LIST OF TABLES

APPENDICES

APPENDICES (Cont.)

APPENDICES

APPENDIX 1

STANDARD OPERATING PROCEDURES FOR SEDIMENT CORE COLLECTION

1. All data from sediment core collection will be recorded in the field database (Microsoft Access®) provided by QEA using a laptop computer on the sampling vessel. Upon completion of sampling at one location, all data from the core will be entered into the database and the field log for that location, printed, and the hard copy stored in the field notebook. This will limit the risk of losing core information due to computer failure. Blank field log sheets that can be used to record information manually also will be provided in case of difficulties with data entry into the computer on the boat are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

2. If the water is too shallow for the sampling vessel to navigate (i.e., less than approximately 2 ft. of water), the location will be temporarily abandoned, and the field sampling coordinator will be notified. A sample will be collected subsequently using either a shallower draft sampling vessel or a push core will be taken from the sample location by wading into the river using chest waders. If the location is reached by wading, the GPS antenna will be hand carried to determine the coordinates of the actual sampling location.

3. Using the on-board GPS system, maneuver the sampling vessel to within 5 ft of the pre-programmed target coordinates for each sample location. Secure the vessel in place using spuds and/or anchors. Record in the field log the actual location from which the core was collected and the target location.

4. Use a calibrated steel rod to probe the sediment surface 3 to 5 ft away from the target location to determine the sediment thickness and type in accordance with the Sediment Probing SOP.

    - If the estimated sediment thickness at the probing area is greater than 6 inches, record probing information in the field log and attempt to collect a core using the vibracorer.

    - If the estimated sediment thickness at the probing area is less than 6 inches, additional probing of the sediment surface will be conducted within 10 ft of the target location for deeper sediments. If thicker sediments are found, relocate the boat to the new coordinates and attempt to collect a core. If sediment depth appears to be systematically less than 6 inches, make one attempt at collection with the vibracorer. If 60% recovery is not achieved after one attempt, collect a sample with a ponar dredge.

5. Once the targeted area is deemed suitable for core collection select an appropriate 3-inch (o.d.) core tube type (Lexan® or aluminum) and length based on the probing information. Use Lexan®

tubing in soft sediments and aluminum tubing for coarse sediments. The majority of the locations will be sampled with core tubes approximately 4 ft. long. Deeper sediments will be sampled with core tubes custom cut on the boat from 10 ft tube sections.

6. Mount a clean coring tube onto the vibracoring device, using extension tubes, as necessary.

7. Lower the coring apparatus with the core tube attached vertically through the water column tube end first, until the river bottom is reached.

8. Gently push the core tube into the river bottom while maintaining the apparatus in a vertical position.

9. Attach the vibracoring apparatus to the aluminum extension tube and vibrate the core into the sediment to refusal. Measure and record the depth of core tube penetration into the sediments in the field database.

10. Pull the apparatus upward out of the river bottom (using a winch as needed), and raise it to the surface, while maintaining the core in a vertical position.

11. Before the bottom of the tube breaks the water surface, place a cap over the bottom to prevent the loss of material from the corer. If boats are properly equipped (i.e., can provide safe access for personnel to reach the water), the cap will be placed on the core by reaching down into the water from the sample vessel, otherwise a second boat may be needed. Secure the cap in place with duct tape when brought on board the vessel.

12. Water overlying the core tube in the coring apparatus will be allowed to drain prior to removal of the core tube.

13. Estimate the recovered length of the sediment core and note it in the electronic field database.

    - The length of the cores recovered in Lexan® tubing will be determined by direct measurement.
    - The length of the cores recovered in aluminum tubing will be determined indirectly by tapping the core with a metal rod from the top to the bottom. The spot where the pitch of the sound changes corresponds to the approximate top of the recovered core.

    The distance between the top of the sediment in the core tube and the bottom of the coring tube corresponds to the estimated length of the recovered core.

14. Compare the length of the recovered core with the core penetration depth.

- If the recovered length of the sediment core is more than 60% of the penetration depth, keep the core.
- If insufficient amount of material is recovered, discard the core into a re-sealable 5-gallon pail and store for subsequent disposal as PCB-waste at the field processing facility. Rinse the core tube with river water and prepare to make an additional attempt.
    - An additional attempt will be made at a minimum distance of 1ft from previously attempted locations.
    - A maximum of three attempts to collect a core will be made for a given location ID.
    - Rinse the core tubes with river water between consecutive attempts.
    - If all three attempts to collect a core are unsuccessful based on recovery alone (i.e., less than 60% recovery), retain the final core for analysis and put flag in the database that indicates that the targeted recovery was not achieved.
    - If an acceptable core cannot be collected within 10 ft of the node location, abandon the location and note conditions preventing core collection in the field database.

15. After a successful core recovery enter additional information into the field database:
    - Date
    - Time of recovery
    - Actual coordinates of the sample location
    - Water depth (ft)
    - Core tube material (aluminum or Lexan®)
    - Core penetration depth (in)
    - Observations, including probing results

16. Remove the core tube from the extension tube and place a second cap on the top of the core tube. Secure the cap in place with duct tape. Rinse the outside of the core tube with a small amount of river water.

17. Draw an arrow on the core tube with permanent marker to mark the top of the core. Label the core with permanent marker indicating station ID, date, and time.

18. Store the core vertically in a core tube rack on ice. Use a tarp to keep the cores in the dark until they are transported to the field processing facility.

19. At locations where core samples cannot be collected and grab samples will be collected by lowering a ponar dredge until it comes in contact with the sediment and the release mechanism trips. Retrieve the ponar dredge and empty the contents into a new aluminum pan. Seal container with lid and duct tape. Label the container with permanent marker indicating station

ID, date, and location. Place aluminum pan on ice in a cooler.

20. Decontaminate the ponar dredge according to the following decontamination procedure:

- Wash with laboratory grade detergent
- Rinse with distilled water
- Rinse with acetone and allow to air dry
- Rinse with hexane and allow to air dry
- Rinse with distilled water and air dry
- Contain rinsate for disposal at the field processing laboratory

20. At the end of each day, an electronic copy (disk) of the field log that includes the information recorded for each core sample collected that day will be provided to the processing laboratory coordinator. Additionally, a hard copy of the field log will be printed out. The hard copy will serve as a back-up to the electronic copy, as well as the chain of custody form from the field to the processing laboratory. This form will be signed by sample collection personnel and core processing personnel at the time that the core processing personnel take custody of the cores. A copy of the signed field log form will be maintained in the processing laboratory.

APPENDIX 2

(The attached SOP includes Attachment A: *Ocean Surveys, Inc. Manual of Standard Operating Procedures.* This attachment contains SOPs for the operation and calibration of navigational and geophysical survey instrumentation. Not all of the SOPs included in this attachment apply to the Bathymetric Survey SOP.)

STANDARD OPERATING PROCEDURE FOR BATHYMETRIC SURVEYS (in the Land Cut)

1. Bathymetric (hydrographic) survey activities will occur over a one day period in the "Land Cut" section of the Champlain Canal that runs outside of the river between the Fort Miller Dam (Lock 6) and Thompson Island Dam - HRM 186 to 189. Since this is a well traveled navigational channel, the work will be coordinated with the Canal Corporation, as required by the Health and Safety Plan and the Community Health and Safety Plan. In addition, the sampling vessels will maintain contact with the Canal Corporation using marine band channel 13.

2. The bathymetric survey will utilize GPS receivers (Trimble 7400 MSi) to acquire navigation data using shore-based reference stations with known coordinates and elevations. Differential correctors determined at these stations will be transmitted to the survey vessel where they will be used by the onboard receiver using Real Time Kinematic OTF software to determine the accurate position of the GPS antenna in the vertical and horizontal planes. These data will be logged on board at one-second intervals for the duration of the survey. Data quality parameters will also be logged and monitored by the onboard navigator with flags put on all data points which do not meet the quality limits set. The specified accuracy for this system is +/- 2 cm when satellite configuration is sufficient.

3. Before leaving dock, the hydrographic crew will check to make sure all navigation and instrument systems are working properly. Calibrate and set navigation instruments based on the instrument-specific standard operating procedures (Attachment A). Prepare survey

equipment for start of daily survey operations including: deployment of 200 kHz transducer into water, measurement of survey equipment offsets, daily speed of sound test (bar check), and other required pre-survey activities.

4. Navigate through the lock to the coordinates of the first transect in the Land Cut. As this is a narrow navigational channel, each transect will run parallel to the canal bank. Approximately 4 longitudinal transects will be surveyed to establish bank-to-bank depth information in the Land Cut. A Coastal Oceanographics "Hypack Max" will be used for trackline design, navigation, trackline control, and digital depth and RTK DGPS data logging.

5. Align survey vessel along transect and confirm heading and equipment operation. Start data acquisition and commence hydrographic survey along transect. Conduct the bathymetric survey using an Innerspace 448 digital depth sounder with a 200 kHz towfish. The average distance between depth soundings should be approximately 2 feet. Log the depth data to the Hypack Max system.

6. Note relevant observations and changes in operational procedures to the field log. These may include: coordinates of observed obstructions or artifacts; areas where interferences or other conditions limit survey resolution or prevent bank-to-bank coverage; and coordinates where adjustments to tow fish height, line spacing, or range scale are made.

7. At the end of each transect, confirm successful data acquisition and storage, navigation and equipment calibrations and settings. Log time and coordinates at end of each transect line surveyed.

8. Prepare equipment for navigation to next transect; navigate to next transect.

9. Repeat steps 4-8 for collecting data along a transect until bank-to-bank coverage has been achieved in each survey section. Maintain a safe operating distance (as determined by boat operator) from lock gates between transects.

10. At the end of each day, backup daily computer data and check for error flags.

11. Output all notes and electronic target files to an ASCII file and store with the raw records.

12. All raw survey data and information (e.g., field notes, instrumentation frequencies) must be documented electronically or in a field notebook. Back-up copies of raw electronic data and copies of field logbooks will be made at the end of each survey day.

ATTACHMENT A

OCEAN SURVEYS, INC.
MANUAL OF
STANDARD OPERATING PROCEDURES

(Geophysical Survey Instruments)

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TABLE OF CONTENTS (Continued)

1.0 INITIAL EQUIPMENT SETUP

This is a draft document. The most recent modification was on 07/31/02 by MLK. New versions will be distributed as they are created.

There are presently several documents that are associated with this that are not included at this time.

1 Caris offset drawing
2 Hypack offset drawing
3 System wiring document
4 System comm. Port settings and data formats

1.1 General Tasks Before Start of Survey

- Notify GE of vessel movement
- Obtain permits for movement through and between locks
- Obtain proper charts and update with all Notice to Mariners
- Verify availability of CG DGPS correctors and RTK stations
- Document equipment installation
    - Establish Boat 0,0,0
        - Vessel fore/aft centerline, aft edge of athwart ship I-Beam on A-Frame, point on aft deck slightly above waterline
    - Measure and record all offsets
        - Trimble 7400 MSi DGPS's
            - Navigation antenna X, Y, Z
            - Reference antenna X, Y, Z
        - Trimble 7400 RTK GPS
            - Antenna to waterline
            - X & Y to boat 0,0
        - Innerspace 448 X, Y, Z
        - TSS DMS 2i-05
            - X, Y, Z
            - Zero out mounting angles with appropriate vessel loading – see procedure in TSS section
        - Robertson Compass
            - X, Y

- Align to true heading of vessel centerline – see procedure in Compass section

- Sidescan Tow Point X, Y, - Z left at 0.0 m for proper Caris import of layback

- Subbottom Profiler Tow Point X, Y, - Z left at 0.0 m for proper Hypack import of layback

1.2 Equipment Setup

1.2.1 Trimble 7400 Receiver

- Initial Settings
  - RTCM Output = off
  - RTCM Input
    - Inputs ON
    - Port = 2
    - Format = USCG
    - ASCII Printout off
    - Beeper Off
    - Station = any
    - Age Limit 20 sec.
    - Integrity Monitor Off
  - Power Up Control
    - Do not default controls at power up
  - SV Enable/Disable
    - Disabled mode = none
  - Adjust local time
    - Time offset EDT-UTC = -4 hrs
    - Time Zone Identifier = EDT
  - Baud Rate Format
    - Port 1 = 9600-N-8-1
    - Port 2 = 9600-N-8-1
  - Remote Protocol
    - Data Collector Compatible
  - Reference Position
    - Lat = 35 50 40.91718
    - Lon = 075 39 19.57021
    - Height = -37.529

        - (Note, may be changed during survey by selecting **HERE** to get local position and current ellipsoid height for Lat/Lon – Fixed height)
      - Masks/Sync Time
        - Elevation Mask = 8
        - PDOP Mask = 5
        - SV Sync Time = 1.0
      - Positioning Modes
        - Weighted solution enabled
      - Lat/Lon Height Always
  - Power Controls
    - Charger and Power output disabled
  - NMEA 183 Output
    - Port 1 Enabled
      - GGA, VTG, ZDA
  - Cycle Printouts = Off
  - 1 pps output = disabled
  - Default controls – **DO NOT USE!!! RESETS TO FACTORY**
  - Modify
    - Units of Measure
      - Lat/Lon Degrees = Deg.Min.Sec.
      - Time = 24 Hr UTC
      - Position = WGS-84 LLH
    - Altitude Reference
      - Height above ellipsoid

1.2.2 MX-51 Beacon Receivers

- Initial Settings - DGPS1

  - **HUDSON FALLS, NY**
    Status: Operational
    RBn Antenna Location: 43° 16.21' N73° 32.31' W
    REFSTA Ant Location (A): 43° 16.2491' N73° 32.34705' W
    REFSTA Ant Location (B): 43° 16.2637' N73° 32.34534' W
    REFSTA RTCM SC-104 ID (A): 94
    REFSTA RTCM SC-104 ID (B): 95
    REFSTA FIRMWARE VERSION: RD00-1C19
    Broadcast Site ID: 844
    Transmission Frequency: 324 KHZ
    Transmission Rate: 200 BPS
    Signal Strength: 100uV/m at 135NM

- CTToolbox should be used to reload H11032R.CNF (config file) if necessary. The following settings are in H11032R.CNF
    - CONTROL/BASE STATION
        - Input using **HERE** at Hudson Falls
        - LAT 35 50 40.77420
        - LON 075 39 19.81768
        - HGT – 0035.870
        - ANT Height 000.000
    - CONTROL/SV ENABLE/DISABLE
        - ALL – ENABLE
    - CONTROL/GENERAL CONTROLS
        - ELEV. MASK: 08
        - PDOP MASK : 05
        - MEAS RATE 1 HZ
        - MOTION: KINEMATIC
    - CONTROL/POWER CHARGER
        - POWER OUTPUT MODE DISABLED
    - CONTROL 1PPS OUTPUT
        - 1 PPS OFF
        - ASCII TIME TAG PORT OFF
    - CONTROL SERIAL PORT OUTPUT
        - NMEA/ASCII OUTPUT
        - GGK
            - PORT 2
            - 1 HZ
        - ZDA
            - PORT 2
            - 1 HZ
        - All others off
    - STREAMED OUTPUT
        - ALL OFF
    - RT17/BINARY OUTPUT
        - ALL OFF
    - CMR/RTCM
        - BASE – MOVING
        - CMR PORT – OFF
        - NAME - cref
        - RTCM PORT – OFF
        - TYPE - 1
    - CONTROL/SERIAL PORT SETUP
        - PORT1 9600 8-NONE-1
        - PORT 2 9600 8-NONE-1 NONE

- PORT 3 9600 8-NONE-1
- PORT 4 9600 8-NONE-1 NONE
- CONTROL/INPUT SETUP
  - USE RTCM STATION – ANY
  - RTK/DGPS AUTO SWITCH RANGE – 20.0 KM

1.2.3 Compass

- Initial Calibration Procedure
  - Load vessel, as it will be for survey ops. Remove any large ferrous objects from the vicinity of the compass.
  - Position the vessel in open water
  - Apply power to the Robertson autopilot
  - Begin by turning the vessel to starboard.
  - Select **INSTALLATION/RFC COMP calibration**.
  - Calibration should complete after ~ 1 ¼ turns and should be verified by a display of **Calibration confirmed**.
- Determine and apply Compass Offset
  - Con the vessel on a straight line while observing the heading computed by the GPS system.
  - Adjust the offset by turning the autopilot knob to match the pilot compass heading to the gps heading. Note the applied offset. (This puts the pilot compass into "TRUE" heading.)

1.2.4 TSS DMS 2i-05

- Initial Settings
  - Set baud rate/format to 19200,N, 8,1
  - Heave bandwidth = SHORT
  - Output Rate = 50 hz.
  - GPS data input settings = NMEA Local 9600, 8, N, 1
    - Check GPS RAW and CALCULATED input
  - GYRO data input settings = NMEA Local 4800, 8, N, 1
    - Check Compass RAW & CALCULATED INPUTS
  - Data output format = TSS1 19200, 8, N, 1
  - Zero out mounting angles. Document mounting angles with screen grab.
    - Stabilize vessel with static loads approximating those that will be experienced during the survey.
    - Access TSS through communication program and set mount angles automatically by averaging data for 5 minutes
    - Accept values and screen grab settings

Restart TSS operation and exit from program

Mount Angle Setting Recorded
06/04/02

```
---------------------------------
DMS 2-05 Version 2.03 Terminal Mode
---------------------------------
Sensor Mounting

Orientation : Vertical
Roll  Mount Angle [  1.741  deg] :
Pitch Mount Angle [  1.711  deg] :
Yaw Mount Angle [  0.000  deg] :
```

- **Do Not Change These Settings!**

•

1.2.5 Innerspace 448

- Initial Settings
  - Verify the following initial settings
    - Gain = Approx. 10 o'clock setting
    - Range = 0-15 M
    - Mode = Meters
    - Chart Speed = 4
    - Range Multiplier = X1
    - Input default speed of sound of 1500 m/s
    - Set draft = 0.0
    - Tide = 0
    - Initial = 5
    - Gate = 2
    - Mode = Gated
    - Reply = 16
    - Alarm on during survey
    - Set variable power TX board to Low, to limit interference with SS and MB
    - Set internal TVG curve switch to open/open or +60 db. This was needed to receive quality data at the above mentioned low power setting with our combination of components
    - Set date & time – See back of paper carrier
    - Load paper per picture on back of paper door
      -

1.2.6 Klein 595

- Initial Recorder Setup

- Set system to factory defaults by pushing left button on the CPU board
    - This resets all values to factory default
    - It also resets all gain curves and other "adaptive controls prior to calibration
        - A calibration should be preformed, per the manuals description any time a component is changed, like a cable or fish
  - Set time/date in submenu
    - Add "*" to time and date to print it when an event is pressed. This can be used to log tuning changes and rub tests
  - Set system to the following values:
    - Auto CPU
        - Altitude = 0,0
        - Return = 0
        - Offset = 2
    - Auto TVG Port
        - Normal
        - Atten. = 9
        - Salt Water
    - Auto TVG Starboard
        - Normal
        - Atten = 9
        - Salt water
    - Printer = Off
    - Range = 25 Add "*" to field
    - Scale lines = 10 Add "*" to field
    - Source = Fish
    - Channel = 1 | 2
    - Speed = Manual –1.0 Set to avoid alarms
    - Altitude = Auto
    - Mapping Mode = Off
    - Altitude Alarm = Off
    - Auto Mark = Off
    - Event Count = Off
    - Event Mark = Off
    - Side Scan Expand = Off
    - Profiler Expand = Off
    - Nav Source = Nav3* - used for external Eventing option

- Follow the calibration found in the operations manual on 3-34 to tune for site conditions
- Document tune-up settings in SSS annotations
- Document tow configuration and Cable out in SSS annotations
    - Tow Point
        - See attached drawing for exact location
        - The tow point is a sheave mounted to a bowsprit. In operation the fish is lowered to1meter in the water as the vessel is moving at survey speed.
        - The cable is fair leaded back to the stern on the outside of the bowsprit mount. Cable out measurement is taken from the point of the sheave closest to the mount point
        - The layback was measured by observing the fish under survey conditions and measuring from the center of the xducers to the tow point.
        - Document any changes made to the recorder online in the Isis notes section
- Initial Fish Setup
    - Depression angle = 20 degree's
    - 500 KHz only
    - 100 KHz disabled in fish – SCR trigger is disconnected.
    - Attach depressor to fish

- Internal Jumpers
    - A/D board jumpers should be set to reflect proper software version (checked 050202)
    - Fish Tape I/O jumper should be set to either 15v for short cable or 24v for long cable (winch) (checked 05/2/02 set to 15v)
    - Verify which channel is tracking altitude on the Connector interface board

1.2.7 Bar Check

- Initial Setup and Calibration
    - Determine maximum depth of survey and depth units
        - Sheet A maximum depth is in the 10 meter range
        - Survey depth units are meters
    - Construct Bar Check per OSI standards
    - Type 1
        - .2 meter diameter lead disk with eye bolt
        - Imprint a "serial number" onto bar
            - "A"

        - "B"
    - Coated aircraft cable
    - Brass marker beads at appropriate intervals
        - Minimum of every 1 meter throughout the survey depths
        - This is to allow use of a "pocket rod" to read inter bead values
    - Also mark cable on both sides of bead with a "sharpie" to help identify bead slips
    - Measure bead locations with steel tape to the nearest 0.01 meter increment
    - Record bar s/n and all other information required on OSI Lead Line Calibration form
  - Recalibration
    - Recalibrate Bar Check every 6 months, or after any action that could possibly affect the condition of the Bar Check, such as snagging line on bottom.
    - Recalibrate at the completion of the survey
  - Maintenance
    - Periodically examine the eye bolts and cables

- Type II
    - Aluminum square-beam > width of boat with target at position of in hull xducer
    - Imprint a "serial number" onto bar
    - Coated aircraft cable
    - Brass marker beads at appropriate intervals
    - Minimum of every 1 meter throughout the survey depths
        - This is to allow use of a "pocket rod" to read inter bead values
    - Also mark cable on both sides of bead with a "sharpie" to help identify bead slips
    - Measure bead locations with steel tape to the nearest 0.01 meter increment
    - Record bar s/n and all other information required on OSI Lead Line Calibration form
  - Recalibration
    - Recalibrate Bar Check every 6 months, or after any action that could possibly affect the condition of the Bar Check, such as snagging line on bottom.
    - Recalibrate at the completion of the survey
  - Maintenance

- Periodically examine the eye bolts and cables

1.2.8 GE 1 Computer System

- Start Up
  - Verify DC Mains and Autopilot are off before powering up, or logging onto, system
  - Log on using default Logon
    - User Name osiuser
    - Password (blank)
- Verify time zone is set to (GMT) Greenwich Mean Time: Dublin, Edinburgh, Lisbon, London.
- DO NOT CHECK "Automatically adjust clock for daylight savings time.

- Start HyPack MAX with appropriate shortcut
  - Open new project named GE-1
    - Create folders in the project folder named DATA1
    - Set geodesy to UTM Zone 18 WGS 84
    - HYPACK HARDWARE SETUP
      - New File
      - NAV - NMEA183.DLL
        - Name = DGPS1
        - Update Frequency = 50ms
        - Type
          - Position
        - Options
          - Record raw data
          - Record quality data
        - Record
          - Always
        - Connect
          - Serial Port
            - COM3, 9600,8,none, 1,Flow Control = none
        - Offsets
          - Starboard = -.35
          - Forward = + .23
          - Height = +1.97
          - Latency = 0.860
        - Setup
          - Standard NMEA 0183 sentences to be used

            - GGA
        - HDOP Limit = 2.5
        - Minimum Satellites = 4
        - Use ZDA message for time tag = Disabled
        - Send alarm when non differential
- Depth – Innerspace 448 {Serial} - IN448.DLL
    - Name = 448
    - Update Frequency = 50
    - Type
        - Echo sounder
    - Options
        - Record raw data
        - Record quality data
        - Paper Annotation
    - Record
        - Always
    - Connect
        - Serial Port
            - COM6, 9600,8,none, 1
    - Offsets
        - Starboard = 0.0
        - Forward = 0.0
        - Height = +.8 NOTE!!! .8 meters used as "display offset". See Draft explanation
        - Latency = 0.000
    - Setup
        - Send annotation string with event mark
        - Multiply not needed
- Auto Pilot Compass – NMEA.DLL
    - Name = AP Compass
    - Update Frequency = 50
    - Type
        - Heading
    - Options
        - Record raw data
        - Record quality data
    - Record
        - Always
    - Connect
        - Serial Port
            - COM5, 4800,8,none, 1

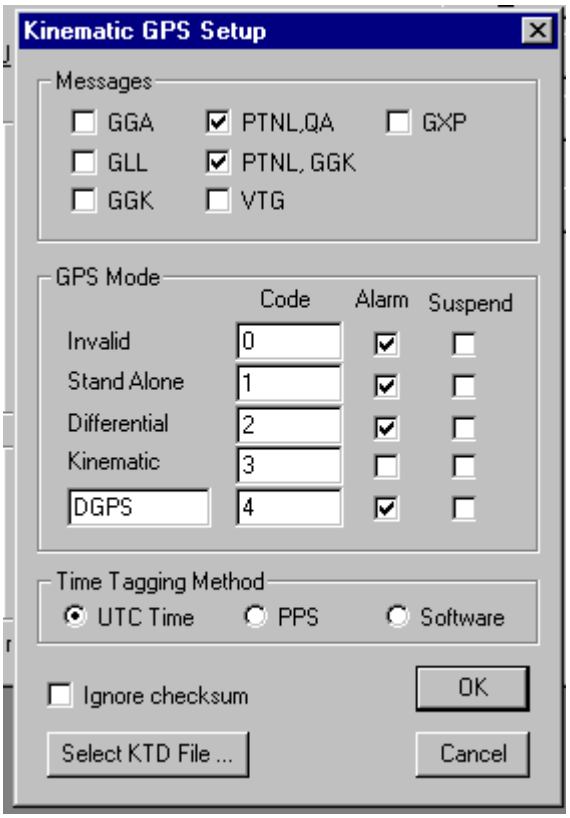
    - Offsets
        - All zero
    - Setup
        - Sentence to be used
- HDG
- Auto Pilot – NMEA.DLL
    - Name = AP XTE
    - Update Frequency = 500
    - Type
        - Output
    - Options
        - Record raw data
        - Record quality data
    - Record
        - Always
    - Connect
        - Serial Port
            - COM8, 4800,8,none, 1
    - Offsets
        - All zero
    - Setup
        - Sentence to be used
- GGA
    - Sentence to generate
    - APB
    - GLL output places = 4
    - XTE (Nautical Miles) checked
    - Output to hundredth decimal place = Enabled
    - XTE Factor = 0.0

- File Server – Delph Output – DELPH.DLL
    - Name = Isis Out
    - Update Frequency = 20000
    - Type
        - (nothing checked)
    - Options
        - Record raw data
        - Record quality data
        - Paper Annotation
    - Record
        - Always
    - Connect
        - Serial Port

        - COM7, 9600,8,none, 1
    - Offsets
        - All Zero

- TSS DMS2i-05 – TSS320.DLL
    - Name = DMS2i-05
    - Update Frequency = 50
    - Type
        - Heave Compensator
        - Other
    - Options
        - Record raw data
        - Record quality data
        - Paper Annotation
    - Setup
        - Motion reference Unit Only
    - Connect
        - COM 1 19200,8,N, 1
    - Record
        - Always
    - Offsets
        - Position
        - Starboard = -.44
        - Forward = +.47
        - Vertical = -.18
        - Yaw = 0
        - Pitch = 0
        - Roll =0
        - Latency =0

- Trimble 7400 RTK OTF - KINEMATIC1.DLL
    - Name – RTK
    - Type
        - Position
        - Echosounder
        - Sync. Clock
        - Tide Gauge
    - Record RAW
    - Record Quality
    - Setup



- SELECT KTD FILE
  - File 02ES007.KTD used for survey ops

- Connect
  - COM2 9600,8,N, 1, Flow Control = none
- Offsets
  - Position
  - Starboard = -1.50
  - Forward = +.25
  - Vertical = + 2.05
  - Yaw = 0
  - Pitch = 0
  - Roll =0
  - Latency =0
- Record
  - Always

- Create a second mobile named RTK. Transfer the RTK device to the second mobile

- URS-1 – VHW.DLL
  - Name = Speedlog
  - Update Frequency = 200
  - Type
    - Speed
    - Other
  - Options
    - Record raw data
    - Record quality data
  - Setup
    - none
  - Connect
    - COM 9 4800,8,N, 1, Flow Control = none
  - Record
    - Always
  - Offsets
    - None
- Settlement – DraftTable.dll
  - Name = Settlement
  - Update frequency = 100
  - Type
    - Draft
  - Setup
    - Create Draft table from Settlement and Squat test
    - Insert Draft table picture – set to 0.0 for squat test
  - Offsets
    - None
  - Connect
    - Ignored
  - Record
    - Always

1.2.9 GE-1 CARRIS OFFSETS to BOAT

DGPS1 (NMEA183.DLL)

STBD	+1.18
FWD	+0.02
Height	+1.97
Latency	+0.00

448 (INN448.DLL)

STBD	+1.53

FWD	-0.21
Height	+0.80
Latency	+0.00

Auto Pilot Compass (NEMA.DLL)

STBD	+0.00
FWD	+0.00
Height	+0.00
Latency	+0.00

Isis Output (DELPH.DLL)

STBD	+0.00
FWD	+0.00
Height	+0.00
Latency	+0.00

Auto Pilot (NEMA.DLL)

STBD	+0.00
FWD	+0.00
Height	+0.00
Latency	+0.00

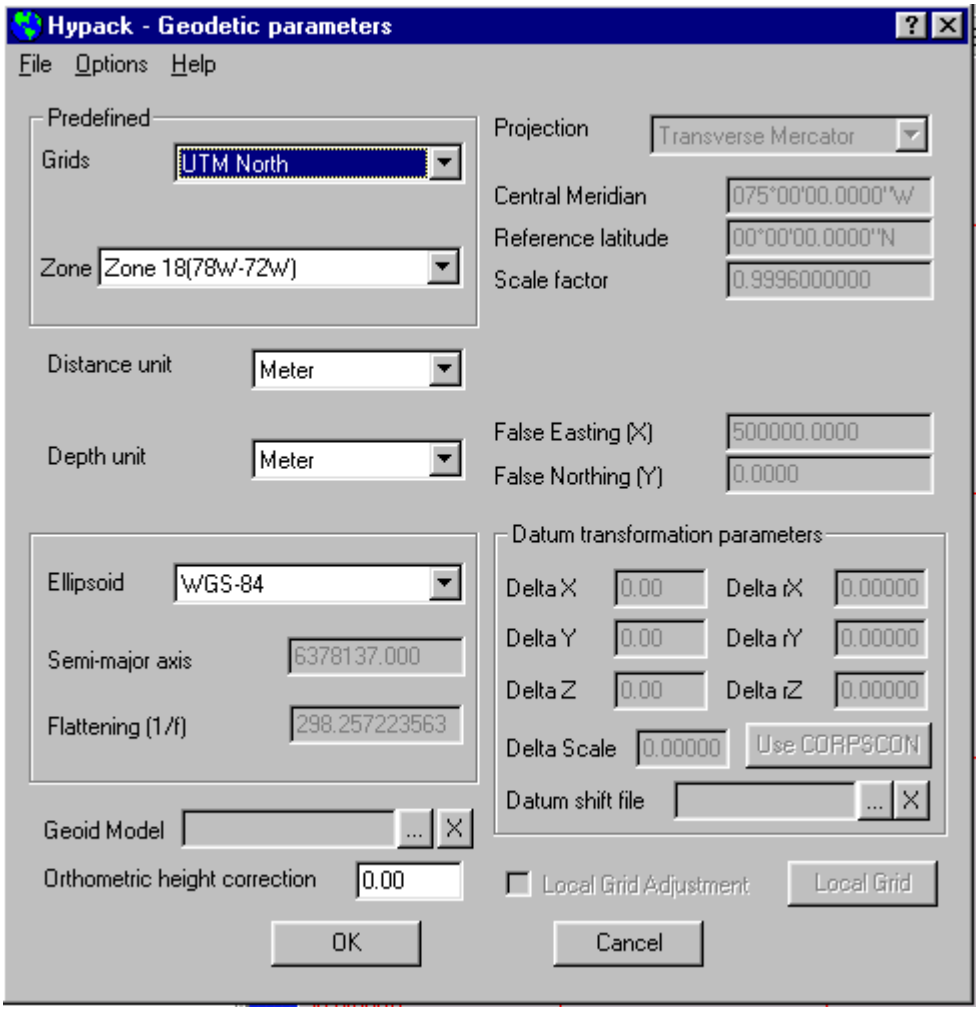
DMS 2i-05 (TSS 320.DLL)

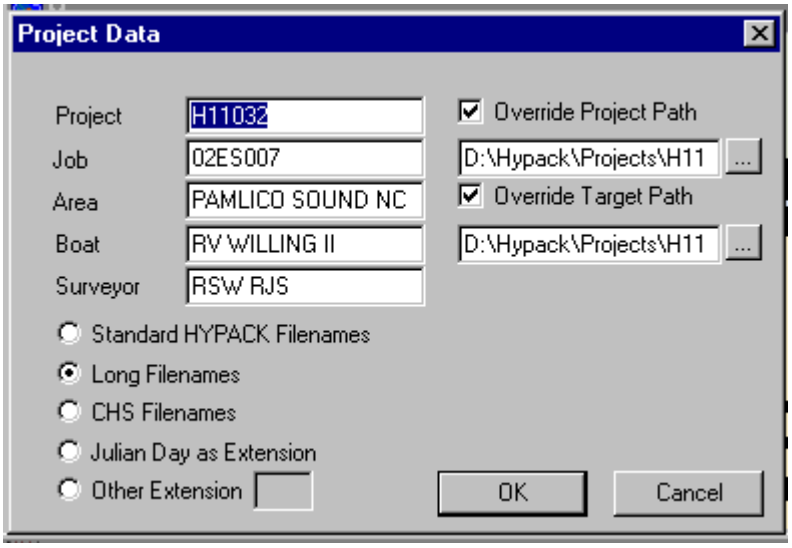
STBD	+1.09
FWD	+0.26
Height	-0.18
Latency	+0.00

RTK GPS_KINEMATIC.DLL

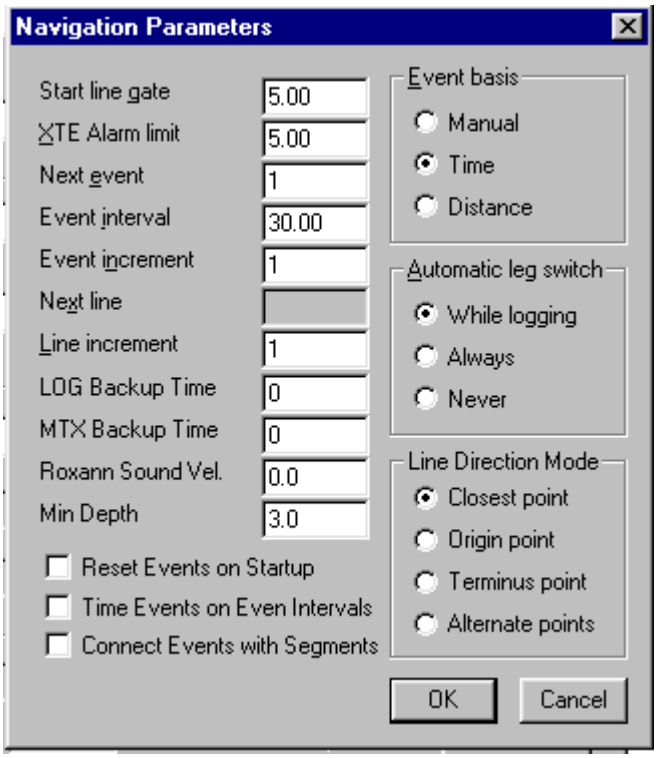
STBD	+0.03
FWD	+0.02
Height	+2.05
Latency	+0.00

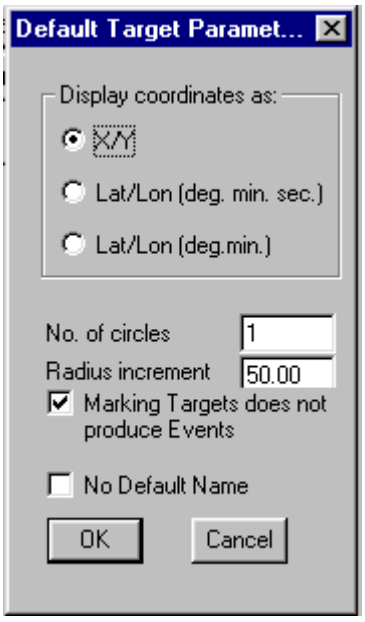
1.2.10 Other Hypack Max Settings


Hypack - Geodetic parameters
File Options Help
Predefined
Grids
UTM North
Zone
Zone 18(78W-72W)
Projection
Transverse Mercator
Central Meridian
075°00'00.0000"W
Reference latitude
00°00'00.0000"N
Scale factor
0.9996000000
Distance unit
Meter
Depth unit
Meter
False Easting (X)
500000.0000
False Northing (Y)
0.0000
Ellipsoid
WGS-84
Semi-major axis
6378137.000
Flattening (1/f)
298.257223563
Datum transformation parameters
Delta X
0.00
Delta rX
0.00000
Delta Y
0.00
Delta rY
0.00000
Delta Z
0.00
Delta rZ
0.00000
Delta Scale
0.00000
Use CORPSCON
Datum shift file
Geoid Model
Orthometric height correction
0.00
Local Grid Adjustment
Local Grid
OK
Cancel


Project Data
Project
H11032
Job
02ES007
Area
PAMLICO SOUND NC
Boat
RV WILLING II
Surveyor
RSW RJS
Override Project Path
D:\Hypack\Projects\H11
Override Target Path
D:\Hypack\Projects\H11
Standard HYPACK Filenames
Long Filenames
CHS Filenames
Julian Day as Extension
Other Extension
OK
Cancel

NOTE: XTE ALARM set to 100000 for Sea Trials





- **1.2.11 ISIS**

o Start Up

- Verify DC Mains and Autopilot are off before powering up, or logging onto, system. Note: if monitor does not come on (yellow power/signal indicator steady yellow on lower right corner of monitor) remove power from monitor for a few seconds, then restore and turn on monitor.

- Start Isis with Isis H11032 shortcut – **Only**
  - This calls up a specific configuration file

- File types and locations
  - H11032 ISIS Short Cut to Start Isis Desktop
  - H11032.LAY Window Layout E:\H11032 ISIS\H11032 Config\
  - H11032_140.CFG Isis configuration file D:\TEI\IsisSona\v5.91\
  - Survey. log Isis session log D:\root
    - Note: unable to redirect this file

- Initial Processor Settings
  - File Menu
    - Playback N/A
    - Record Setup
      - Sonar Setup
        - Pick standard analog
        - Select CHICO/CHICO PLUS Board
          - Channel 1 edit
            - Status = On
            - Name = Port
            - Type = Port SSS
            - Trigger = 1
          - Channel 2 edit
            - Status = On
            - Name = Stbd
            - Type = Starboard SSS
            - Trigger = 1
          - All other channels disabled
          - Sonar name to H11032 Klein 595 2 CH 500Khz
          - Frequency = 384.0,384.0
          - Horizontal Beam Angle = 0.2,0.2
          - Beam Width = 50.0, 50.0
          - Tilt angle = 20.0, 20.0
          - Name of server = ISISCHICO.EXE
          - Automatic control disabled
      - Serial Port 1 Heave, Pitch, Roll
        - Status = On

- Settings = 19200, 8, N, 1
- Template = TSS
- Convert Lat - Long = Disabled
- Filter Speed = Disabled
- Navigation Latency = 0.0

- Serial Port 2 Not used
- Serial Port 3 GPS for SSS
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = NMEA0183 NOCLOCK
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 4 GPS for Single Beam
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = NMEA0183
    - NMEA0183 SHIPPOS NOVTG
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 5 Compass
  - Status = On
  - Settings = 4800, 8, N, 1
  - Template = NMEA0183 NOCLOCK NORMC NOGLL NOVTG
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 6 May be used for Fish Altitude input
  - Better Tuning Has Made This Option Unused
    - Manual SSS Bottom Tracking Option
  - Status = Off
  - Settings = 9600 8, N, 1
  - Template = Manual
    - Modify Default = {/100}{-1.3}7
      - Change 1.3 to value needed to get correct altitude
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0

- Serial Port 7 Hypack feed for Line Control
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = (Leave Blank)
    - Allows events and start/stop info in from Hypack
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 8 448 feed to Aux Sensor 1
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = Manual
    - Modify Default = {/100}1
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
  - Serial Port 9 RTK INPUT
- Serial Port 10 Speed Log
  - Status = On
  - Settings = 4800, 8, N, 1
  - Template = {pattern=m}s
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0

- File Format
  - Format = XTF
  - Media = Disable
  - Sample Size to Record = 16 bit
  - Samples per Channel = 1024
  - Processing Method = MAX
  - XTF File Header Notes
    - Vessel Name
    - Survey Area
    - Operator

- Configure
  - Playback Speed – as desired
    - Real Time Scrolling
      - Scroll without restoring covered data
        - This keeps system from locking up
    - Transducer Depth = 0.0
    - Ocean Tide

        - Apply Corrector = Disabled
        - Verify = 0.0
    - Sound Velocity = Average from first cast of the day
    - Multiple Pings = 1
    - Hypack DDE
        - Accept from Hypack = Disable All
        - Automatically Start Saving At Start of Line
            - Use File Name from Hypack = Enable
            - Generate File Names = Disable
            - Start Each File with = Enter Daily Directory Info
    - Cue Boxed = Disabled
    - Set Date and Time = Ignore – Will be automatically set during operation
    - Save Setup = Prompt User at Exit

- Color
    - Palette
        - SSS Colors = Grey Scale
        - Squelch = 0.0
        - Reverse Palette = Enabled
        - Strong Returns Red = Disabled
    - Grid Color
        - Voltage Grid
            - Line = Blue
            - Data = White
            - Dim = Both Enabled
        - Scale Lines Red

- View
    - Scale Lines
        - Apply Settings to = All the same
        - Scale line Unit = Distance
            - Spacing = 10
    - Depth Delay and Duration
        - Apply Settings to = All the same
        - Units = Off
    - Overlay
        - Show on Waterfall
            - Event Marks = Disabled
            - Event Text = Disabled
            - Bottom Track = Enable
        - Bookmarks

- Save Bookmarks = Enabled
- Display Bookmarks = Enabled

- Down Sample = Max
- Speed
  - Automatic = Enabled
  - Filter = Disabled
- Heading = Automatic
- Layback Correction
  - Apply Delta XY = Disabled
  - Apply Layback = Enable
    - Use Logged Layback = Disabled
    - Enter layback manually = Enabled
    - Compute layback from Cable Out = Disabled
    - Enter layback value in box provided (Currently 1.0M)
      - This field with be empty, enter value
        - Obtain value from chart
      - Click ACCEPT, current value changes to entry
      - NOTE: **DO NOT CLOSE WINDOW**
      - NOTE: CHECK AT START OF EACH LINE
      - NOTE: HAVE OPEN DURING CONTACT PICKING

- Tools
  - Target Setup
    - TargetPro.exe only
  - Target Setup
    - Height = 512
    - Width = 2048
    -
  - Target
    - File
      - **Set working Directory = Enter Daily Data Directory**
    - Tools
      - Configuration
      - Speed auto
      - Speed Corrected display = yes
      - Layback = manual
      - Horizontal beamwidth
        - Manual, 0.0
      - Local variation = 0.00
      - Latitude/longtitude
        - Deg Min Sec

        - Northing/Easting Display
            - Meters
        - Range Display Units
            - Meters
        - Speed display Units
            - Knots
        - Misc.
            - Automatic Audit Trail = yes
            - Object Detection on image load
                - None
    - Units = Meters
    - Constants = Use defaults
    - Set Contact Number = Start with 1 – Ensure number is consistent with contacts logged to date.
    - Speed Correct = Enabled

- Parameter Window – Current File Section
    - Switch Button
        - Record Data to File Name = Blank
        - Remaining storage = Enable D: and E:
        - File Grows larger than = Disable

Altitude - Absolute

Based on 595 Range Scale

Range	8% Minimum Altitude	20% Maximum Altitude
25	2.00	5.00

Maximum System Speed

Based on 595 Ping Rate

Range	Ping Rate / Second (Measured)	Maximum Speed (Knots)
25	27.00	17.50

Maximum Survey Speed

Based on 10% Buffer

Range	Maximum Speed (Knots)	90 %Maximum Speed (Knots)
25	17.50	15.75

- **1.2.12 Robertson Autopilot**

Introduction:
The factory technical representative for the parent company Simrad, is Rich Barnes (425-778-8821) who is located at Simrad, Inc., 19210 33rd Avenue West, Suite A, Lynwood, WA. 98036. The pilot was interfaced to NOAA1 to receive NMEA (modified) standard messages from Coastal Oceanographics HYPACK MAX Survey program. The vessel captain performs all operations related to the pilot.

Interface:
The pilot receives the following NMEA-0183 messages;
APB (modified by Coastal to send .#### nm of cross track error vs. .## nm, the NMEA standard)
VTG (standard)
GGA (standard)
Baud rate is 4800/N/8/1
NMEA input to the pilot is through TB 10 on the Junction Unit, Pins RX 1(+) and RX1 (-). There is no handshaking or error correction used. The Robertson RFC35R rate compass is used to provide vessel heading to all systems and outputs a NMEA message through TB10on the Junction Unit, Pins TX2(+) and TX2(-).

Operation:
The pilot starts in the **Helmsman** mode. The captain steers the vessel on to the trackline well ahead of the actual BOL and attempts to track down the line. When the vessel has stabilized online the pilot is put into the **Auto** mode. The pilot is "course steering" at this point. The captain observes the vessel motion and line tracking while adjusting the "course" using the left/right buttons on the control unit or remote control. When the vessel is steering the line and cross-track error has been reduced to a minimum (typically less than 1 meter), the captain changes to the **NAV** mode. The pilot will continue to steer in "course steering" mode for a period of time determined by an internal setting (currently at minimum – 100 sec). Then it will use the XTE value received from HYPACK MAX and attempt to adjust it's course to achieve zero XTE.

Some conditions prohibit the use of the **NAV** mode. One example is the use of a drogue chute to slow the vessel. Sea conditions that cause sudden large heading changes are another example. In these cases the pilot is left in the **Auto** mode and the left/right buttons on the control unit or remote control unit are used to con the vessel down the line.

Initial Setup:

Mechanical setup and alignment are performed at the time of installation and should require no further adjustment. There are many electronic settings that affect pilot operation. They fall in to several categories:

- Front Panel
    - Rudder – used to set the amount of rudder used by steering commands
    - Counter Rudder – used to set the opposing rudder used when crossing a course line
    - Weather – used to reduce pilot sensitivity in heavy seas
- Info Loop
- Weather Loop
- Debug Loop

Normally, only the Rudder setting is changed throughout the day. More rudder (higher #) causes closer tracking and quicker steering response. Too much rudder causes large heading swings. Too little rudder and the vessel will fail to closely follow the line.

2.0 PRE SURVEY OPERATIONS

2.1 Navigation System Check

Upon arrival in Hudson Falls a third order control disk will be located to facilitate the performance of a navigation confidence test. Two separate procedures will be performed. The first procedure is to determine the horizontal and vertical position of the project RTK GPS base station and certify it. The second procedure involves using the Trimble 7400Msi L!/L2 Kinematic OTF system to locate a check point in proximity of the survey vessel for future confidence checks.

The first procedure involves the following.

A RTK base will be set up with it's antenna positioned at a known height over a GE/QEA supplied point. The Trimble 7400Msi reference receiver is then configured to provide CMR correctors based on the following parameters.

Configuration Toolbox file D24_Base.cfg

1. Generate CMR correctors on Port 1
2. Kinematic base unit
3. A elevation mask of 13 degree's
4. A PDOP mask of 5
5. Reference position of 35 50 40.87561 Lat, 075 39 15.38597 Long, -37.75 Elev. (WGS-84 Ellipsoid height)
6. Antenna height set to 2.000 meters, Antenna mounted on a 2.00 meter rod
7. Antenna type set to L1/L2 compact resulting in a True Vertical Height of 2.062 meters

The project RTK base will be set up as a rover station, receiving corrections from the station set at various stations using the following parameters:

Configuration Toolbox file RTK_ROV.cfg

1. Receive CMR corrections on Port 1
2. Kinematic rover
3. A elevation mask of 13 degree's
4. A PDOP mask of 5
5. Output GGK on Port 2.

For reference, the RTCM-104 correctors will be relayed from the reference station to the project base station location with Pacific Crest Radio Modems Model RFM96W.

Finally, a Hypack Project will be setup to monitor the position in both WGS-84 Lat, Long and UTM Zone 18 NAD-83. The following parameters will be used.

1. Project = Base_Average
2. Kinematic DLL for GPS input configuration
3. System offsets were set to 0,0,0 for this test
4. Geodesy was set for the above listed UTM Grid.

Position observations will be recorded for a sixty minute period. These observations will then be averaged and assigned as the project RTK base stations horizontal (WGS-84 Lat Lon) and vertical elevation (WGS-84 Ellipsoid).

The project RTK base will then be set up as a reference station, sending corrections based upon the assigned position. The following parameters will be used:

Configuration Toolbox file BASE.cfg

1. Generate CMR correctors on Port 1
2. Kinematic base unit
3. A elevation mask of 8 degree's
4. A PDOP mask of 5
5. Reference position of Lat 35 50 37.98404 N , Long, 075 39 15.87987 , -23.826 Elev. (NAVD88)
6. Antenna height set to 000.00 and antenna type set to **UNKNOWN (0.0 offset)**

The data from each file will be processed through SB-MAX where it will be filtered to only GPS Mode 3 points with an HDOP of <=2.0. These values will then be averaged and also the min & max values will be observed.

2.2 Static Draft Measurement

- **Establishment of Vessel Reference Position**

Prior to survey operations, a Vessel Reference Position was set for use in post processing. Survey data will be collected by an Isis v5.91 system for processing under the Caris HIPS/SIPS software package. Single beam only data will be collected by a Coastal Oceanographics HyPack MAX v0.5b system for processing under the Caris HIPS/SIPS software package. During survey operations, no physical offsets will be entered into the Isis system. Therefore, all offsets and corrections should be handled by the Caris package. It should be noted that an average sound speed for the water column and Side Scan "Horizontal Layback" will be input into the Isis raw data package. This information will be discussed in the appropriate system sections.

With this in mind the following Reference Position was established based on the definition of a Vessel Coordinate System provided in the HIPS User's Guide.

> **Vessel Coordinate System**
> Vessel configuration is based upon an instantaneous, three-dimensional, vessel coordinate system. The
> Origin of the coordinate system is the reference position (RP). The axis is defined as follows:
> The Y-axis is oriented along the vessel's fore/aft axis, positive forward.
> The X-axis is oriented along the vessel's port/starboard axis, perpendicular to the Y-axis, positive
> to starboard.
> The Z-axis is perpendicular to the X-Y plane, and positive down (into the water).

The Y-axis is located approximately mid ship at the fore/aft centerline created perpendicular to the location of the A-Frame.
The X-axis is located at the approximate port/starboard center of the vessel.
The Z-axis was located at the rear deck level, slightly above the water line of the vessel during setup and sea trials

Once this point was established, measurements were made to determine the physical offsets of all survey equipment based on this coordinate system. These measurements were compiled and displayed in the AutoCAD 2000 file called R/V Willing.dwg. This drawing contains all sensor offsets.

During the establishment of system offsets a "Reference Mark" was set to aid in monitoring vessel Static Draft. The Reference Marks are located on the starboard single beam transducer mount vertical member, The distance from the Reference Mark to the Z-axis is 1.20 meters.

2.3 Monitoring Vessel Static Draft

To correctly process soundings, Caris needs to know the position of the Reference Point during survey operations. This point will move as equipment load, personnel, and fuel levels change. To

compensate for these changes the Static Draft is monitored daily. At the start of every survey day the motion sensor is monitored to determine vessel attitude and a measurement is made from the Reference Mark to the present waterline. If the vessel is experiencing a roll bias, due to fuel load, personnel are moved to steady the vessel at its standard attitude. This attitude was established during sea trials, by approximating vessel loads and "zeroing" the motion sensor.

- **Appling Static Draft**

The measurement is logged in the daily spreadsheet and is reduced to a static draft value that is subtracted from the distance to the zero vertical reference and the difference entered in Caris.

- **Static Draft Variation**

The Static Draft is monitored daily as mentioned above. The Static Draft of the vessel appears to have a maximum deviation of 0.01 meters. The data to date is summarized below:

Fuel Load	Static Draft (meters)
Full	0.080
.9	0.080
.8	0.080
7	0.079
.6	0.079
.5	0.079
4	0.079
.3	0.079
.25	0.079

2.4 KTD File Development for RTK GPS Water Level Data Collection and Raw Data Collection

We will be collecting RTK GPS water level elevations throughout the survey area and will be saving them as water elevations referenced to the NAVD 88 datum. This requires the preparation and use of a .KTD file. The KTD file models the difference between the ellipsoid height and the collection datum (NAVD 88) throughout the site.

3.0 HYDROGRAPHER OPERATIONS

3.1 Start of Day - System Start-up and Dock Side Checks

Upon arrival to the vessel on a planned survey day, perform the following functions or verify their occurrence. These items should be done every day before departure.

- Start generator and switch system power from shore to generator.
- If system was shut down the night before, turn on both UPS main power switches and wait for the units to power up. Trip the TEST switch once on both units to apply power to the outlets.

3.2 Start of Day – Electronics Systems Start-Up

- Verify DC Mains, 448, 595, and Autopilot are off before powering up, or logging onto, the computer systems.
- Verify that the monitors are all off via the switch on the monitor outlet strip.
- Power up the Triton Elics, NOAA 1 & NOAA 2 computers.
- Turn on the monitors via the switch on the outlet strip.
- Computer 1 & 2
  - Log on using default Logon
    - User Name osiuser
    - Password (blank)
- The Triton Elics machine is Windows 2000 and has no log on screen
- Wait for all three computer systems to fully boot
- Turn on DC Mains switch. This powers the DMS2i-05, 7400, T4000s, MX51s, CTD and radio modem
- Put the Autopilot in standby
  - Observe compass = 244 - 250 degrees
- Verify computer date/time on each system
  - Open the H11032 vessel log.xls and enter the crew arrival time, vessel departure time, and crew initials.

3.3 Start of Day - GPS Systems Check

- Activate REMCON
  - Select CLEAR to acknowledge power-up
  - Select POSITION
    - Verify Mode is RTK FIX
    - Verify position
      - Lat ~ 35 50 40.8
      - Lon ~ 75 39 19.6
- Minimize REMCON

3.4 Start of Day – Klein 595

- Check mount
- Check connector
- Check cable and lock ring

- Check Fish body screws
- Apply power to unit
- Press "any" button to start system
- Press enter once, and left arrow once to stop printer

3.5 Start of Day – Innerspace 448

- Verify paper supply in unit
- Set power to on to verify date and time – correct if necessary
- Set power back to standby
- Add Start of Day Annotation
    - Registry #
    - Julian Date
    - Calendar Date
    - Vessel
    - Transducer in use
    - Operators
    - Roll #

3.6 Start of Day – Logging

Open Survey Log
Log date and personnel on board
Log WX observations at start of day
Log activities at dock

3.7 Start of Day – HYPACK MAX

- Open Explorer
- Create a folders in the HYPACK/PROJECTS//DATA1/ folder with a naming scheme of ###MAX1 where ### is the Julian date of the survey day. (Daily survey directory) Create a separate folder for each survey day.
- Start Hypack MAX
    - Verify that correct Line File is Enabled
    - Verify that correct background chart is enabled
    - Verify Geodesy
- Start Survey
    - Open Dialog box under Options/Project Options
        - Set Project directory to the daily survey directory.
        - Set the Target directory to the daily survey directory.
        - Verify that the other information is correct and that Long Filenames are enabled.
    - Verify all alarms are off (except 448)

- Verify that all equipment is in normal locations (generator, etc.)
- Ensure vessel is in Reference position. Have vessel captain move the vessel as needed. In Survey, click on Targets, Select, and then Change File. Select the file NAVCHK.TGT from the project directory. Select the dockside nav-check point and right click on it to "select" target. Observe distance to target. If distance is excessive. (Value +/- 1.5 meters) determine what the problem is and correct it. Take a target (F5).
- Modify the target properties (F6) to name it *XXX AM NAV CHK* where XXX is the Julian Date. Add entries in Comments section: *Pitch X.X Roll X.X Hdg XXX.X* in which you record the observed pitch, roll, and heading as observed at the dock.
- Dockside Limits:
  - Pitch 0.0 +/- .2
  - Roll 0.0 +/- .5
  - Heading 246 +/-5 deg.
- Evaluate if values exceed the limits.
- Log the time in the "activity sheet" of the H11032 survey. Also, place an "x" in the roll, pitch, and heading columns on the same sheet to indicate they have been checked.

- **Dockside static draft:**
  - Observe the ROLL value from the MRU and move people to normal positions within the vessel, or as necessary to compensate for fuel load, to achieve a "zero" roll while measuring the static draft from "Reference Mark" to the water's surface. Record the measured value in survey log. Correct the measurement to true static draft value with formula provided. Also note the RTK tide displayed on the NOAA1 Hypack Max data display and enter it in the daily log sheet.
- **Dockside RTK water level check**
  - Observe the local water level reading and enter it in the RTK vs. Observed section of the daily log sheet. Compare the NAVD-88 value calculated by the log sheet with the value recorded from Hypack Max.

3.8 Start of Day – ISIS

- Open Windows Explorer
- Verify space unavailable on data drive E: > 10 GB. If less than 10 GB you need to clear out older (already archived) files to make space.
- Create a new directory on that drive in the H11032 ISIS folder based on the following format:
  - XXXISIS - With X = to Julian day
- Minimize Windows Explorer

- Start ISIS system from the H11032 ISIS shortcut. (This starts ISIS with the correct config file)
    - Set working directory for Isis under Configure>Hypack DDE> *Start each filename with* to daily directory
    - Set Target working directory under Tools>Target>File>Set Working Directory
- Verify next contact number is set in Tools>Target> Edit>Set Contact Number
- Set unit to Start Record to screen only- File>Start Recording>Display Only
- Set Layback—View>Layback>Enter value>Accept
- Set threshold in waterfall by right click—Threshold =1
- Set waterfall window values as shown below
- Open Sensor window- Windows>Status & Control>Sensors
- If you want to view 448 depth - Aux 1 displays depth
- Open Altitude window
- Click on symbol of Alt: in Telemetry window of Parameter Display

- **Annotations**
    - Annotations are kept in a WordPad document name JD###.TXT where ### is the Julian Date. This file is kept open on the Isis machine and annotations are copied and "pasted" into the **NOTE:** section of the .XTF.
    - SSS annotations must be recorded in the notes section of the Isis box at:
        - At start of line
        - When surface objects are noted
        - When SS tuning, range, cable out, or any other parameters are changed

4.0 CONFIDENCE CHECKS

Confidence Checks H11032-JD160-06092002-RV WILLING II/PORT

Confidence Checks H11032-JD160-06092002-RV WILLING II/STBD

Confidence Checks H11032-JD160-06092002-RV WILLING II/BOTH

Registry#/Julian Date/Calendar day/Towing Vessel/Channel

5.0 INTERFERENCE

H11032-JD160-06092002-RV WILLING II/Wake

H11032-JD160-06092002-RV WILLING II/Biologic

Registry#/Julian Date/Calendar day/Towing Vessel/Type of Interference

- **6.0 DURING TRANSIT TO SITE**

  - Ensure the shore power cable is stowed.
  - Remove all dock lines and depart.

7.0 ON-SITE – PRIOR TO SURVEYING

- Determine sound velocity and enter into machines
- Isis – **Configure/Sound Velocity**
- Hypack Max – **Options/Navigation/Roxann Sound Velocity**
- Innerspace 448 – Dial in as **Speed of Sound**
- Bar Check
- Depth confidence check
- Deploy SSS for appropriate tow
- Check SSS Range

7.1 Daily Average Speed of Sound

- Obtain speed of sound readings. Enter in 448, Isis, and in HYPACK MAX - Survey, under OPTIONS, Navigation Parameters as "Roxann Sound Vel. Verify value is representative of prior values.

- **7.2 BAR Check (Depth)**
  - Verify that the average speed of sound from the days first cast is entered into the 448
  - Lower the barcheck to the lowest 1.0 meter increment available referencing the 1 meter marks to the 448 draft mark on the transducer vertical pole.
  - Start the 448 paper and record the bar at one meter intervals to 1.0 meters.

- **7.3 Confidence Check (Depth)**

  - Check 448 to insure correct sound velocity entered, draft=0.0, tide=0. Mode Auto, gate 4, replies 8. Turn 448 from STBY to ON just prior to check to record date, time, speed of sound, and draft on paper record.
  - Record depth on paper record as Hydrographer lowers bar to seafloor. On the "MARK" given by the hydrographer as the bar is touching the seafloor, toggle the FIX MARK switch on the 448. The hydrographer will measure the distance from the seafloor to the water surface using the barcheck marks and

by measuring between marks. Take target.(F5) Name target XXX Depth Confidence Check. Return 448 to STBY mode.

- Annotate paper record with:
  - Depth Confidence Check
  - H11032
  - Julian Date XXX
  - Operator Initials
  - Bar Check = X.X m (meters)
  - Calculated 448 depth by adding displayed depth to daily static draft.

7.4 Confidence Check (Sidescan)

- While collecting data:
- ISIS operator will enter the appropriate annotation into the **NOTE:** section of the .XTF while online. The time is entered into the daily log and noted as a confidence check .
- At times other than during regular data collection
- A line can be run outside of regular data collection to demonstrate that the sidescan sonar system is able to detect targets out to the full extent of the selected range. The Hypack operator selects line 900 to record the data. The XTE value in *Survey/Options/Navigation Parameters* should be changed to 200000 to avoid unnecessary TEXT log entries. Start the line when ISIS is ready.

8.0 BEFORE ON LINE DATA COLLECTION

8.1 Computer 1 - Hypack Max

Start Survey

Verify correct line entered, and line azimuth is correct. Change if necessary.

8.2 Computer 2 - Hypack Max

Start Survey – start logging prior to BOL.

8.3 Innerspace 448

Turn 448 alarms on (if off) – verify digital depth is ok Start Paper

8.4 ISIS

Verify ISIS is ready.

8.5 Heave

Verify Heave is ready.

Create a target (F5) and change it's properties (F6) to DECK CTD = XXXX.X. (The value observed at the beginning of line)

9.0 START OF LINE

- Save / Clear any contacts in the Target window
- Verify SSS data quality and bottom track prior to start
- Verify coastal line start of Isis
    - Watch file size increment
    - Check destination directory for file

10.0 ONLINE

Observe digital depths, heave, and profile window to verify proper operation. In shallow areas assist the vessel helmsman by closely monitoring the depth of water. Immediately notify helmsman of hazardous condition. Watch water depth to QA/QC alt. of SSS. Watch vessel speed.

Observe Sidescan record in Isis. Mark targets & put target in Hypack so as to allow checking the target on the next pass.

Periodically observe Deck CTD value, DIM value, heave, vessel speed, and CTD time interval. Observe Navigation map for holes in Isis.

10.1 Gap Tracking - Sidescan

If a condition is observed that may create a gap in the Sidescan data the operator hits F5 on Computer 1 to create target. The operator then evaluates further. If a gap is declared the target will be called up for modification (F6). The default name in the target name field will be changed to XXX SS GAP; where XXX is the julian date. Further info will be entered into the notes field as follows:

Start & end time of gap, channel (port/stbd) Line designation
Example:
034 SS GAP
Notes: 16:37:00 to 16:37:45, Port Channel, Line 201_1549.034, type of interference
Ensure that Gap is entered in H11032 daily log.

10.2 Gap Tracking - Singlebeam

Hypack operator hits F5 and creates a target as SB gap is seen. Operator modifies target (F6) to change name to XXX SB GAP. (XXX is the Julian date) Ensure that Gap is entered in survey daily log file.

- **11.0 END OF LINE**

  - Save all contacts as follows, and report final contact number in log
    - Target>File>Save All>Yes if not saved already

12.0 END OF DAY

Review ASCII text file for alarms

12.1 End Of Day - ISIS

- Exit from Isis
- Close Target window if still active
- Log off machine or shut down based on required backup situation

12.2 Archiving Procedure

- Data from all sources is colleted in Computer 1archive for archiving and data transmittal preparation
- A separate directory is established for each survey day with a subdirectory structure where each type of data is stored
- The structure and file types are outlines below

DIRECTORY NAME		FILE NAMES	
XXX Data\Docs	All documents created	H11032 Survey Log.XLS	Summary of all activities
		Willing II_offsets_1_19.DWG	Vessel layout and system offsets
XXX Data\XXXisis	All Isis data files	*.XTF XXX.LOG *.CON, XXX-00-contact.TXT	All .XTF files from the day Daily Isis survey log Original Isis contact files

XXX Data\Max_Support	Hypack MAX support files	Varied file types	Setup and support files for Hypack MAX operation Hypack MAX operations and alarms summary .INI files used for MAX
XXX Data\XXXmax1	Hypack MAX data files and .log file	*.RAW *.TGT	All Hypack data lines .TGT is MAX target file

- A directory template is available with all subdirectories established with an XXX, copy this template to Computer 1 and replace XXX with Julian day.
- Removable Hard Drive
  - A copy of each days data are copied from Computer 1 to a removable hard drive at the end of each survey day.
  - The Drive is then taken to the project office where the data is archived.
- XTF Data
  - Move the survey log from D:\root to daily directory at the end of the survey day
- Hypack Data
  - Copy both the TGT and the TXT file for the day to the data archive.
- Document Files
  - Copy the Daily Survey Log to the Daily Directory Doc section
  - Copy the Master Log.XLS to the Daily Directory Doc section
  - Copy any other relevant documents or drawings to this section
- Misc Section
  - Place any other non-standard files into this directory.

- **12.3 <u>End of Day: System Shut Down and Dock Side Checks</u>**

Upon arrival at the dock, perform the following functions or verify their occurrence. These items should be done every day before departure from the vessel.

- Secure all dock lines and hook up the shore power cable upon arrival at the dock, log arrival time in vessel log.
-
- Read the vessel fuel gauge and enter the value in “Activities Section” of Daily Log
- Capacity is approximately 120 gallons

- Ensure vessel has all appropriate supplies for the next day. Fuel, disks, FEDEX supplies, food, paper supplies, and water.
- Switch the system over to shore power after verify unneeded systems are off.
- Turn off the DC Mains and Autopilot.
- Verify you have the Data package and any files that will be e-mailed with you.
- Ensure all lights and boat electronics are off. Check all windows. Ensure bilge pumps are on. Lock back door upon departure.

12.4 Misc. System Operations

12.4.1 Klein 595

- Lower fish into the water to test operation

- Deploy fish and note cable out for layback calculations.
- Verify SSS image quality on Isis

- End of Day
  - Power Off
  - Recover Fish
  - Inspect entire wet end of system for wear – damage

12.4.2 Innerspace 448

- On-site
  - Input average speed of sound from first SVP and verify entry into all other systems
    - 448 – Hypack – Isis
- Start of Line
  - Alarm on
    - Good bottom lock
  - Verify range, gain, mode, and gate settings for upcoming line conditions.
  - Verify proper sound velocity based on first cast
  - Unit in standby power unless performing confidence check or time check

- End of day
  - Turn unit off
  - Remove and archive sounding roll
  - Verify Sounding pole is raised
  - Verify paper supply on board

- Periodic Maintenance

- Clean print head

APPENDIX 3

(The attached SOP includes Attachment A: *Ocean Surveys, Inc. Manual of Standard Operating Procedures.* This attachment contains SOPs for the operation and calibration of navigational and geophysical survey instrumentation. Not all of the SOPs included in this attachment apply to the Sub-Bottom Profiling Test SOP.)

STANDARD OPERATING PROCEDURE FOR SUB-BOTTOM PROFILING SURVEYS

1. Tests of acoustic- and GPR-based sub-bottom profiling equipment will occur over two to three week period on the Upper Hudson River just north of the Northumberland Dam near Hudson River Mile (HRM) 184 and in the Thompson Island Pool, near HRM 190 at Griffin Island, and near HRM 189.4 at Moses Kill. Since this is a well-traveled navigational channel, the work will be coordinated with the Canal Corporation, as required by the Health and Safety Plan and the Community Health and Safety Plan. In addition, the sampling vessels will maintain contact with the Canal Corporation using marine band channel 13.

2. The sub-bottom profiling tests will utilize GPS receivers (Trimble 7400 MSi) to acquire navigation data using shore-based reference stations with known coordinates and elevations. Differential correctors determined at these stations will be transmitted to the survey vessel where they will be used by the onboard receiver using Real Time Kinematic OTF software to determine the accurate position of the GPS antenna in the vertical and horizontal planes. These data will be logged on board at one-second intervals for the duration of the survey. Data quality parameters will also be logged and monitored by the onboard navigator with flags put on all data points which do not meet the quality limits set. The specified accuracy for this system is +/- 2 cm when satellite configuration is sufficient.

3. The sub-bottom profiling tests will focus on one technique at a time – either acoustic or GPR. Tests of the acoustic sub-bottom profiling equipment will be tested along 4-5 transects at each survey location using an EdgeTech Geostar Chirp sub-bottom profiler with both 4-24 kHz and 2-16 kHz transducers. Once the acoustic survey is completed, tests of GPR sub-bottom profiling techniques will be conducted along the same transects using a

GSSI SIR 2000 Ground Penetrating Radar system with 100, 200, 300 and 500 MHz antenna.

4. Before leaving dock, the sub-bottom survey crew will check to make sure all navigation and instrument systems are working properly. Calibrate and set navigation instruments based on the instrument-specific standard operating procedures (Attachment A). Prepare survey equipment for start of daily survey operations including: deployment of sonar tow fish into water (or deployment of GPR antenna), measurement of survey equipment offsets, daily speed of sound test, and other required pre-survey activities.

5. Navigate to coordinates of first transect. Transect coordinates and headings are based on tracklines that intersect Sediment Sampling and Analysis Program (SSAP) coring locations in the vicinity of historical coring locations that show stratification of a variety of sediment types. Transect coordinates and headings will be provided to the sub-bottom survey crew for import into the navigation computer. A Coastal Oceanographics "Hypack Max" will be used for trackline design, navigation, trackline control, and digital depth and RTK DGPS data logging.

6. Align survey vessel along longitudinal transect and confirm autopilot heading and operation. Start data acquisition and commence sub-bottom survey tests along transect. Conduct acoustic (or GPR) sub-bottom profiling tests. Test multiple frequencies along transect and note frequencies of highest resolution. Export and log the sub-bottom imagery to the ISIS data acquisition platform. Enter all system annotations in the ISIS XTF notes field.

7. Use a digital depth sounder to collect water depth information along each transect. Log depth data to the Hypack Max system.

8. During the survey, perform periodic manual probing and visual characterization of sediments. Note coordinates and results of probing or characterization in the field log. Note coordinates of areas that may need additional confirmatory sampling and sediment grain size analysis to ground-truth the sub-bottom data in the field log.

9. Note relevant observations and changes in operational procedures to the field log. These may include: coordinates of observed obstructions or artifacts; areas where interferences or other conditions limit survey resolution, and coordinates where adjustments to the tow fish or GPR antenna are made. Repeat survey of the entire transect using acoustic (or GPR) frequencies that showed highest resolution during preliminary survey tests.

10. At the end of each transect, confirm successful data acquisition and storage, navigation and equipment calibrations and settings. Log time and coordinates at end of each transect line surveyed.

11. Prepare equipment for navigation to next transect; navigate to next transect.

12. Repeat steps 4-12 and collect sub-bottom data along each transect until representative sub-bottom data for each has been acquired in each survey section for each survey technique - both acoustic and GPR.

13. All raw survey data and information (e.g., field notes, instrumentation frequencies) must be documented electronically or in a field note book. At the end of each day, check daily computer data from the Hypack Max and ISIS systems for error flags. Output all notes to an ASCII file and store with the raw records. Back-up copies of the raw electronic data and make copies of all field log entries.

ATTACHMENT A

OCEAN SURVEYS, INC.
MANUAL OF
STANDARD OPERATING PROCEDURES

(Geophysical Survey Instruments)

1.1.1.1.1 TABLE OF CONTENTS

Page

1.0 INITIAL EQUIPMENT SETUP

This is a draft document. The most recent modification was on 07/31/02 by MLK. New versions will be distributed as they are created.

There are presently several documents that are associated with this that are not included at this time.

1 Caris offset drawing
2 Hypack offset drawing
3 System wiring document
4 System comm. Port settings and data formats

1.1 General Tasks Before Start of Survey

- Obtain reviewed Survey Plan
- Notify GE of vessel movement
- Obtain permits for movement through and between locks
- Obtain proper charts and update with all Notice to Mariners
- Verify availability of CG DGPS correctors and RTK stations
- Document equipment installation
    - Establish Boat 0,0,0
        - Vessel fore/aft centerline, aft edge of athwart ship I-Beam on A-Frame, point on aft deck slightly above waterline
    - Measure and record all offsets
        - Trimble 7400 MSi DGPS's
            - Navigation antenna X, Y, Z
            - Reference antenna X, Y, Z
        - Trimble 7400 RTK GPS
            - Antenna to waterline
            - X & Y to boat 0,0
        - Innerspace 448 X, Y, Z

- TSS DMS 2i-05
  - X, Y, Z
  - Zero out mounting angles with appropriate vessel loading – see procedure in TSS section

- Robertson Compass
  - X, Y
  - Align to true heading of vessel centerline – see procedure in Compass section

- Sidescan Tow Point X, Y, - Z left at 0.0 m for proper Caris import of layback

- Subbottom Profiler Tow Point X, Y, - Z left at 0.0 m for proper Hypack import of layback

1.2 Equipment Setup

1.1.1.1.2 ***1.2.1 Trimble 7400 Receiver***

- Initial Settings
  - RTCM Output = off
  - RTCM Input
    - Inputs ON
    - Port = 2
    - Format = USCG
    - ASCII Printout off
    - Beeper Off
    - Station = any
    - Age Limit 20 sec.
    - Integrity Monitor Off
  - Power Up Control
    - Do not default controls at power up
  - SV Enable/Disable
    - Disabled mode = none
  - Adjust local time

        - Time offset EDT-UTC = -4 hrs
        - Time Zone Identifier = EDT
    - Baud Rate Format
        - Port 1 = 9600-N-8-1
        - Port 2 = 9600-N-8-1
    - Remote Protocol
        - Data Collector Compatible
    - Reference Position
        - Lat = 35 50 40.91718
        - Lon = 075 39 19.57021
        - Height = -37.529
        - (Note, may be changed during survey by selecting **HERE** to get local position and current ellipsoid height for Lat/Lon – Fixed height)
    - Masks/Sync Time
        - Elevation Mask = 8
        - PDOP Mask = 5
        - SV Sync Time = 1.0
    - Positioning Modes
        - Weighted solution enabled
    - Lat/Lon Height Always
- Power Controls
    - Charger and Power output disabled
- NMEA 183 Output
    - Port 1 Enabled
        - GGA, VTG, ZDA
- Cycle Printouts = Off
- 1 pps output = disabled
- Default controls – **DO NOT USE!!! RESETS TO FACTORY**
- Modify
    - Units of Measure
        - Lat/Lon Degrees = Deg.Min.Sec.
        - Time = 24 Hr UTC
        - Position = WGS-84 LLH
    - Altitude Reference
        - Height above ellipsoid

1.2.2 MX-51 Beacon Receivers

- Initial Settings - DGPS1

- **HUDSON FALLS, NY**
  Status: Operational
  RBn Antenna Location: 43° 16.21' N73° 32.31' W
  REFSTA Ant Location (A): 43° 16.2491' N73° 32.34705' W
  REFSTA Ant Location (B): 43° 16.2637' N73° 32.34534' W
  REFSTA RTCM SC-104 ID (A): 94
  REFSTA RTCM SC-104 ID (B): 95
  REFSTA FIRMWARE VERSION: RD00-1C19
  Broadcast Site ID: 844
  Transmission Frequency: 324 KHZ
  Transmission Rate: 200 BPS
  Signal Strength: 100uV/m at 135NM

- CTToolbox should be used to reload H11032R.CNF (config file) if necessary. The following settings are in H11032R.CNF
  - CONTROL/BASE STATION
    - Input using **HERE** at Hudson Falls
    - LAT 35 50 40.77420
    - LON 075 39 19.81768
    - HGT – 0035.870
    - ANT Height 000.000
  - CONTROL/SV ENABLE/DISABLE
    - ALL – ENABLE
  - CONTROL/GENERAL CONTROLS
    - ELEV. MASK: 08
    - PDOP MASK : 05
    - MEAS RATE 1 HZ
    - MOTION: KINEMATIC
  - CONTROL/POWER CHARGER
    - POWER OUTPUT MODE DISABLED
  - CONTROL 1PPS OUTPUT
    - 1 PPS OFF
    - ASCII TIME TAG PORT OFF
  - CONTROL SERIAL PORT OUTPUT
    - NMEA/ASCII OUTPUT
    - GGK
      - PORT 2
      - 1 HZ
    - ZDA
      - PORT 2
      - 1 HZ

    - All others off
- STREAMED OUTPUT
    - ALL OFF
- RT17/BINARY OUTPUT
    - ALL OFF
- CMR/RTCM
    - BASE – MOVING
    - CMR PORT – OFF
    - NAME - cref
    - RTCM PORT – OFF
    - TYPE - 1
- CONTROL/SERIAL PORT SETUP
    - PORT1 9600 8-NONE-1
    - PORT 2 9600 8-NONE-1 NONE
    - PORT 3 9600 8-NONE-1
    - PORT 4 9600 8-NONE-1 NONE
- CONTROL/INPUT SETUP
    - USE RTCM STATION – ANY
    - RTK/DGPS AUTO SWITCH RANGE – 20.0 KM

1.2.3 Compass (Side scan sonar operations)

- Initial Calibration Procedure
  - Load vessel, as it will be for survey ops. Remove any large ferrous objects from the vicinity of the compass.
  - Position the vessel in open water
  - Apply power to the Robertson autopilot
  - Begin by turning the vessel to starboard.
  - Select **INSTALLATION/RFC COMP calibration**.
  - Calibration should complete after ~ 1 ¼ turns and should be verified by a display of **Calibration confirmed**.
- Determine and apply Compass Offset
  - Con the vessel on a straight line while observing the heading computed by the GPS system.
  - Adjust the offset by turning the autopilot knob to match the pilot compass heading to the gps heading. Note the applied offset. (This puts the pilot compass into "TRUE" heading.)

1.2.4 TSS DMS 2i-05 (Hydrographic survey operations)

- Initial Settings
  - Set baud rate/format to 19200,N, 8,1
  - Heave bandwidth = SHORT
  - Output Rate = 50 hz.
  - GPS data input settings = NMEA Local 9600, 8, N, 1
    - Check GPS RAW and CALCULATED input
  - GYRO data input settings = NMEA Local 4800, 8, N, 1
    - Check Compass RAW & CALCULATED INPUTS
  - Data output format = TSS1 19200, 8, N, 1
  - Zero out mounting angles. Document mounting angles with screen grab.
    - Stabilize vessel with static loads approximating those that will be experienced during the survey.
    - Access TSS through communication program and set mount angles automatically by averaging data for 5 minutes
    - Accept values and screen grab settings

Restart TSS operation and exit from program

Mount Angle Setting Recorded

06/04/02

```
---------------------------------
DMS 2-05 Version 2.03 Terminal Mode
---------------------------------
Sensor Mounting

Orientation : Vertical
Roll  Mount Angle [  1.741  deg] :
Pitch Mount Angle [  1.711  deg] :
Yaw Mount Angle [  0.000  deg] :
```

- **Do Not Change These Settings!**

1.1.1.1.3

1.2.5 Innerspace 448 (Hydrographic survey operations)

- Initial Settings
  - Verify the following initial settings
    - Gain = Approx. 10 o'clock setting
    - Range = 0-15 M
    - Mode = Meters
    - Chart Speed = 4
    - Range Multiplier = X1
    - Input default speed of sound of 1500 m/s
    - Set draft = 0.0
    - Tide = 0
    - Initial = 5
    - Gate = 2
    - Mode = Gated
    - Reply = 16
    - Alarm on during survey
    - Set variable power TX board to Low, to limit interference with SS and MB
    - Set internal TVG curve switch to open/open or +60 db. This was needed to receive quality data at the above mentioned low power setting with our combination of components
    - Set date & time – See back of paper carrier
    - Load paper per picture on back of paper door

1.1.1.2

1.2.6 Klein 595 (Side scan sonar operations)

- Initial Recorder Setup
  - Set system to factory defaults by pushing left button on the CPU board
    - This resets all values to factory default
    - It also resets all gain curves and other "adaptive controls prior to calibration
      - A calibration should be preformed, per the manuals description any time a component is changed, like a cable or fish
  - Set time/date in submenu
    - Add "*" to time and date to print it when an event is pressed. This can be used to log tuning changes and rub tests
  - Set system to the following values:
    - Auto CPU
      - Altitude = 0,0
      - Return = 0
      - Offset = 2
    - Auto TVG Port
      - Normal
      - Atten. = 9
      - Salt Water
    - Auto TVG Starboard
      - Normal
      - Atten = 9
      - Salt water
    - Printer = Off
    - Range = 25 Add "*" to field
    - Scale lines = 10 Add "*" to field
    - Source = Fish
    - Channel = 1 | 2
    - Speed = Manual –1.0 Set to avoid alarms
    - Altitude = Auto
    - Mapping Mode = Off
    - Altitude Alarm = Off
    - Auto Mark = Off
    - Event Count = Off
    - Event Mark = Off

        - Side Scan Expand = Off
        - Profiler Expand = Off
        - Nav Source = Nav3* - used for external Eventing option
    - Follow the calibration found in the operations manual on 3-34 to tune for site conditions
    - Document tune-up settings in SSS annotations
    - Document tow configuration and Cable out in SSS annotations
        - Tow Point
            - See attached drawing for exact location
            - The tow point is a sheave mounted to a bowsprit. In operation the fish is lowered to1meter in the water as the vessel is moving at survey speed.
            - The cable is fair leaded back to the stern on the outside of the bowsprit mount. Cable out measurement is taken from the point of the sheave closest to the mount point
            - The layback was measured by observing the fish under survey conditions and measuring from the center of the xducers to the tow point.
            - Document any changes made to the recorder online in the Isis notes section
    - Initial Fish Setup
        - Depression angle = 20 degree's
        - 500 KHz only
        - 100 KHz disabled in fish – SCR trigger is disconnected.
        - Attach depressor to fish

    - Internal Jumpers
        - A/D board jumpers should be set to reflect proper software version (checked 050202)
        - Fish Tape I/O jumper should be set to either 15v for short cable or 24v for long cable (winch) (checked 05/2/02 set to 15v)
        - Verify which channel is tracking altitude on the Connector interface board

1.2.7 EdgeTech Geostar (Sub-bottom profiling operations)

The power amplifier power input is manually set to 110 or 220VAC. To access the switch on the amplifier, it must be removed from the 19" rack, the switch is located on the right side of the unit. The monitor and the computer are auto sensing.

1.2 Operator Controls (refer to GeoStar manual before modifying any of the default control parameters)

Review the following parameters and select to optimize data quality:

a) Normalize gain control
b) Select display gain for either or both channels (From 1 to 97, in increments of 3 dB)
c) Set Time Varying Gain (TVG) for either or both channels (From 0 to 30, in single increments)
d) Select one or two channel display based on transducer number
e) Bandwith selection (Full, High or Low)
f) Set vertical zoom (1/2, 1, 2 or 4 times) based on range and water depth
g) Set Mode selection (Acquire or Playback), acquire for data collection
h) Select Time and Data source (CPU or GPS)
i) Select Start depth (A/D delay) of display and acquisition 0 to 200m below the fish
j) Review Pulse selection (3 pulses for each towfish)
k) Set data storage selection (Iomega Jaz or hard-drive)
l) Data file management (deleting unnecessary files)
m) Set decimation factor
n) Select printer (EPC 1086) if using printer
o) Quit to shut down the system

1.2.8 GSSI SIR 2000 (Subbottom profile operations)

2.

3. Startup System

- Connect antenna.

- Connect power source.

- Press Power button. The green light above the power button should be steady. If the green light is not steady, your power source is faulty, change power source.

4. Data Collection Setup

- The blue SIR-2000 Startup Screen will appear.

- Press Enter for Standard operation.

- Press the Left arrow for Previous Setup or the Right arrow for Stored Setups.

    - Previous Setup will recall the last used operating parameter.

    - Stored Setups provide a list of factory- and user-defined settings.

- Select a factory setup based on antenna frequency or user defined setup from window using arrow keys.

    - Press the Enter to recall the setup file and then press Enter to confirm.

    - System will initialize (you will see "servo in process") according to selected setup.

5. Data Collect Setup

- The Screen will open with a Linescan display on the left and the O-Scope window on the right. The User menu is navigated with arrow keys.

- The auto setting recalled will set data collection parameters according to "rule of thumb" guidelines. All settings can be changed by the user, if desired. Refer to SIR 2000 manual for additional information

1.2.9 Bar Check

- Initial Setup and Calibration
  - Determine maximum depth of survey and depth units
    - Sheet A maximum depth is in the 10 meter range
    - Survey depth units are meters
  - Construct Bar Check per OSI standards
  - Type 1
    - .2 meter diameter lead disk with eye bolt
    - Imprint a "serial number" onto bar
      - "A"
      - "B"
    - Coated aircraft cable
    - Brass marker beads at appropriate intervals
      - Minimum of every 1 meter throughout the survey depths
      - This is to allow use of a "pocket rod" to read inter bead values
    - Also mark cable on both sides of bead with a "sharpie" to help identify bead slips
    - Measure bead locations with steel tape to the nearest 0.01 meter increment
    - Record bar s/n and all other information required on OSI Lead Line Calibration form
  - Recalibration
    - Recalibrate Bar Check every 6 months, or after any action that could possibly affect the condition of the Bar Check, such as snagging line on bottom.
    - Recalibrate at the completion of the survey
  - Maintenance
    - Periodically examine the eye bolts and cables

  - Type II
    - Aluminum square-beam > width of boat with target at position of in hull xducer
    - Imprint a "serial number" onto bar
    - Coated aircraft cable
    - Brass marker beads at appropriate intervals
    - Minimum of every 1 meter throughout the survey depths
      - This is to allow use of a "pocket rod" to read inter bead values

        - Also mark cable on both sides of bead with a "sharpie" to help identify bead slips
        - Measure bead locations with steel tape to the nearest 0.01 meter increment
        - Record bar s/n and all other information required on OSI Lead Line Calibration form
    - Recalibration
        - Recalibrate Bar Check every 6 months, or after any action that could possibly affect the condition of the Bar Check, such as snagging line on bottom.
        - Recalibrate at the completion of the survey
    - Maintenance
    - Periodically examine the eye bolts and cables

1.2.10 GE 1 Computer System

- Start Up
    - Verify DC Mains and Autopilot are off before powering up, or logging onto, system
    - Log on using default Logon
        - User Name osiuser
        - Password (blank)
- Verify time zone is set to (GMT) Greenwich Mean Time: Dublin, Edinburgh, Lisbon, London.
- DO NOT CHECK "Automatically adjust clock for daylight savings time.

- Start HyPack MAX with appropriate shortcut
    - Open new project named GE-1
        - Create folders in the project folder named DATA1
        - Set geodesy to UTM Zone 18 WGS 84
        - HYPACK HARDWARE SETUP
            - New File
            - NAV - NMEA183.DLL
                - Name = DGPS1
                - Update Frequency = 50ms
                - Type
                    - Position
                - Options
                    - Record raw data
                    - Record quality data

    - Record
        - Always
    - Connect
        - Serial Port
            - COM3, 9600,8,none, 1,Flow Control = none
    - Offsets
        - Starboard = -.35
        - Forward = + .23
        - Height = +1.97
        - Latency = 0.860
    - Setup
        - Standard NMEA 0183 sentences to be used
            - GGA
        - HDOP Limit = 2.5
        - Minimum Satellites = 4
        - Use ZDA message for time tag = Disabled
        - Send alarm when non differential
- Depth – Innerspace 448 {Serial} - IN448.DLL
    - Name = 448
    - Update Frequency = 50
    - Type
        - Echo sounder
    - Options
        - Record raw data
        - Record quality data
        - Paper Annotation
    - Record
        - Always
    - Connect
        - Serial Port
            - COM6, 9600,8,none, 1
    - Offsets
        - Starboard = 0.0
        - Forward = 0.0
        - Height = +.8 NOTE!!! .8 meters used as “display offset”. See Draft explanation
        - Latency = 0.000
    - Setup

        - Send annotation string with event mark
        - Multiply not needed
- Auto Pilot Compass – NMEA.DLL
    - Name = AP Compass
    - Update Frequency = 50
    - Type
        - Heading
    - Options
        - Record raw data
        - Record quality data
    - Record
        - Always
    - Connect
        - Serial Port
            - COM5, 4800,8,none, 1
    - Offsets
        - All zero
    - Setup
        - Sentence to be used
- HDG
- Auto Pilot – NMEA.DLL
    - Name = AP XTE
    - Update Frequency = 500
    - Type
        - Output
    - Options
        - Record raw data
        - Record quality data
    - Record
        - Always
    - Connect
        - Serial Port
            - COM8, 4800,8,none, 1
    - Offsets
        - All zero
    - Setup
        - Sentence to be used
- GGA
    - Sentence to generate
    - APB
    - GLL output places = 4
    - XTE (Nautical Miles) checked

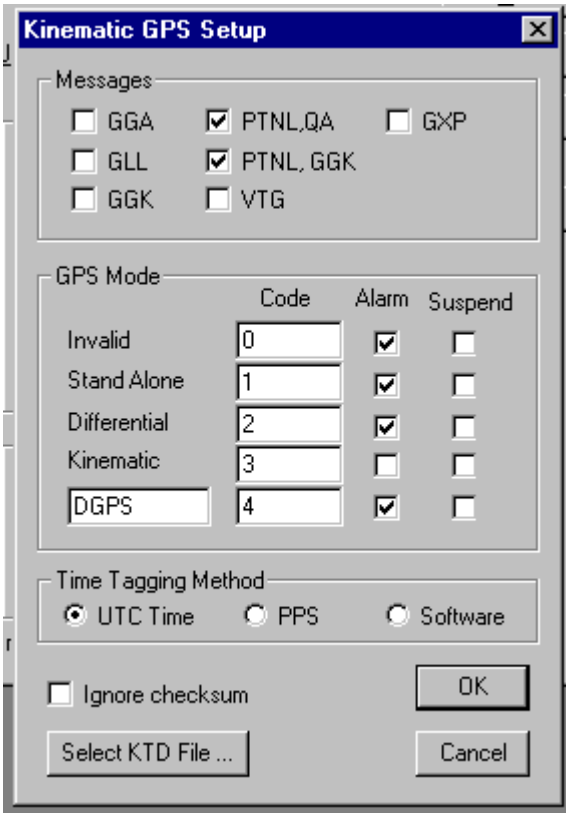
  - Output to hundredth decimal place = Enabled
  - XTE Factor = 0.0

- File Server – Delph Output – DELPH.DLL
  - Name = Isis Out
  - Update Frequency = 20000
  - Type
    - (nothing checked)
  - Options
    - Record raw data
    - Record quality data
    - Paper Annotation
  - Record
    - Always
  - Connect
    - Serial Port
      - COM7, 9600,8,none, 1
  - Offsets
    - All Zero

- TSS DMS2i-05 – TSS320.DLL
  - Name = DMS2i-05
  - Update Frequency = 50
  - Type
    - Heave Compensator
    - Other
  - Options
    - Record raw data
    - Record quality data
    - Paper Annotation
  - Setup
    - Motion reference Unit Only
  - Connect
    - COM 1 19200,8,N, 1
  - Record
    - Always
  - Offsets
    - Position
    - Starboard = -.44
    - Forward = +.47
    - Vertical = -.18

- Yaw = 0
- Pitch = 0
- Roll =0
- Latency =0

- Trimble 7400 RTK OTF - KINEMATIC1.DLL
  - Name – RTK
  - Type
    - Position
    - Echosounder
    - Sync. Clock
    - Tide Gauge
  - Record RAW
  - Record Quality
  - Setup



  - SELECT KTD FILE

        - File 02ES007.KTD used for survey ops

    - Connect
        - COM2 9600,8,N, 1, Flow Control = none
    - Offsets
        - Position
        - Starboard = -1.50
        - Forward = +.25
        - Vertical = + 2.05
        - Yaw = 0
        - Pitch = 0
        - Roll =0
        - Latency =0
    - Record
        - Always

    - Create a second mobile named RTK. Transfer the RTK device to the second mobile

- URS-1 – VHW.DLL
    - Name = Speedlog
    - Update Frequency = 200
    - Type
        - Speed
        - Other
    - Options
        - Record raw data
        - Record quality data
    - Setup
        - none
    - Connect
        - COM 9 4800,8,N, 1, Flow Control = none
    - Record
        - Always
    - Offsets
        - None
- Settlement – DraftTable.dll
    - Name = Settlement
    - Update frequency = 100
    - Type

- Draft
- Setup
  - Create Draft table from Settlement and Squat test
  - Insert Draft table picture – set to 0.0 for squat test
- Offsets
  - None
- Connect
  - Ignored
- Record
  - Always

1.2.9 GE-1 CARRIS OFFSETS to BOAT

DGPS1 (NMEA183.DLL)

STBD	+1.18
FWD	+0.02
Height	+1.97
Latency	+0.00

448 (INN448.DLL)

STBD	+1.53
FWD	-0.21
Height	+0.80
Latency	+0.00

Auto Pilot Compass (NEMA.DLL)

STBD	+0.00
FWD	+0.00
Height	+0.00
Latency	+0.00

Isis Output (DELPH.DLL)

STBD	+0.00
FWD	+0.00
Height	+0.00
Latency	+0.00

Auto Pilot (NEMA.DLL)

STBD	+0.00
FWD	+0.00
Height	+0.00
Latency	+0.00

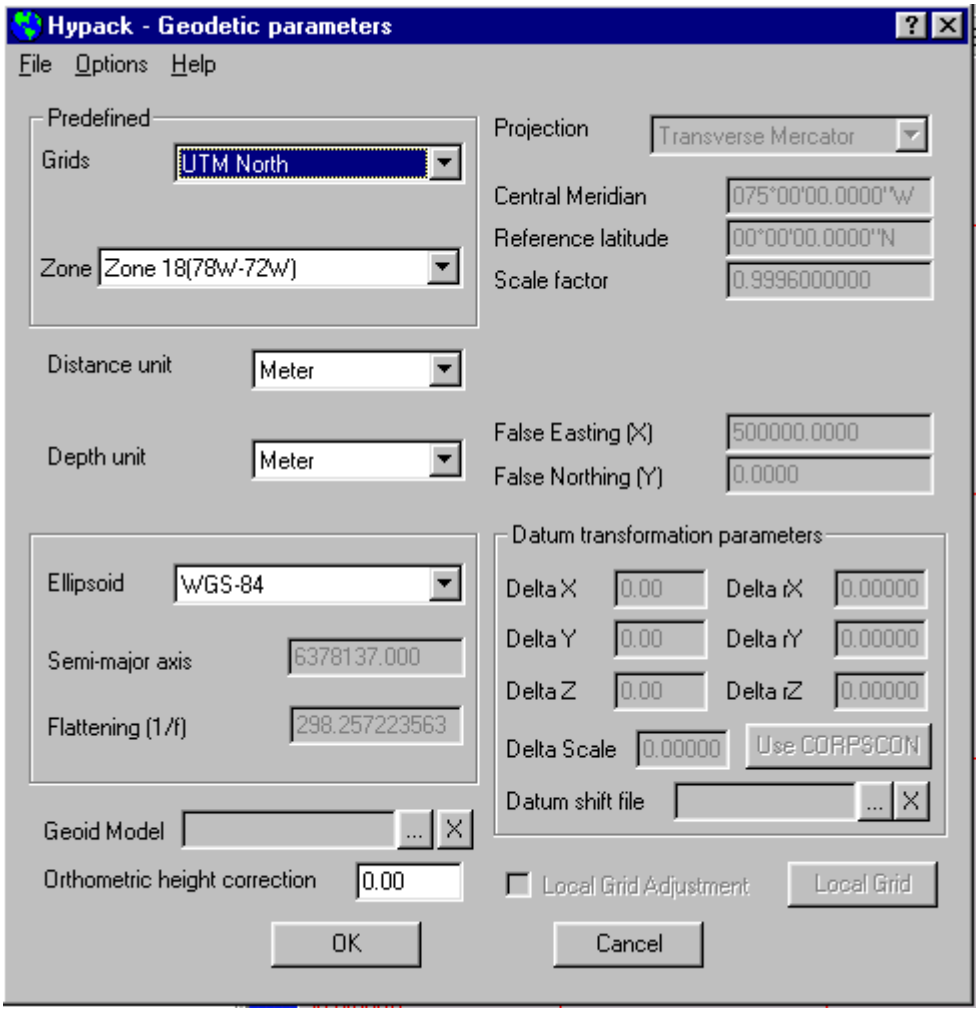
DMS 2i-05 (TSS 320.DLL)

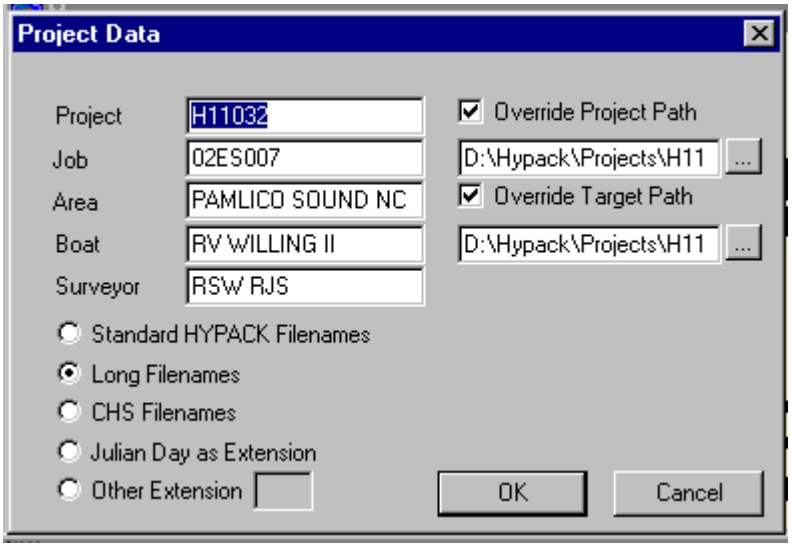
STBD	+1.09
FWD	+0.26
Height	-0.18
Latency	+0.00

RTK GPS KINEMATIC.DLL

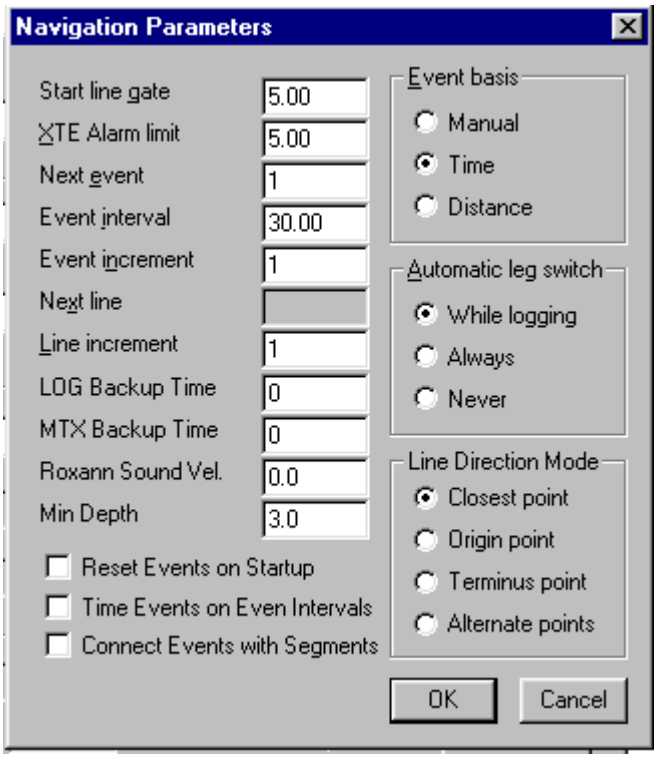
STBD	+0.03
FWD	+0.02
Height	+2.05
Latency	+0.00

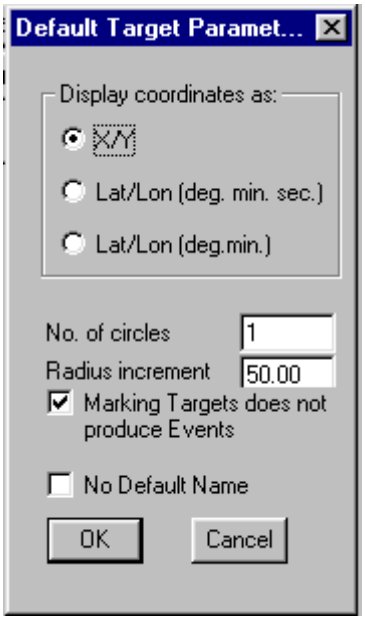
1.2.10 Other Hypack Max Settings


Hypack - Geodetic parameters
File
Options
Help
Predefined
Grids
UTM North
Zone
Zone 18(78W-72W)
Projection
Transverse Mercator
Central Meridian
075°00'00.0000"W
Reference latitude
00°00'00.0000"N
Scale factor
0.9996000000
Distance unit
Meter
Depth unit
Meter
False Easting (X)
500000.0000
False Northing (Y)
0.0000
Ellipsoid
WGS-84
Semi-major axis
6378137.000
Flattening (1/f)
298.257223563
Datum transformation parameters
Delta X
0.00
Delta rX
0.00000
Delta Y
0.00
Delta rY
0.00000
Delta Z
0.00
Delta rZ
0.00000
Delta Scale
0.00000
Use CORPSCON
Datum shift file
Geoid Model
Orthometric height correction
0.00
Local Grid Adjustment
Local Grid
OK
Cancel



NOTE: XTE ALARM set to 100000 for Sea Trials





5.1.1.1 **1.2.11 ISIS**

- Start Up
  - Verify DC Mains and Autopilot are off before powering up, or logging onto, system. Note: if monitor does not come on (yellow power/signal indicator steady yellow on lower right corner of monitor) remove power from monitor for a few seconds, then restore and turn on monitor.

  - Start Isis with Isis H11032 shortcut – **Only**
    - This calls up a specific configuration file

- File types and locations
  - H11032 ISIS Short Cut to Start Isis Desktop
  - H11032.LAY Window Layout E:\H11032 ISIS\H11032 Config\
  - H11032_140.CFG Isis configuration file D:\TEI\IsisSona\v5.91\
  - Survey. log Isis session log D:\root
    - Note: unable to redirect this file

- Initial Processor Settings
  - File Menu

- Playback N/A
- Record Setup
    - Sonar Setup
        - Pick standard analog
        - Select CHICO/CHICO PLUS Board
            - Channel 1 edit
                - Status = On
                - Name = Port
                - Type = Port SSS
                - Trigger = 1
            - Channel 2 edit
                - Status = On
                - Name = Stbd
                - Type = Starboard SSS
                - Trigger = 1
            - All other channels disabled
            - Sonar name to H11032 Klein 595 2 CH 500Khz
            - Frequency = 384.0,384.0
            - Horizontal Beam Angle = 0.2,0.2
            - Beam Width = 50.0, 50.0
            - Tilt angle = 20.0, 20.0
            - Name of server = ISISCHICO.EXE
            - Automatic control disabled
    - Serial Port 1 Heave, Pitch, Roll
        - Status = On
        - Settings = 19200, 8, N, 1
        - Template = TSS
        - Convert Lat - Long = Disabled
        - Filter Speed = Disabled
        - Navigation Latency = 0.0
    - Serial Port 2 Not used
    - Serial Port 3 GPS for SSS
        - Status = On
        - Settings = 9600, 8, N, 1
        - Template = NMEA0183 NOCLOCK
        - Convert Lat - Long = Disabled
        - Filter Speed = Disabled
        - Navigation Latency = 0.0
    - Serial Port 4 GPS for Single Beam
        - Status = On
        - Settings = 9600, 8, N, 1

- Template = NMEA0183
  - NMEA0183 SHIPPOS NOVTG
- Convert Lat - Long = Disabled
- Filter Speed = Disabled
- Navigation Latency = 0.0

- Serial Port 5 Compass
  - Status = On
  - Settings = 4800, 8, N, 1
  - Template = NMEA0183 NOCLOCK NORMC NOGLL NOVTG
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 6 May be used for Fish Altitude input
  - Better Tuning Has Made This Option Unused
    - Manual SSS Bottom Tracking Option
    - Status = Off
    - Settings = 9600 8, N, 1
    - Template = Manual
      - Modify Default = {/100}{-1.3}7
        - Change 1.3 to value needed to get correct altitude
    - Convert Lat - Long = Disabled
    - Filter Speed = Disabled
    - Navigation Latency = 0.0
- Serial Port 7 Hypack feed for Line Control
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = (Leave Blank)
    - Allows events and start/stop info in from Hypack
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 8 448 feed to Aux Sensor 1
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = Manual
    - Modify Default = {/100}1
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled

- Navigation Latency = 0.0
- Serial Port 9 RTK INPUT

- Serial Port 10 Speed Log
  - Status = On
  - Settings = 4800, 8, N, 1
  - Template = {pattern=m}s
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0

- File Format
  - Format = XTF
  - Media = Disable
  - Sample Size to Record = 16 bit
  - Samples per Channel = 1024
  - Processing Method = MAX
  - XTF File Header Notes
    - Vessel Name
    - Survey Area
    - Operator

- Configure
  - Playback Speed – as desired
    - Real Time Scrolling
      - Scroll without restoring covered data
        - This keeps system from locking up
    - Transducer Depth = 0.0
    - Ocean Tide
      - Apply Corrector = Disabled
      - Verify = 0.0
    - Sound Velocity = Average from first cast of the day
    - Multiple Pings = 1
    - Hypack DDE
      - Accept from Hypack = Disable All
      - Automatically Start Saving At Start of Line
        - Use File Name from Hypack = Enable
        - Generate File Names = Disable
        - Start Each File with = Enter Daily Directory Info
    - Cue Boxed = Disabled
    - Set Date and Time = Ignore – Will be automatically set during operation
    - Save Setup = Prompt User at Exit

- Color
  - Palette
    - SSS Colors = Grey Scale
    - Squelch = 0.0
    - Reverse Palette = Enabled
    - Strong Returns Red = Disabled
  - Grid Color
    - Voltage Grid
      - Line = Blue
      - Data = White
      - Dim = Both Enabled
    - Scale Lines Red

- View
  - Scale Lines
    - Apply Settings to = All the same
    - Scale line Unit = Distance
      - Spacing = 10
  - Depth Delay and Duration
    - Apply Settings to = All the same
    - Units = Off
  - Overlay
    - Show on Waterfall
      - Event Marks = Disabled
      - Event Text = Disabled
      - Bottom Track = Enable
    - Bookmarks
      - Save Bookmarks = Enabled
      - Display Bookmarks = Enabled
  - Down Sample = Max
  - Speed
    - Automatic = Enabled
    - Filter = Disabled
  - Heading = Automatic
  - Layback Correction
    - Apply Delta XY = Disabled
    - Apply Layback = Enable
      - Use Logged Layback = Disabled
      - Enter layback manually = Enabled

- Compute layback from Cable Out = Disabled
- Enter layback value in box provided (Currently 1.0M)
    - This field with be empty, enter value
        - Obtain value from chart
    - Click ACCEPT, current value changes to entry
    - NOTE: **DO NOT CLOSE WINDOW**
    - NOTE: CHECK AT START OF EACH LINE
    - NOTE: HAVE OPEN DURING CONTACT PICKING

- Tools
    - Target Setup
        - TargetPro.exe only
        - Target Setup
            - Height = 512
            - Width = 2048
            -
        - Target
            - File
                - **Set working Directory = Enter Daily Data Directory**
            - Tools
                - Configuration
                - Speed auto
                - Speed Corrected display = yes
                - Layback = manual
                - Horizontal beamwidth
                    - Manual, 0.0
                - Local variation = 0.00
                - Latitude/longtitude
                    - Deg Min Sec
                - Northing/Easting Display
                    - Meters
                - Range Display Units
                    - Meters
                - Speed display Units
                    - Knots
                - Misc.
                    - Automatic Audit Trail = yes
                    - Object Detection on image load
                        - None
            - Units = Meters

- Constants = Use defaults
- Set Contact Number = Start with 1 – Ensure number is consistent with contacts logged to date.
- Speed Correct = Enabled

- Parameter Window – Current File Section
  - Switch Button
    - Record Data to File Name = Blank
    - Remaining storage = Enable D: and E:
    - File Grows larger than = Disable

Altitude - Absolute

Based on 595 Range Scale

Range	8% Minimum Altitude	20% Maximum
25	2.00	5.00

Maximum System Speed

Based on 595 Ping Rate

Range	Ping Rate / Second	Maximum Speed
25	27.00	17.50

Maximum Survey Speed

Based on 10% Buffer

Range	Maximum Speed (Knots)	90 %Maximum Speed (Knots)
25	17.50	15.75

5.1.1.2 1.2.12 Robertson Autopilot

Introduction:

The factory technical representative for the parent company Simrad, is Rich Barnes (425-778-8821) who is located at Simrad, Inc., 19210 33rd Avenue West, Suite A, Lynwood, WA. 98036. The pilot was interfaced to NOAA1 to receive NMEA (modified) standard messages from Coastal Oceanographics HYPACK MAX Survey program. The vessel captain performs all operations related to the pilot.

Interface:

The pilot receives the following NMEA-0183 messages;

APB (modified by Coastal to send .#### nm of cross track error vs. .## nm, the NMEA standard)

VTG (standard)

GGA (standard)

Baud rate is 4800/N/8/1

NMEA input to the pilot is through TB 10 on the Junction Unit, Pins RX 1(+) and RX1 (-). There is no handshaking or error correction used. The Robertson RFC35R rate compass is used to provide vessel heading to all systems and outputs a NMEA message through TB10on the Junction Unit, Pins TX2(+) and TX2(-).

Operation:

The pilot starts in the **Helmsman** mode. The captain steers the vessel on to the trackline well ahead of the actual BOL and attempts to track down the line. When the vessel has stabilized online the pilot is put into the **Auto** mode. The pilot is "course steering" at this point. The captain observes the vessel motion and line tracking while adjusting the "course" using the left/right buttons on the control unit or remote control. When the vessel is steering the line and cross-track error has been reduced to a minimum (typically less than 1 meter), the captain changes to the **NAV** mode. The pilot will continue to steer in "course steering" mode for a period of time determined by an internal setting (currently at minimum – 100 sec). Then it will use the XTE value received from HYPACK MAX and attempt to adjust it's course to achieve zero XTE.

Some conditions prohibit the use of the **NAV** mode. One example is the use of a drogue chute to slow the vessel. Sea conditions that cause sudden large heading changes are another example. In these cases the pilot is left in the **Auto** mode and the left/right buttons on the control unit or remote control unit are used to con the vessel down the line.

Initial Setup:

Mechanical setup and alignment are performed at the time of installation and should require no further adjustment. There are many electronic settings that affect pilot operation. They fall in to several categories:

- Front Panel
  - Rudder – used to set the amount of rudder used by steering commands
  - Counter Rudder – used to set the opposing rudder used when crossing a course line
  - Weather – used to reduce pilot sensitivity in heavy seas
- Info Loop
- Weather Loop
- Debug Loop

Normally, only the Rudder setting is changed throughout the day. More rudder (higher #) causes closer tracking and quicker steering response. Too much rudder causes large heading swings. Too little rudder and the vessel will fail to closely follow the line.

2.0 PRE SURVEY OPERATIONS

2.1 Navigation System Check

Upon arrival in Hudson Falls a third order control disk will be located to facilitate the performance of a navigation confidence test. Two separate procedures will be performed. The first procedure is to determine the horizontal and vertical position of the project RTK GPS base station and certify it. The second procedure involves using the Trimble 7400Msi L!/L2 Kinematic OTF system to locate a check point in proximity of the survey vessel for future confidence checks.

The first procedure involves the following.

A RTK base will be set up with it's antenna positioned at a known height over a GE/QEA supplied point. The Trimble 7400Msi reference receiver is then configured to provide CMR correctors based on the following parameters.

Configuration Toolbox file D24_Base.cfg

1. Generate CMR correctors on Port 1
2. Kinematic base unit
3. A elevation mask of 13 degree's
4. A PDOP mask of 5
5. Reference position of 35 50 40.87561 Lat, 075 39 15.38597 Long, -37.75 Elev. (WGS-84 Ellipsoid height)
6. Antenna height set to 2.000 meters, Antenna mounted on a 2.00 meter rod
7. Antenna type set to L1/L2 compact resulting in a True Vertical Height of 2.062 meters

The project RTK base will be set up as a rover station, receiving corrections from the station set at various stations using the following parameters:

Configuration Toolbox file RTK_ROV.cfg

1. Receive CMR corrections on Port 1
2. Kinematic rover
3. A elevation mask of 13 degree's
4. A PDOP mask of 5
5. Output GGK on Port 2.

For reference, the RTCM-104 correctors will be relayed from the reference station to the project base station location with Pacific Crest Radio Modems Model RFM96W.

Finally, a Hypack Project will be setup to monitor the position in both WGS-84 Lat, Long and UTM Zone 18 NAD-83. The following parameters will be used.

1. Project = Base_Average
2. Kinematic DLL for GPS input configuration
3. System offsets were set to 0,0,0 for this test
4. Geodesy was set for the above listed UTM Grid.

Position observations will be recorded for a sixty minute period. These observations will then be averaged and assigned as the project RTK base stations horizontal (WGS-84 Lat Lon) and vertical elevation (WGS-84 Ellipsoid).

The project RTK base will then be set up as a reference station, sending corrections based upon the assigned position. The following parameters will be used:

Configuration Toolbox file BASE.cfg

1. Generate CMR correctors on Port 1
2. Kinematic base unit
3. A elevation mask of 8 degree's
4. A PDOP mask of 5
5. Reference position of Lat 35 50 37.98404 N , Long, 075 39 15.87987 , -23.826 Elev. (NAVD88)
6. Antenna height set to 000.00 and antenna type set to **UNKNOWN (0.0 offset)**

The data from each file will be processed through SB-MAX where it will be filtered to only GPS Mode 3 points with an HDOP of <=2.0. These values will then be averaged and also the min & max values will be observed.

2.2 Static Draft Measurement

6. Establishment of Vessel Reference Position

Prior to survey operations, a Vessel Reference Position was set for use in post processing. Survey data will be collected by an Isis v5.91 system for processing under the Caris HIPS/SIPS software package. Single beam only data will be collected by a Coastal Oceanographics HyPack MAX v0.5b system for processing under the Caris HIPS/SIPS software package. During survey operations, no physical offsets will be entered into the Isis system. Therefore, all offsets and corrections should be handled by the Caris package. It should be noted that an average sound speed for the water column and Side Scan "Horizontal Layback" will be input into the Isis raw data package. This information will be discussed in the appropriate system sections.

With this in mind the following Reference Position was established based on the definition of a Vessel Coordinate System provided in the HIPS User's Guide.

Vessel Coordinate System

Vessel configuration is based upon an instantaneous, three-dimensional, vessel coordinate system. The

Origin of the coordinate system is the reference position (RP). The axis is defined as follows:

The Y-axis is oriented along the vessel's fore/aft axis, positive forward.

The X-axis is oriented along the vessel's port/starboard axis, perpendicular to the Y-axis, positive

to starboard.

The Z-axis is perpendicular to the X-Y plane, and positive down (into the water).

The Y-axis is located approximately mid ship at the fore/aft centerline created perpendicular to the location of the A-Frame.

The X-axis is located at the approximate port/starboard center of the vessel.

The Z-axis was located at the rear deck level, slightly above the water line of the vessel during setup and sea trials

Once this point was established, measurements were made to determine the physical offsets of all survey equipment based on this coordinate system. These measurements were compiled and displayed in the AutoCAD 2000 file called R/V Willing.dwg. This drawing contains all sensor offsets.

During the establishment of system offsets a "Reference Mark" was set to aid in monitoring vessel Static Draft. The Reference Marks are located on the starboard single beam transducer mount vertical member, The distance from the Reference Mark to the Z-axis is 1.20 meters.

2.3 Monitoring Vessel Static Draft

To correctly process soundings, Caris needs to know the position of the Reference Point during survey operations. This point will move as equipment load, personnel, and fuel levels change. To compensate for these changes the Static Draft is monitored daily. At the start of every survey day the motion sensor is monitored to determine vessel attitude and a measurement is made from the Reference Mark to the present waterline. If the vessel is experiencing a roll bias, due to fuel load, personnel are moved to steady the vessel at its standard attitude. This attitude was established during sea trials, by approximating vessel loads and "zeroing" the motion sensor.

7.

8. Appling Static Draft

The measurement is logged in the daily spreadsheet and is reduced to a static draft value that is subtracted from the distance to the zero vertical reference and the difference entered in Caris.

9.

10. Static Draft Variation

The Static Draft is monitored daily as mentioned above. The Static Draft of the vessel appears to have a maximum deviation of 0.01 meters. The data to date is summarized below:

Fuel Load	Static Draft (meters)
Full	0.080
.9	0.080
.8	0.080
7	0.079
.6	0.079
.5	0.079
4	0.079
.3	0.079
.25	0.079

2.4 KTD File Development for RTK GPS Water Level Data Collection and Raw Data Collection

We will be collecting RTK GPS water level elevations throughout the survey area and will be saving them as water elevations referenced to the NAVD 88 datum. This requires the preparation and use of a .KTD file. The KTD file models the difference between the ellipsoid height and the collection datum (NAVD 88) throughout the site.

3.0 HYDROGRAPHER OPERATIONS

11.

3.1 Start of Day - System Start-up and Dock Side Checks

Upon arrival to the vessel on a planned survey day, perform the following functions or verify their occurrence. These items should be done every day before departure.

- Start generator and switch system power from shore to generator.
- If system was shut down the night before, turn on both UPS main power switches and wait for the units to power up. Trip the TEST switch once on both units to apply power to the outlets.

3.2 Start of Day – Electronics Systems Start-Up

11.1

- Verify DC Mains, 448, 595, and Autopilot are off before powering up, or logging onto, the computer systems.
- Verify that the monitors are all off via the switch on the monitor outlet strip.
- Power up the Triton Elics, NOAA 1 & NOAA 2 computers.
- Turn on the monitors via the switch on the outlet strip.
- Computer 1 & 2
  - Log on using default Logon
    - User Name osiuser
    - Password (blank)
- The Triton Elics machine is Windows 2000 and has no log on screen
- Wait for all three computer systems to fully boot
- Turn on DC Mains switch. This powers the DMS2i-05, 7400, T4000s, MX51s, CTD and radio modem
- Put the Autopilot in standby
  - Observe compass = 244 - 250 degrees

- Verify computer date/time on each system
  - Open the H11032 vessel log.xls and enter the crew arrival time, vessel departure time, and crew initials.

3.3 Start of Day - GPS Systems Check

- Activate REMCON
  - Select CLEAR to acknowledge power-up
  - Select POSITION
    - Verify Mode is RTK FIX
    - Verify position
      - Lat ~ 35 50 40.8
      - Lon ~ 75 39 19.6
- Minimize REMCON

11.1.1.1

3.4 Start of Day – Klein 595

- Check mount
- Check connector
- Check cable and lock ring
- Check Fish body screws
- Apply power to unit
- Press “any” button to start system
- Press enter once, and left arrow once to stop printer

3.5 Start of Day – Innerspace 448

- Verify paper supply in unit
- Set power to on to verify date and time – correct if necessary
- Set power back to standby
- Add Start of Day Annotation
  - Registry #
  - Julian Date
  - Calendar Date
  - Vessel
  - Transducer in use
  - Operators

- Roll #

3.6 Start of Day – EdgeTech GeoStar

- Check mount
- Check connector
- Check cable and tow line
- Check Transducer housing
- Apply power to unit

3.7 Start of Day – GSSI SIR 2000

- Check mount
- Check connector
- Check cable and tow line
- Check Transducer housing
- Apply power to unit

3.8 Start of Day – Logging

- Open Survey Log
- Log date and personnel on board
- Log WX observations at start of day
- Log activities at dock

11.2 **3.9 Start of Day – HYPACK MAX**

- Open Explorer
- Create a folders in the HYPACK/PROJECTS//DATA1/ folder with a naming scheme of ###MAX1 where ### is the Julian date of the survey day. (Daily survey directory) Create a separate folder for each survey day.
- Start Hypack MAX
    - Verify that correct Line File is Enabled

  - Verify that correct background chart is enabled
  - Verify Geodesy
- Start Survey
  - Open Dialog box under Options/Project Options
    - Set Project directory to the daily survey directory.
    - Set the Target directory to the daily survey directory.
    - Verify that the other information is correct and that Long Filenames are enabled.
  - Verify all alarms are off (except 448)
  - Verify that all equipment is in normal locations (generator, etc.)
  - Ensure vessel is in Reference position. Have vessel captain move the vessel as needed. In Survey, click on Targets, Select, and then Change File. Select the file NAVCHK.TGT from the project directory. Select the dockside nav-check point and right click on it to "select" target. Observe distance to target. If distance is excessive. (Value +/- 1.5 meters) determine what the problem is and correct it. Take a target (F5).
  - Modify the target properties (F6) to name it *XXX AM NAV CHK* where XXX is the Julian Date. Add entries in Comments section: *Pitch X.X Roll X.X Hdg XXX.X* in which you record the observed pitch, roll, and heading as observed at the dock.
  - Dockside Limits:
    - Pitch 0.0 +/- .2
    - Roll 0.0 +/- .5
    - Heading 246 +/-5 deg.
  - Evaluate if values exceed the limits.
  - Log the time in the "activity sheet" of the H11032 survey. Also, place an "x" in the roll, pitch, and heading columns on the same sheet to indicate they have been checked.

- **Dockside static draft:**
  - Observe the ROLL value from the MRU and move people to normal positions within the vessel, or as necessary to compensate for fuel load, to achieve a "zero" roll while measuring the static draft from "Reference Mark" to the water's surface. Record the measured value in survey log. Correct the measurement to true static draft value with formula provided. Also note the RTK tide displayed on the NOAA1 Hypack Max data display and enter it in the daily log sheet.
- **Dockside RTK water level check**
  - Observe the local water level reading and enter it in the RTK vs. Observed section of the daily log sheet. Compare the NAVD-88 value calculated by the log sheet with the value recorded from Hypack Max.

11.3

11.3.1.1 **3.10 Start of Day – ISIS**

- Open Windows Explorer
- Verify space unavailable on data drive E: > 10 GB. If less than 10 GB you need to clear out older (already archived) files to make space.
- Create a new directory on that drive in the H11032 ISIS folder based on the following format:
    - XXXISIS - With X = to Julian day
- Minimize Windows Explorer
- Start ISIS system from the H11032 ISIS shortcut. (This starts ISIS with the correct config file)
    - Set working directory for Isis under Configure>Hypack DDE> *Start each filename with* to daily directory
    - Set Target working directory under Tools>Target>File>Set Working Directory
- Verify next contact number is set in Tools>Target> Edit>Set Contact Number
- Set unit to Start Record to screen only- File>Start Recording>Display Only
- Set Layback—View>Layback>Enter value>Accept
- Set threshold in waterfall by right click—Threshold =1
- Set waterfall window values as shown below
- Open Sensor window- Windows>Status & Control>Sensors
- If you want to view 448 depth - Aux 1 displays depth
- Open Altitude window
- Click on symbol of Alt: in Telemetry window of Parameter Display

- **Annotations**
    - Annotations are kept in a WordPad document name JD###.TXT where ### is the Julian Date. This file is kept open on the Isis machine and annotations are copied and "pasted" into the **NOTE:** section of the .XTF.
    - SSS annotations must be recorded in the notes section of the Isis box at:
        - At start of line
        - When surface objects are noted
        - When SS tuning, range, cable out, or any other parameters are changed

4.0 CONFIDENCE CHECKS

Confidence Checks H11032-JD160-06092002-RV WILLING II/PORT

Confidence Checks H11032-JD160-06092002-RV WILLING II/STBD

Confidence Checks H11032-JD160-06092002-RV WILLING II/BOTH

Registry#/Julian Date/Calendar day/Towing Vessel/Channel

5.0 INTERFERENCE

H11032-JD160-06092002-RV WILLING II/Wake

H11032-JD160-06092002-RV WILLING II/Biologic

Registry#/Julian Date/Calendar day/Towing Vessel/Type of Interference

11.4 **6.0 DURING TRANSIT TO SITE**

- Ensure the shore power cable is stowed.
- Remove all dock lines and depart.

7.0 ON-SITE – PRIOR TO SURVEYING

- Determine sound velocity and enter into machines
- Isis – **Configure/Sound Velocity**
- Hypack Max – **Options/Navigation/Roxann Sound Velocity**
- Innerspace 448 – Dial in as **Speed of Sound**
- Bar Check
- Depth confidence check
- Deploy SSS for appropriate tow
- Check SSS Range

11.4.1

7.1 Daily Average Speed of Sound

- Obtain speed of sound readings. Enter in 448, Isis, and in HYPACK MAX - Survey, under OPTIONS, Navigation Parameters as "Roxann Sound Vel. Verify value is representative of prior values.

11.4.2 7.2 BAR Check (Depth)

- Verify that the average speed of sound from the days first cast is entered into the 448
- Lower the barcheck to the lowest 1.0 meter increment available referencing the 1 meter marks to the 448 draft mark on the transducer vertical pole.
- Start the 448 paper and record the bar at one meter intervals to 1.0 meters.

11.4.3 7.3 Confidence Check (Depth)

- Check 448 to insure correct sound velocity entered, draft=0.0, tide=0. Mode Auto, gate 4, replies 8. Turn 448 from STBY to ON just prior to check to record date, time, speed of sound, and draft on paper record.
- Record depth on paper record as Hydrographer lowers bar to seafloor. On the "MARK" given by the hydrographer as the bar is touching the seafloor, toggle the FIX MARK switch on the 448. The hydrographer will measure the distance from the seafloor to the water surface using the barcheck marks and by measuring between marks. Take target.(F5) Name target XXX Depth Confidence Check. Return 448 to STBY mode.
- Annotate paper record with:
  - Depth Confidence Check
  - H11032
  - Julian Date XXX
  - Operator Initials
  - Bar Check = X.X m (meters)
  - Calculated 448 depth by adding displayed depth to daily static draft.

7.4 Confidence Check (Sidescan)

- While collecting data:

- ISIS operator will enter the appropriate annotation into the **NOTE:** section of the .XTF while online. The time is entered into the daily log and noted as a confidence check .
- At times other than during regular data collection
- A line can be run outside of regular data collection to demonstrate that the sidescan sonar system is able to detect targets out to the full extent of the selected range. The Hypack operator selects line 900 to record the data. The XTE value in *Survey/Options/Navigation Parameters* should be changed to 200000 to avoid unnecessary TEXT log entries. Start the line when ISIS is ready.

11.4.4

11.4.5 **8.0 BEFORE ON LINE DATA COLLECTION**

8.1 Computer 1 - Hypack Max

Start Survey

Verify correct line entered, and line azimuth is correct. Change if necessary.

8.2 Computer 2 - Hypack Max

Start Survey – start logging prior to BOL.

8.3 Innerspace 448

Turn 448 alarms on (if off) – verify digital depth is ok Start Paper

8.4 ISIS

Verify ISIS is ready.

8.5 Heave

Verify Heave is ready.

Create a target (F5) and change it's properties (F6) to DECK CTD = XXXX.X. (The value observed at the beginning of line)

9.0 START OF LINE

- Save / Clear any contacts in the Target window
- Verify SSS data quality and bottom track prior to start
- Verify coastal line start of Isis
    - Watch file size increment
    - Check destination directory for file

11.5 10.0 ONLINE

Observe digital depths, heave, and profile window to verify proper operation. In shallow areas assist the vessel helmsman by closely monitoring the depth of water. Immediately notify helmsman of hazardous condition. Watch water depth to QA/QC alt. of SSS. Watch vessel speed.

Observe Sidescan record in Isis. Mark targets & put target in Hypack so as to allow checking the target on the next pass.

Periodically observe Deck CTD value, DIM value, heave, vessel speed, and CTD time interval. Observe Navigation map for holes in Isis.

11.5.1 10.1 Gap Tracking - Sidescan

If a condition is observed that may create a gap in the Sidescan data the operator hits F5 on Computer 1 to create target. The operator then evaluates further. If a gap is declared the target will be called up for modification (F6). The default name in the target name field will be changed to

XXX SS GAP; where XXX is the julian date. Further info will be entered into the notes field as follows:

Start & end time of gap, channel (port/stbd) Line designation

Example:

034 SS GAP

Notes: 16:37:00 to 16:37:45, Port Channel, Line 201_1549.034, type of interference

Ensure that Gap is entered in H11032 daily log.

10.2 Gap Tracking - Singlebeam

Hypack operator hits F5 and creates a target as SB gap is seen. Operator modifies target (F6) to change name to XXX SB GAP. (XXX is the Julian date) Ensure that Gap is entered in survey daily log file.

12. 11.0 END OF LINE

- Save all contacts as follows, and report final contact number in log
  - Target>File>Save All>Yes if not saved already

12.0 END OF DAY

Review ASCII text file for alarms

12.1 End Of Day - ISIS

- Exit from Isis
- Close Target window if still active
- Log off machine or shut down based on required backup situation

12.2 Archiving Procedure

- Data from all sources is colleted in Computer 1archive for archiving and data transmittal preparation
- A separate directory is established for each survey day with a subdirectory structure where each type of data is stored
- The structure and file types are outlines below

DIRECTORY NAME		FILE NAMES	
XXX Data\Docs	All documents created	H11032 Survey Log.XLS	Summary of all activities
		Willing II_offsets_1_19.DWG	Vessel layout and system offsets
XXX Data\XXXisis	All Isis data files	*.XTF XXX.LOG *.CON, XXX-00-contact.TXT	All .XTF files from the day Daily Isis survey log Original Isis contact files
XXX Data\Max_Support	Hypack MAX support files	Varied file types	Setup and support files for Hypack MAX operation Hypack MAX operations and alarms summary

			.INI files used for MAX
XXX Data\XXXmax1	Hypack MAX data files and .log file	*.RAW *.TGT	All Hypack data lines .TGT is MAX target file

- A directory template is available with all subdirectories established with an XXX, copy this template to Computer 1 and replace XXX with Julian day.
- Removable Hard Drive
  - A copy of each days data are copied from Computer 1 to a removable hard drive at the end of each survey day.
  - The Drive is then taken to the project office where the data is archived.
- XTF Data
  - Move the survey log from D:\root to daily directory at the end of the survey day
- Hypack Data
  - Copy both the TGT and the TXT file for the day to the data archive.
- Document Files
  - Copy the Daily Survey Log to the Daily Directory Doc section
  - Copy the Master Log.XLS to the Daily Directory Doc section
  - Copy any other relevant documents or drawings to this section
- Misc Section
  - Place any other non-standard files into this directory.

13. 12.3 End of Day: System Shut Down and Dock Side Checks

Upon arrival at the dock, perform the following functions or verify their occurrence. These items should be done every day before departure from the vessel.

- Secure all dock lines and hook up the shore power cable upon arrival at the dock, log arrival time in vessel log.
- Read the vessel fuel gauge and enter the value in “Activities Section” of Daily Log
- Capacity is approximately 120 gallons

- Ensure vessel has all appropriate supplies for the next day. Fuel, disks, FEDEX supplies, food, paper supplies, and water.
- Switch the system over to shore power after verify unneeded systems are off.
- Turn off the DC Mains and Autopilot.
- Verify you have the Data package and any files that will be e-mailed with you.
- Ensure all lights and boat electronics are off. Check all windows. Ensure bilge pumps are on. Lock back door upon departure.

12.4 Misc. System Operations

13.1.1.1

13.1.1.2 **12.4.1 Klein 595**

- Lower fish into the water to test operation

- Deploy fish and note cable out for layback calculations.
- Verify SSS image quality on Isis

- End of Day
  - Power Off
  - Recover Fish
  - Inspect entire wet end of system for wear – damage

13.1.1.2.1.1 **12.4.2 Innerspace 448**

- On-site
  - Input average speed of sound from first SVP and verify entry into all other systems
    - 448 – Hypack – Isis
- Start of Line
  - Alarm on
    - Good bottom lock
  - Verify range, gain, mode, and gate settings for upcoming line conditions.
  - Verify proper sound velocity based on first cast

- Unit in standby power unless performing confidence check or time check

- End of day
  - Turn unit off
  - Remove and archive sounding roll
  - Verify Sounding pole is raised
  - Verify paper supply on board

- Periodic Maintenance
  - Clean print head

12.4.3 EdgeTech GeoStar subbottom profiling system

- End of Day
  - Power Off
  - Recover Transducer

  Inspect entire wet end of system for wear – damage

12.4.4 GSSI SIR 2000 ground penetrating radar system

- End of Day
  - Power Off
  - Recover Antenna

  Inspect entire wet end of system for wear – damage

APPENDIX 4

STANDARD OPERATING PROCEDURES FOR SEDIMENT PROBING

1. Using the on-board GPS system, maneuver the sampling vessel to within 5 ft of the pre-programmed target coordinates for each sample location. Secure the vessel in place using spuds and/or anchors.

2. Use a 3/8 in. steel rod or equivalent to probe the sediment. The probe will be sharpened at one end, and calibrated in 6 in. intervals.

3. Probing will be conducted a minimum of 3 - 5 ft away from the target core location to avoid disturbing the sediment at the sampling location.

4. Advance the probe into the river bed, noting the depth of penetration and type of resistance met by the probe.

5. Move the probe laterally several feet (while maintaining the minimum 3 ft distance from the target core location) and repeat the probing at least 3 times.

6. Record the approximate average sediment thickness (to the nearest 1/2 ft.) and estimated sediment type (e.g., rock, fine-grained, coarse-grained) in the field log. If results of probing are inconsistent between the three attempts; record the inconsistency in the manual description of the field database. Record the estimated sediment type as the most representative one of the three attempts.

7. Prepare to collect a core in accordance with the procedures specified in the Sediment Core Collection SOP.

APPENDIX 5

STANDARD OPERATING PROCEDURE (SOP) GEHR8082

1.0 Title: General Electric (GE) Hudson River Design Support Sediment Sampling and Analysis Program Standard Operating Procedure for the analysis of Polychlorinated Biphenyls (PCBs) by SW-846 Method 8082

Capillary Column

Standard operating procedure for the analysis of Polychlorinated Biphenyls by Gas Chromatography with Electron Capture Detection and Total Aroclor Quantification.

(Acknowledgment: This SOP is based substantially on internal method SOPs provided by Northeast Analytical, Inc. of Schenectady, N.Y.)

2.0 Purpose

The purpose of this SOP is to provide a detailed written document for measurement of Polychlorinated Biphenyls (PCBs) according to SW-846 Method 8082 specifications.

3.0 Scope

3.1 This SOP is applicable to the determination and quantification of PCBs as outlined in EPA SW-846 Method 8082 for the GE Hudson River Design Support Sediment Sampling and Analysis Program. It is applicable to the sediment/solid samples.

3.2 The following compounds can be determined by this method:

Compound	CAS Number
Aroclor-1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

3.3 In general, samples are extracted, with a pesticide-grade solvent. The extracts are further processed by concentrating or diluting, depending on the PCB concentration, and carried through a series of clean-up techniques. The sample is then analyzed by injecting the extract onto a gas chromatographic system and detected by an electron capture detector.

3.4 This SOP provides detailed instructions for gas chromatographic conditions, calibration, and analysis of PCBs by gas chromatography. Sediment extraction procedures are covered in separate standard operating procedures.

4.0 Comments

4.1 One of the major sources of interference in the analysis of PCBs is that organochlorine pesticides are co-extracted from the samples. Several of the commonly found pesticides and associated degradation products (DDT, DDE, DDD) overlap the PCB profile envelope and co-elute with several PCB GC peaks and therefore cannot be accurately measured. The analyst must be careful in chromatographic pattern review and flag peaks that are suspected

of being contaminated so that they are not included in the total PCB values generated.

4.2 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters respond on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification.

5.0 Safety

5.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

5.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. The analyst should minimize manipulation of sample extracts outside of a fume hood.

5.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions of handling applicable solvents and chemicals used to process samples. The analyst should refer to the project laboratory's internal chemical hygiene plan for further safety information.

5.4 Samples remaining after analysis should be disposed of through the project laboratory's internal disposal plan. Refer to the project laboratory's internal standard operating procedures for disposal of laboratory waste.

6.0 Requirements

6.1 Extensive knowledge of this standard operating procedure and SW-846 Method 8082 is required.

6.2 The analysis portion of this method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

7.0 Equipment

7.1 Instrumentation

7.1.1 Gas chromatograph: Varian Model 3400 or equivalent, equipped with Model 1077 split/splitless injector or equivalent, temperature programmable oven, electron capture detector, and Model 8100 autosampler or equivalent.

7.1.1.1 Column - A 30 meter, 0.25 mm ID, 0.25-micron phase DB-1 capillary column is used for analysis.

7.1.2 Chromatographic Data System: A data system for measuring peak height and peak area. A Millennium_32 computer network based workstation (Waters Associates) or equivalent, will be employed to capture detector response and digitally store the chromatographic information. This system will allow for chromatographic review of data from the gas chromatograph, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

7.2 Glassware and Accessories

7.2.1 25-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-25 or equivalent)

7.2.2 5-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-5 or equivalent)

7.2.3 10-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-10 or equivalent)

7.2.4 50-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-50 or equivalent)

7.2.5 100-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-100 or equivalent)

7.2.6 4-dram vials for sample extract storage (Kimble Opticlear, part no. 60910, code no. 60910-4 or equivalent)

7.2.7 8-dram vials for sample extract storage (Kimble Opticlear, part no. 60910, code no. 60910-8 or equivalent)

7.2.8 Pasteur pipettes (Kimble, part no. 72050 or equivalent)

7.2.9 250-mL beakers, glass (Baxter Cat. No. B2650-250 or equivalent)

7.2.10 100-mL beakers, glass (Baxter Cat. No. B2650-100 or equivalent)

7.2.11 Disposable 10-mL pipettes (Baxter P4650-110 or equivalent)

7.2.12 Disposable 5-mL pipettes (Baxter P4650-15 or equivalent)

7.2.13 Disposable 1.0-mL pipette (Baxter P4650-11X or equivalent)

7.3 Chemicals

7.3.1 Pesticide-Grade Hexane, Burdick and Jackson, (Cat. No. 216-4) or equivalent

7.3.2 Pesticide-Grade Acetone, Burdick and Jackson, (Cat.No.010-4) or equivalent

7.3.3 Pesticide-Grade Toluene, Baker, (Cat. No. 9336-03) or equivalent

7.3.4 Pesticide-Grade Methylene Chloride, Burdick and Jackson, (Cat. No. 300-4) or equivalent

7.4 Analytical Standard Solutions

7.4.1 Aroclor Stock Standard Solutions

7.4.1.1 Polychlorinated Biphenyls - Neat commercial material for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as electric power transformers and capacitors. Commercially-prepared stock standards can be used if they are certified by the manufacturer or by an independent source and traceable to National Standards of Measurement.

7.4.1.2 Stock standards are prepared from individual Aroclor formulations by weighing an exact amount of the neat material to the nearest 0.1 mg, and dissolving and diluting to volume in a 100 mL volumetric flask with hexane. See Attachment A, Table 1 for an example of exact weights of each compound. For decachlorobiphenyl (DCB), dissolve

neat formulation in 10 mL of toluene and then transfer to a 100 mL volumetric flask bringing to volume with hexane. Alternatively, commercially-prepared stock standards may be used providing they are traceable to National Standards of Measurement.

7.4.1.3 The stock standards are transferred into Boston bottles and stored in a refrigerator at 0-6°C, protected from light.

7.4.1.4 Stock PCB standards must be replaced after one year, or sooner if comparison with certified check standards indicate a problem. See 8.5.3 for limits.

7.4.1.5 The labeling and tracking of standards should be in accordance with the project laboratory's internal standard operating procedures for preparation of standards. Labeling of standards should also be in accordance with NELAC standards, section 5.10.5.

7.4.2 Calibration Standards

7.4.2.1 Calibration standards are prepared at five concentration levels using a prepared working standard. See Attachment A, Table 2 for an example of the preparation and exact concentrations of the working standards. The following five standards make

up the initial calibration curve standard set for each of Aroclor-1221, Aroclor-1242, and Aroclor-1254: 20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, and 1000 ng/mL. One calibration standard at 50 ng/mL which is below the reporting limit (80 ng/mL) will be prepared for each of Aroclor-1016, Aroclor-1232, Aroclor-1248, and Aroclor-1260 (unless observed to be present in a project sample which would require recalibration for the detected Aroclor at the five standard levels used for Aroclor-1221, Aroclor-1242, and Aroclor-1254).

7.4.2.2 The two surrogates tetrachloro-*meta*-xylene (TCMX) and DCB are included in the Aroclor-1254 calibration standards. The stock standard for TCMX is prepared by diluting 1 mL of TCMX solution (ULTRA, cat. #IST-440 or equivalent, at 2000 μg/mL) into a 100-mL volumetric flask resulting in a solution of TCMX at 20 ppm.

7.4.2.3 To prepare the working surrogate standard, pipet 5.0 mL of the 100ppm DCB stock standard and 2.5 mL of the 20 ppm TCMX stock standard into a 100 mL volumetric flask and bring to volume with hexane. The final concentration of this solution will be 5.0 ppm of DCB and 0.5 ppm of TCMX.

7.4.2.4 Refer to Attachment A, Table 4 for an example of the instructions on preparation of the calibration standards

containing Aroclor-1254 and the surrogates. Refer to Attachment A, Table 3 for an example of the instructions on preparing the remaining calibration standards.

7.4.2.5 Transfer all calibration standards to 8-dram vials (or equivalent) and store in a refrigerator at 0-6°C, protected from light. Calibration standards must be replaced after six months, or sooner, if comparison with check standards indicates a problem. See 8.5.3 for acceptance limits.

7.4.3 Continuing Calibration Check Standards

7.4.3.1 Continuing calibration check standards are prepared independently from calibration standards, by using an alternate source purchased from standard vendors. Continuing calibration check standards will be prepared for Aroclor-1221, Aroclor-1242, and Aroclor-1254 (and other Aroclors, if detected). All continuing calibration check standards will contain the surrogate compounds TCMX and DCB. Refer to Attachment B, Tables 1-3 for instructions on preparation of these standards.

8.0 Procedure

8.1 Gas Chromatographic Operating Conditions

8.1.1 Establish the gas chromatograph (GC) operating parameters as follows:

Autosampler parameters: Multi-vial mode, ECD Attenuation and range are 1.

Refer to Attachment C for all other GC operating procedures.

Note: GC helium gas flow is optimized after instrument maintenance by adjusting nitrogen flow to elute a PCB calibration standard to a known retention time.

8.2 Data Acquisition

8.2.1 Chromatographic information will be collected and processed utilizing a computer based data acquisition workstation (Waters Associates, Millennium_32 computer network based workstation or equivalent). The GC workstation acquires the millivolt detector signal, performs an analog to digital conversion and stores the digital chromatogram on the computer network's disk. The chromatography software performs all data reduction including, long term data storage on magnetic media, chromatographic peak integration, all calculations, report generation, chromatogram plots, and calibration functions.

8.3 Initial GC Calibration

8.3.1 GC calibration will be performed by the external calibration procedure. Prior to running samples the system must be calibrated and system performance must be verified.

8.3.2 Establish the gas chromatographic operating parameters outlined in Section 8.1. Five calibration standard levels are to be prepared for each Aroclor-1221, Aroclor-1242, and Arclor-1254 and the surrogate compounds TCMX and DCB and one calibration standard level (at 50 ng/mL) is to be prepared initially for each Aroclor-1016, Aroclor-1232, Aroclor-1248 and Aroclor-1260 as discussed in section 7.4.2. If Aroclor-1016, Aroclor-1232, Aroclor-1248 or Aroclor-1260 is detected in any project sample based on the single-point calibration, the affected samples must be reanalyzed after a five-point calibration for the detected Aroclor.

8.3.3 Inject each calibration standard using the GC autosampler and the parameters outlined in section 8.1, which are those used for actual samples.

8.3.4 For each Aroclor, 5 peaks are selected to prepare calibration curves (or calibration factor for single-point calibrations). The peaks selected from the multi-component Aroclor formulations were based on maximizing the separation for each Aroclor (*i.e.*, minimizing peak overlap in retention time). Consideration was also given to selecting peaks that normally did not have problems with co-elution with interfering peaks or possible co-elution with

organochlorine pesticides. The determined area of the five peaks selected for calibration is processed by the data workstation as a group, combining the area for calculations of the calibration factors. The following table lists the Aroclors that are included in the initial calibration and group number that represents the group of peaks selected for that Aroclor for calibration purpose.

Aroclor	Group Number
A1221	1
A1232	2
A1016	3

Aroclor	Group Number
A1242	4
A1248	5
A1254	6
A1260	7

8.3.5 Attachment D is an example of chromatograms of standards of each Aroclor for a DB-1 column with peaks selected for calibration labeled.

8.3.6 For the initial calibration curve to be considered valid, the percent relative standard deviation must be less than 20% over the working range. In addition, the correlation coefficient for the linear calibration curve must be greater than or equal to 0.99. The linear-fit calibration curve (not forced

through zero) is used for quantification in every case and is not replaced with the average calibration factor.

8.4 Retention Time Windows

8.4.1 The GC system should be checked by the analyst to make sure it is functioning properly before establishing retention time windows. Make three injections of each Aroclor at a mid-level concentration throughout a minimum 72-hour time period.

8.4.2 For the 5 peaks selected for calibration of each Aroclor, calculate the standard deviation resulting from the variation in the three retention times for that peak.

8.4.3 The retention time window is defined as plus or minus three times the standard deviation of the three retention time determinations.

8.4.4 If the standard deviation of the selected peak is zero, the standard deviation of the peak eluting after it is used. If it is the last eluting peak that has zero for the standard deviation, then substitute the standard deviation of the peak eluting before the last peak.

8.4.5 Retention time (R.T.) windows established in section 8.4.3 to 8.4.4 may not be practical when samples containing matrix interferences are injected onto the GC column. The default R.T. window of ± 0.08 minutes is employed

when the established windows are below ±0.08 minutes. Besides using retention time windows to assign peaks for quantification, the analyst should rely on their experience in pattern recognition of multi-response chromatographic response exhibited by PCB Aroclors.

8.4.6 Attachment E provides examples of calculated retention time windows generated by the above outlined procedures.

8.5 Gas Chromatographic Analysis

8.5.1 Prior to conducting any analyses on samples, calibrate the system as specified in Section 8.3

8.5.2 To start an analytical sequence, the 500 ppb calibration standard is injected and analyzed for the Aroclor-1221, Aroclor-1242, and Aroclor-1254 after the initial calibration and if more than 24-hours has elapsed since the last valid continuing calibration check standard. If less than 24-hours has elapsed since the last valid continuing calibration check standard, select one 500 ppb continuing calibration check standard (Aroclor-1221, Aroclor-1242, or Aroclor-1254, each containing the surrogate compounds TCMX and DCB). Selection of continuing calibration check standards other than Aroclor-1221, Aroclor-1242, or Aroclor-1254 should be based on anticipated Aroclor contamination that the samples may exhibit. Selection of the continuing calibration check standard after the start of a sequence should also be alternated among the three Aroclors.

8.5.3 The calculated value for each Aroclor and surrogate in the continuing calibration check standard must be ±15% of the true value for it to be valid and analysis to proceed. If this criterion is exceeded, the analyst should inspect the system to determine the cause and perform maintenance as necessary. The system can then be recalibrated and sample analysis can proceed. **Note:** If a failed continuing calibration check returns to acceptable calibration later in the sequence, samples following the acceptable continuing calibration check will be reported; and samples between the failed continuing calibration check and subsequent compliant continuing calibration check will be reanalyzed. All samples which are not bracketed by valid continuing calibration check standards must be reanalyzed when the system is in-control. The analytical sequence must end with the analysis of the CCCs for each Aroclors-1221, -1242, and -1254 (and/or other Aroclors if to be quantitated).

8.5.4 The daily retention time windows must be established. Use the retention time for the selected 5 peaks of the continuing calibration check standard as the midpoint of the window for that day. If all seven Aroclors were analyzed as the initial calibration or continuing calibration check standard, then establish retention time windows using the retention time plus or minus the windows established in Section 8.4. If not all Aroclors were analyzed as the initial calibration or continuing calibration check standard, use the retention time from these Aroclor standard(s) as the midpoint plus or minus the windows established in Section 8.4 to establish the daily retention time windows. For

the remaining Aroclors, go back to the previous time the remaining Aroclors were analyzed as the initial or continuing calibration check standards in the past 24 hours and use those retention times plus or minus the windows established in Section 8.4 to develop daily retention time windows. If greater than 24 hours have elapsed since a particular Aroclor was analyzed as part of the initial or continuing calibration check, the daily retention time window for that Aroclor will be updated by reference to the surrogate or Aroclor continuing calibration check shift(s).

8.5.6 Each Aroclor and surrogate in all succeeding continuing calibration check standards analyzed during an analysis sequence must also have a percent difference of 15% or less when compared to the initial calibration generated from the 5-point calibration curve.

8.5.7 All succeeding standards in an analysis sequence should exhibit retention times that fall within the daily retention time window established by the first continuing calibration check standard(s) of that analytical sequence. If the retention times are outside the established windows instrument maintenance must be performed and recalibration may be required.

8.5.8 The following is the order that initial calibration standards, continuing calibration check standards, method blanks, QC samples, and samples are placed in an analytical sequence. A continuing calibration check standard is run after every ten injections in the analytical sequence. All analytical

sequences must end with a continuing calibration check standard regardless of the number of samples analyzed.

ANALYTICAL SEQUENCE

INJECTION	MATERIAL INJECTED
1	Hexane Blank
2-20	Initial Calibration Standards
21-23	Continuing Calibration Check Standards (Aroclor-1221, Aroclor-1242, and Aroclor-1254 and other Aroclors if reanalysis occurs if other Aroclors were observed in the samples)
24-33	Sample analyses, including method blanks, matrix spikes, matrix spike duplicates, and QC reference check standard (LCS). A maximum of 10 samples between continuing calibration check standards.
34	Continuing calibration check standard

ANALYTICAL SEQUENCE (CONTINUED)

INJECTION	MATERIAL INJECTED
45 and higher	Repeat inject. 24-34 sequence (Alternating continuing calibration check standards between Aroclor-1221, Aroclor-1242, and Aroclor-1254 and other Aroclors [reanalysis occurs if other Aroclors were observed in the samples])
Closing injections:	Continuing calibration check standards (Aroclor-1221, Aroclor-1242, and Aroclor-1254 and other Aroclors [reanalysis occurs if other Aroclors were observed in the samples])

8.6 Quality Control (Refer to Attachment F for a summary of the quality control requirements.)

8.6.1 This section outlines the necessary quality control samples that need to be instituted at the time of sample extraction. The data from these quality control samples is maintained to document the quality of the data generated.

8.6.2 Each analyst must demonstrate competence in accuracy and precision on quality control samples before beginning analysis on samples. This demonstration must be on-going and be repeated if there is any modification to the method.

8.6.3 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For sediment/solid samples, a laboratory sodium sulfate blank is processed.

8.6.4 The method blank must exhibit PCB levels less than the matrix-defined reporting limit. If the method blank exhibits PCB contamination above the reporting limit, the samples associated with the contaminated blank should be re-extracted and analysis repeated. If there is no original sample available for re-extraction, then the results should be flagged with a "B" indicating blank contamination. The value measured in the blank is reported for those samples associated with the particular blank out of criteria.

8.6.5 At this time, the GE Hudson River Design Support Sediment Sampling and Analysis Program does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, a matrix spike for Aroclor-1242 is to be analyzed at a rate of 1 matrix spike per every 20 samples at a concentration of 20,000 ng/mL in the extract (**Note:** this spike concentration will require a sample dilution to be performed). Also a matrix spike duplicate sample is to be analyzed at a rate of 1 per every 20 samples.

8.6.6 If requested, analyze one unspiked and two spiked samples. Calculate the percent recovery based on Aroclor concentration of both samples as follows:

A = concentration of spiked sample
B = concentration of unspiked sample (background)
T = known true value of the spike

Percent Recovery (p) = 100 (A-B) %/T

Compare the percent recovery calculated with the project limits of 60-140%. If the concentrations of the matrix spikes are *greater* than four times the calculated sample amount then the quality control limits should be applied. If the concentrations of the matrix spikes are *less* than four times the sample than there are no established limits applicable. If the percent recovery falls outside the acceptance range for the given Aroclor used as the spiking analyte, then the matrix spike recovery failed the acceptance criteria. Check for documentable errors (*e.g.,* calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated QC reference check standard (Laboratory Control Sample [LCS]) is within 60-140%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

A relative percent difference (RPD) must also be calculated on the matrix spike set recoveries. This is calculated as follows:

A = % recovery of matrix spike sample
B = % recovery of matrix spike duplicate sample

RPD = [(A-B)/{(A+B)/2}] x 100
where (A-B) *is taken as an absolute value*

If the concentrations of the matrix spike set are *greater* than four times the calculated sample amount, then an RPD of 40% or less is acceptable. If the concentrations of the matrix spike set are *less* than four times the calculated sample amount than there are no established limits applicable to the RPD. If the criterion is not met, check for documentable errors (*e.g.,* calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated LCS is within 60-140%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

8.6.7 A QC reference check standard (LCS) is also prepared and analyzed for Aroclor-1242 at a concentration of 500 ng/mL in the extract. For sediment/solid samples, sodium sulfate is used for the QC reference check standard (LCS). Calculate the percent recovery for the Aroclor spike and compare to the project limits of 60-140%. If the percent recovery for the QC reference check standard (LCS) is out of criteria, the analysis is out of the control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be re-extracted and re-run (Exception: If the LCS recovery is high and there were no associated positive results for any Aroclor, then address the issue in the Case Narrative and no further action is needed).

8.6.8 Surrogate compounds are added to each sample, matrix spike, matrix spike duplicate, method blank, and QC reference check standard (LCS) at time of extraction. The surrogate compounds TCMX and DCB are to be added prior to extraction for final extract concentrations of 10 ng/mL and 100 ng/mL, respectively (refer to extraction SOPs).

8.6.9 Only one surrogate analyte needs to meet established control limits for the analysis to be valid. For samples analyzed at a five-fold dilution of the extract or less, the data is compared to the project limits of 60-140%. If percent surrogate recovery is not within limits for either surrogate, the following steps are required.

8.6.9.1 Review calculations that were used to generate surrogate percent recovery values to make certain there are no errors.

8.6.9.2 Check by GC analysis surrogate solutions used during sample extraction steps to ensure that no problems exist with spiking solutions.

8.6.9.3 Re-analyze the extracts that did not meet control limits at the previously analyzed dilution to assess if the sample matrix interfered with surrogate measurement.

8.6.9.4 If the above steps do not give satisfactory results, re-extract and re-analyze the sample. Report this data if surrogate recovery is within limits. If surrogate percent recovery is out of limits for the re-extracted samples, low or high surrogate recovery is due to matrix affects and the data can be reported as estimated and the data user is notified in the form of a case narrative.

8.7 Qualitative/Quantitative Issues

8.7.1 Quantitation of Aroclors is complex. In each case, the Aroclor is made up of numerous compounds and, consequently, the chromatograms are multi-peak; also, in each case, the chromatogram of the residue may not match that of the standard. These residues are quantitated by comparison to one or more of the Aroclor mixtures, depending on the chromatographic pattern of the

residue. A choice must be made as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the residue.

8.7.2 If Aroclors-1016, -1232, -1248, and/or -1260 are detected in a project sample, the instrument must be calibrated using 5 concentration levels (20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, and 1000 ng/mL) for the detected Aroclor(s) and the sample reanalyzed for quantitation by a 5-point linear fit calibration curve. The same acceptance criteria that applied to initial calibration and continuing calibration check standard analysis for Aroclors -1221, -1242, and -1254 will apply to Aroclors-1016, -1232, -1248, and/or -1260 when samples are reanalyzed for quantitation of any of these Aroclors.

8.7.3 All quantitations are to be based on 5-point initial calibrations (using external standard calibration techniques). The concentration of each Aroclor and surrogate in the sample will be determined by using the linear-fit calibration curve (see section 8.7.5) determined from the initial calibration standards. Refer to section 8.3 for initial calibration procedures. The final calculated sample concentration will take into account the sample-specific dilution factor, initial sample weight, final extract volume, and percent solids. All solids will be reported on a dry-weight basis.

8.7.4 If the instrument level of any Aroclor in a sample exceeds the instrument level of that Aroclor in the highest level standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed for quantitation.

8.7.5 Calibration Curve by First Order Linear Regression External Standard Calibration.

Five selected Aroclor quantitation peaks are calibrated by first order linear regression with intercept. The surrogates TCMX and DCB are calibrated and quantified in the same manner using the individual peak areas for these analytes:

Equation of Line: $Y = aX + b$

where:

Y = summed total peak area of quantitation peaks used (uV-sec)
a = coefficient constant (slope)
X = calibration concentration (ng/mL)
b = first order coefficient (intercept)

8.7.6 Sample Concentration result calculation (solid samples)

$$C = \frac{(Y_i - b) * V_e * df}{a * M * \%TS * 1000}$$

where:

C = sample concentration (μg/g)
Y_i = summed total area of quantitation peaks in sample. (uV-sec)
b = intercept from (#1 above) (uV-sec)
V_e = concentrated extract volume (mL)
df = analytical dilution factor of extract
a = slope (from #1 above)
M = mass of sample in (g)
%TS = Percent Total Solid (in decimal format)
1000 = units conversion ng to μg

9.0 References

9.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update, December 1996.

9.2 U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants", July 1988.

9.3 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual", Wadsworth Center for laboratories and Research, 1988, updated 1998.

9.4 "Guide to Environmental Analytical Methods", fourth edition, Genium Publishing Corporation, 1998.

10.0 Attachments (**Note:** Attachments are not paginated.)

10.1 Attachment A: Example PCB Standards Preparation Tables

10.2 Attachment B: PCB Continuing Calibration Tables

10.3 Attachment C: Gas Chromatograph Operating Procedures

10.4 Attachment D: Chromatograms of PCB standards.

10.5 Attachment E: Retention Time Windows

10.6 Attachment F: Quality Control Requirements Summary Table for SOP GEH8082

ATTACHMENT A

Table 1
Example PCB Stock Standard Preparation Table

PCB Formulation	Supplier	Catalog #	Std. weight (mg)	Conc.(PPM)
A1016	Neat Material Source	NA	93.2	932.0
A1221	Neat Material Source	NA	106.8	1068.0
A1232	Neat Material Source	NA	103.3	1033.0
A1242	Neat Material Source	NA	99.0	990.0
A1248	Neat Material Source	NA	101.9	1019.0
A1254	Neat Material Source	NA	99.6	996.0
A1260	Neat Material Source	NA	99.2	992.0
DCB	Chem Service	F2170	10	100.0

Unless otherwise noted hexane is the solution used to make all dilutions.

Table 2
Example PCB Working Standard Preparation Table

PCB Stock Standards	Init. Volume(mL)	Final Volume(mL)	Conc.(PPM)
A1016	1.0	100	9.32
A1221	1.0	100	10.68
A1232	1.0	100	10.33
A1242	1.0	100	9.90
A1248	1.0	100	10.19
A1254	1.0	100	9.96
A1260	1.0	100	9.92

ATTACHMENT A cont'd

Table 3
Example PCB Calibration Standard Preparation Table

Init. Volume (mL)	Final Volume (mL)	Final Concentration (PPM)					
		A1016	A1221	A1232	A1242	A1248	A1260
5.0	50	0.932	1.068	1.033	0.990	1.019	0.992
2.5	50	0.466	0.534	0.5165	0.495	0.5095	0.496
1.25	50	0.233	0.267	0.25825	0.2475	0.2548	0.248
1.00	50	0.1864	0.2136	0.2066	0.198	0.2038	0.1984
0.500	50	0.0932	0.1068	0.1033	0.0990	0.1019	0.0992
5.0*	50	0.01864	0.02136	0.02066	0.0198	0.02038	0.01984

*This initial volume is of the nominal 0.250 ppm standard. All others are from the nominal 10 ppm standard.

Table 4
Example PCB Aroclor-1254 Calibration Standard Preparation Table

Init. Volume (mL) A1254	Init. Volume (mL) Surrogate	Final Volume (mL)	Final Concentration(PPM)		
			A1254	TCMX	DCB
5.0	0	50	0.996	0	0
10.0	4.0	100	0.996	0.020	0.200
25.0*	0	50	0.498	0.010	0.100
1.25	0.800	50	0.249	0.008	0.080
0.500	0.500	50	0.0996	0.005	0.050
0.100**	0.200	50	0.01992	0.002	0.020

*This initial volume is of the A1254 0.996ppm solution with surrogates.
**This initial volume is of the A1254 0.996ppm solution without surrogates.
All others are from the A1254 9.96ppm working standard.

ATTACHMENT B

Table 1
PCB Continuing Calibration Stock Standards

PCB	Supplier*	Catalog #*	Conc. (μg/mL)
A1016	Chem Service	F107AS	1000
A1221	Chem Service	F108AS	1000
A1232	Chem Service	F113AS	1000
A1242	Chem Service	F109AS	1000
A1248	Chem Service	F110AS	1000
A1254	Chem Service	F111AS	1000
A1260	Chem Service	F112BS	1000

*Or Equivalent.

Table 2
PCB Continuing Calibration Working Standards

PCB	Initial Volume(mL)	Final Volume(mL)	Concentration(PPM)
A1016	1.0	100	10
A1221	1.0	100	10
A1232	1.0	100	10
A1242	1.0	100	10
A1248	1.0	100	10
A1254	1.0	100	10
A1260	1.0	100	10

ATTACHMENT B cont'd

Table 3
PCB Continuing Calibration Standards

PCB	Initial Volume(mL)	Final Volume(mL)	Concentration (PPM)
A1016	2.5	50	0.500
A1221	2.5	50	0.500
A1232	2.5	50	0.500
A1242	2.5	50	0.500
A1248	2.5	50	0.500
A1254	2.5	50	0.500
A1260	2.5	50	0.500

ATTACHMENT C

Gas Chromatograph Operating Procedures[1]

Column Type	Capillary
Column ID	DB-1
Vendor	J&W (or equivalent)
Part Number	122-1032
Column Length(m)	30
ID(mm)	0.25
Film Thick.(um)	0.25
1)Initial Col. Temp. (^{o}C)	140
1)Col. Hold Time (min.)	1.0
1)Col. Temp. Rate (^{o}C/min.)	10
1)Final Col. Temp. (^{o}C)	200
1)Col. Hold Time (min.)	NA
2)Col. Temp. Rate (^{o}C/min.)	5
2)Final Col. Temp. (^{o}C)	245
2)Col. Hold Time (min.)	14.50
GC Col. gas flow rate (mL/min.)	17-24
ECD autozero	Yes
Detector Temp.(^{o}C)	300
Init. Injector Temp. (^{o}C)	300
A/S Vial Needle Depth	85
A/S Solvent Select	3
A/S Upper Air Gap	Yes
A/S Lower Air Gap	Yes
A/S Viscosity Factor	1

ATTACHMENT C cont'd

Gas Chromatograph Operating Procedures[1]

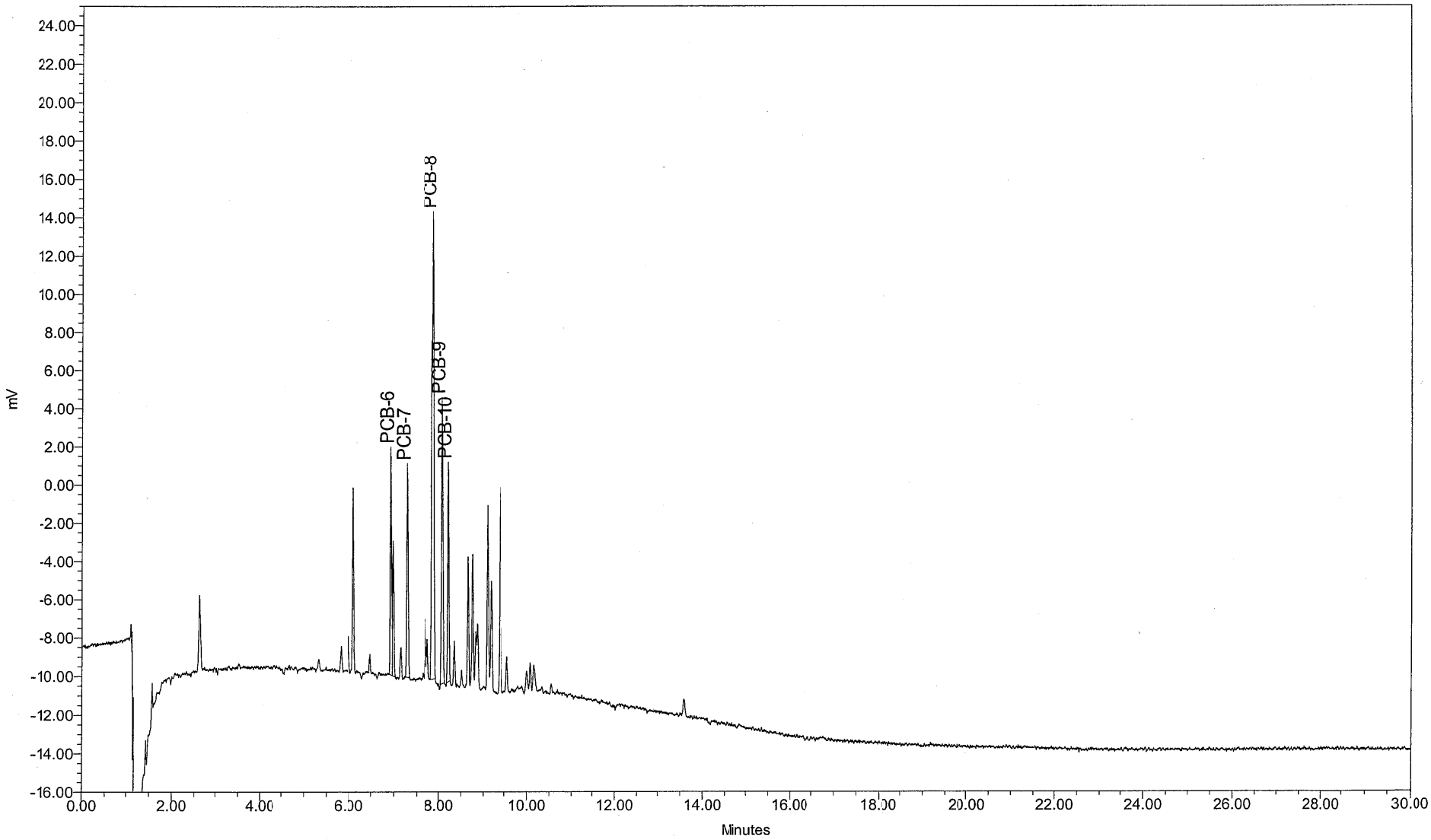
A/S Hot Needle Time (min.)	0.05
Autosampler (A/S) Model Number	8100 (or equivalent)
A/S Injection Volume (uL)	Lab-determined
A/S Injection Time (min.)	0.01
A/S Injection Rate (uL/sec.)	Fast 4.0
A/S Solvent Inj. plug size (uL)	0.2

Note:
1 – Parameters can be adjusted as necessary for the specific instrument used by the laboratory provided that chromatography for quantitation peaks is consistent with the examples in this SOP.

ATTACHMENT D
DB-1 CHROMATOGRAMS

Chromatogram Report, PCB by SW846 Method 8082

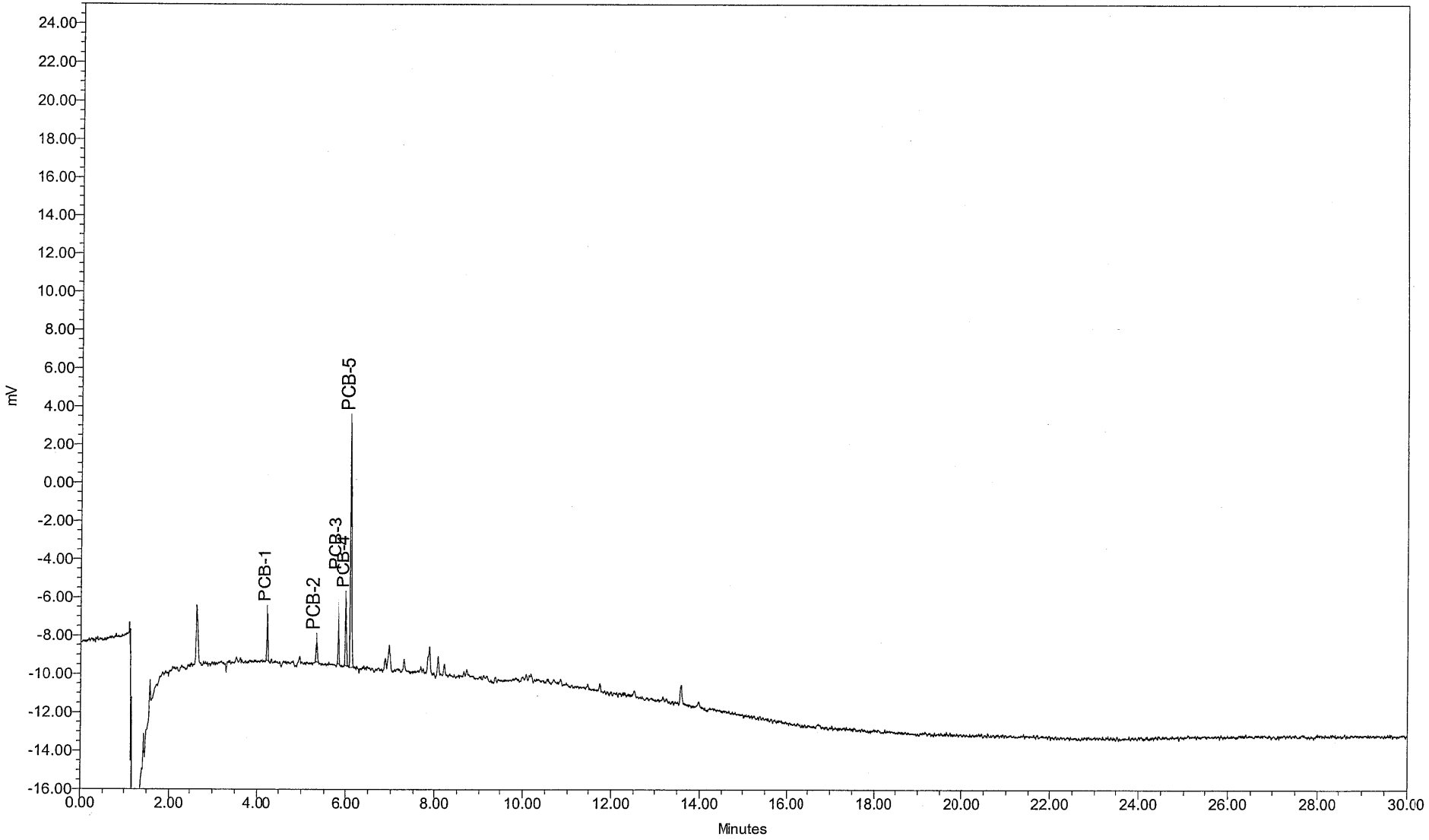
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS160725	Sample Amount:	1
Sample ID:	A1016 500 PPB	Dilution:	1
Date Acquired:	07/26/1999 09:32:16	Processing Method:	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

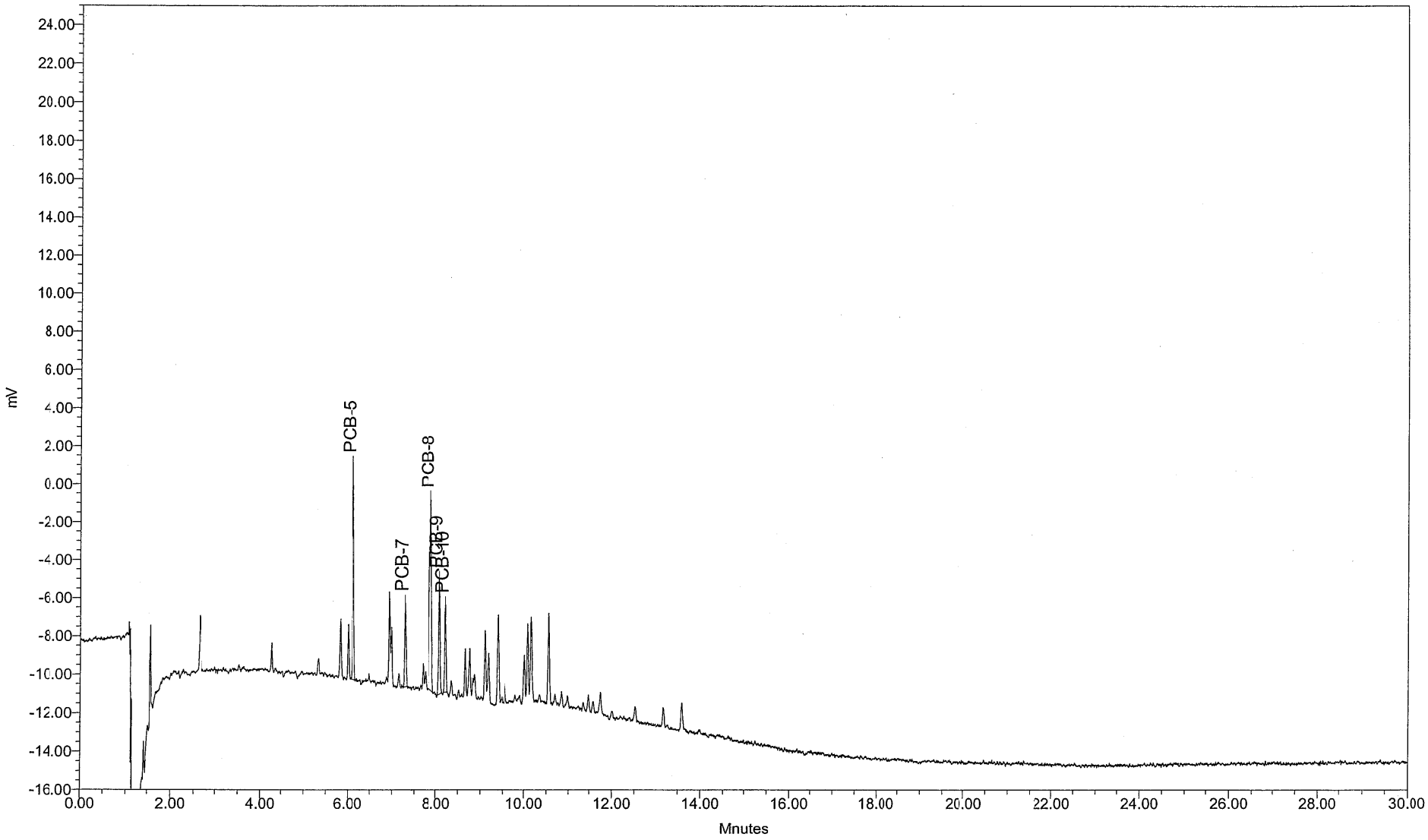
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS210725	**Sample Amount:**	1
Sample ID:	A1221 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 10:08:26	**Processing Method:**	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

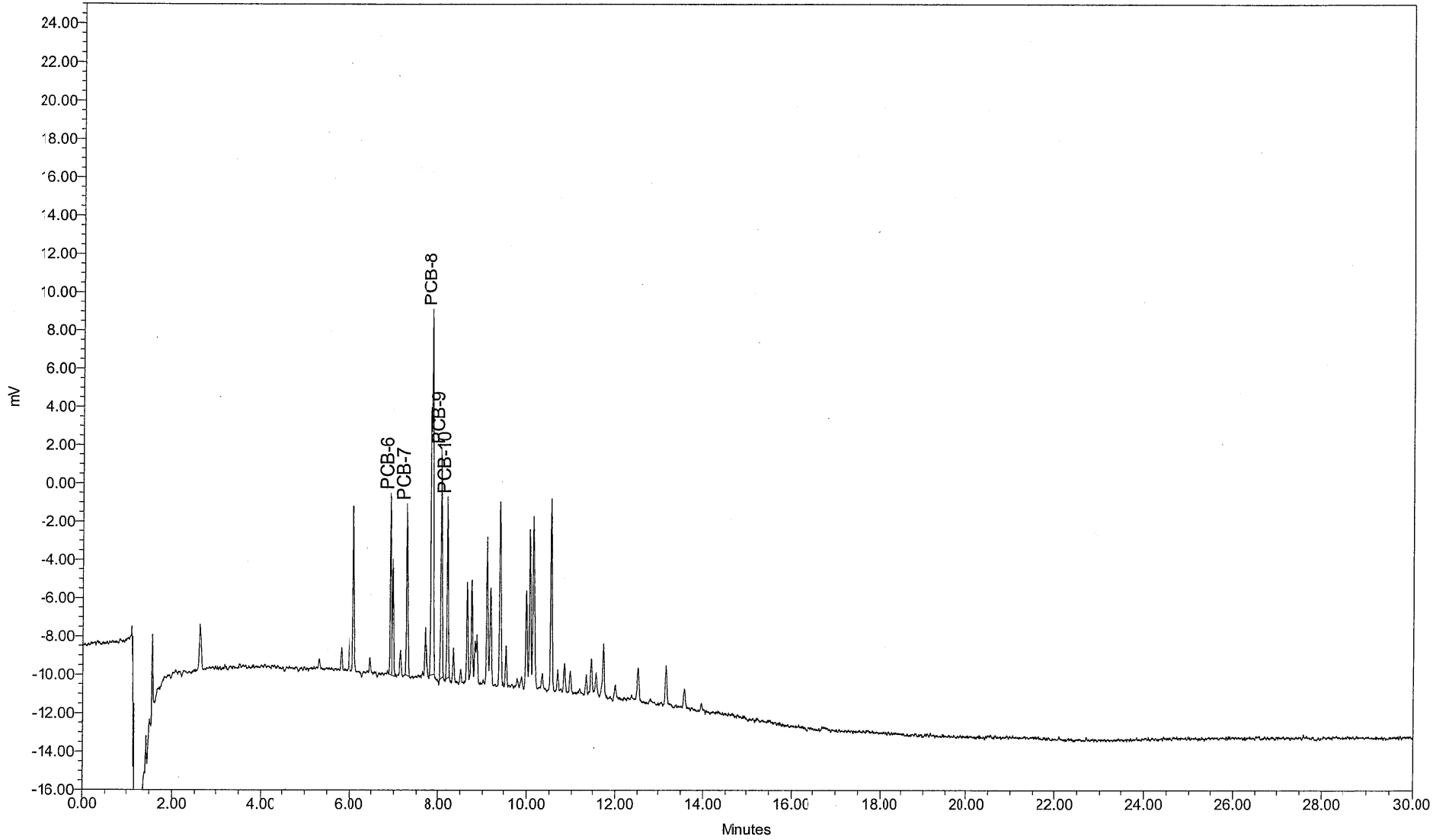
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS320725	**Sample Amount:**	1
Sample ID:	A1232 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 11:09:59	**Processing Method:**	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

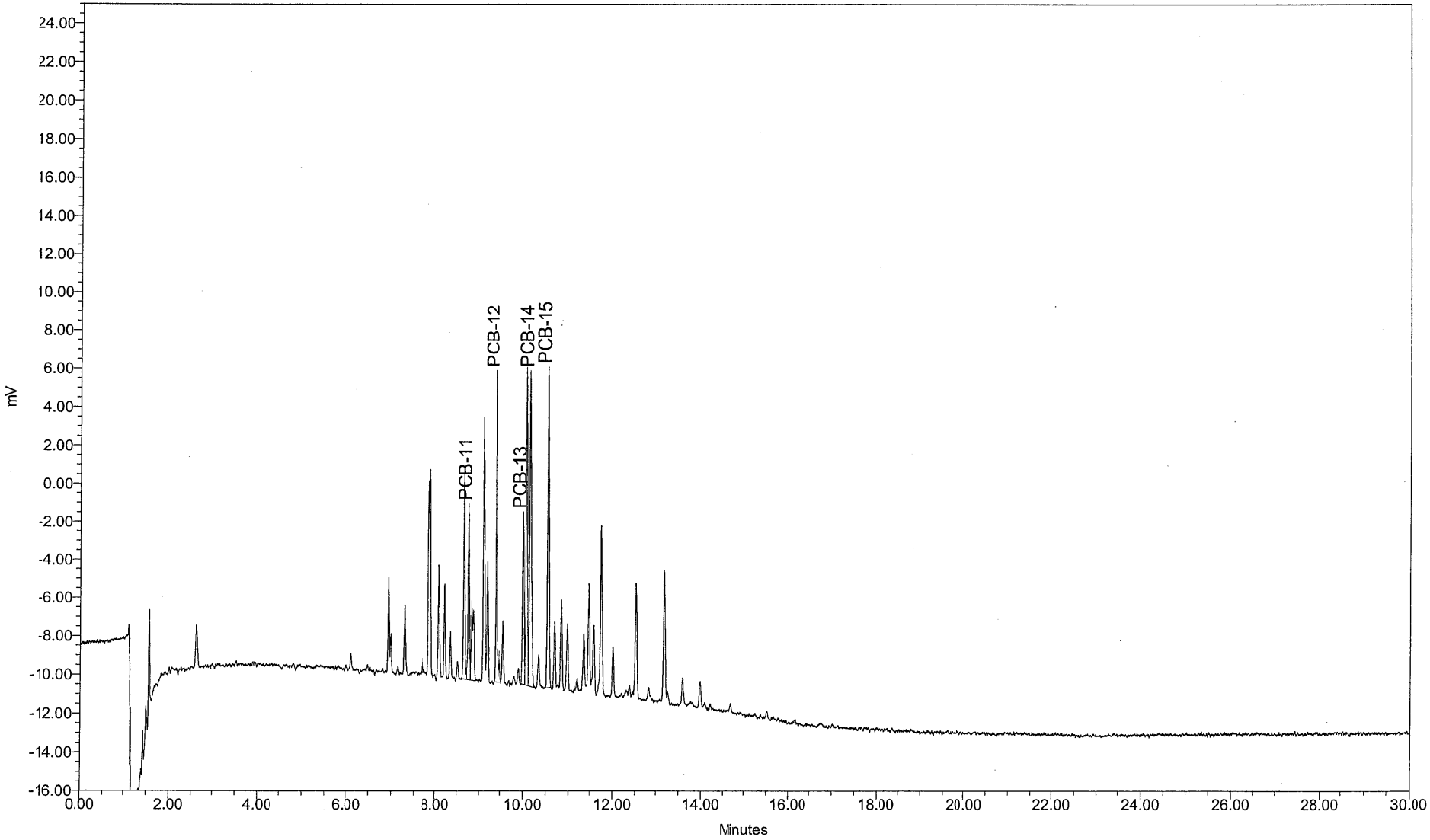
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS420725	Sample Amount:	1
Sample ID:	A1242 500 PPB	Dilution:	1
Date Acquired:	07/26/1999 11:46:07	Processing Method:	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

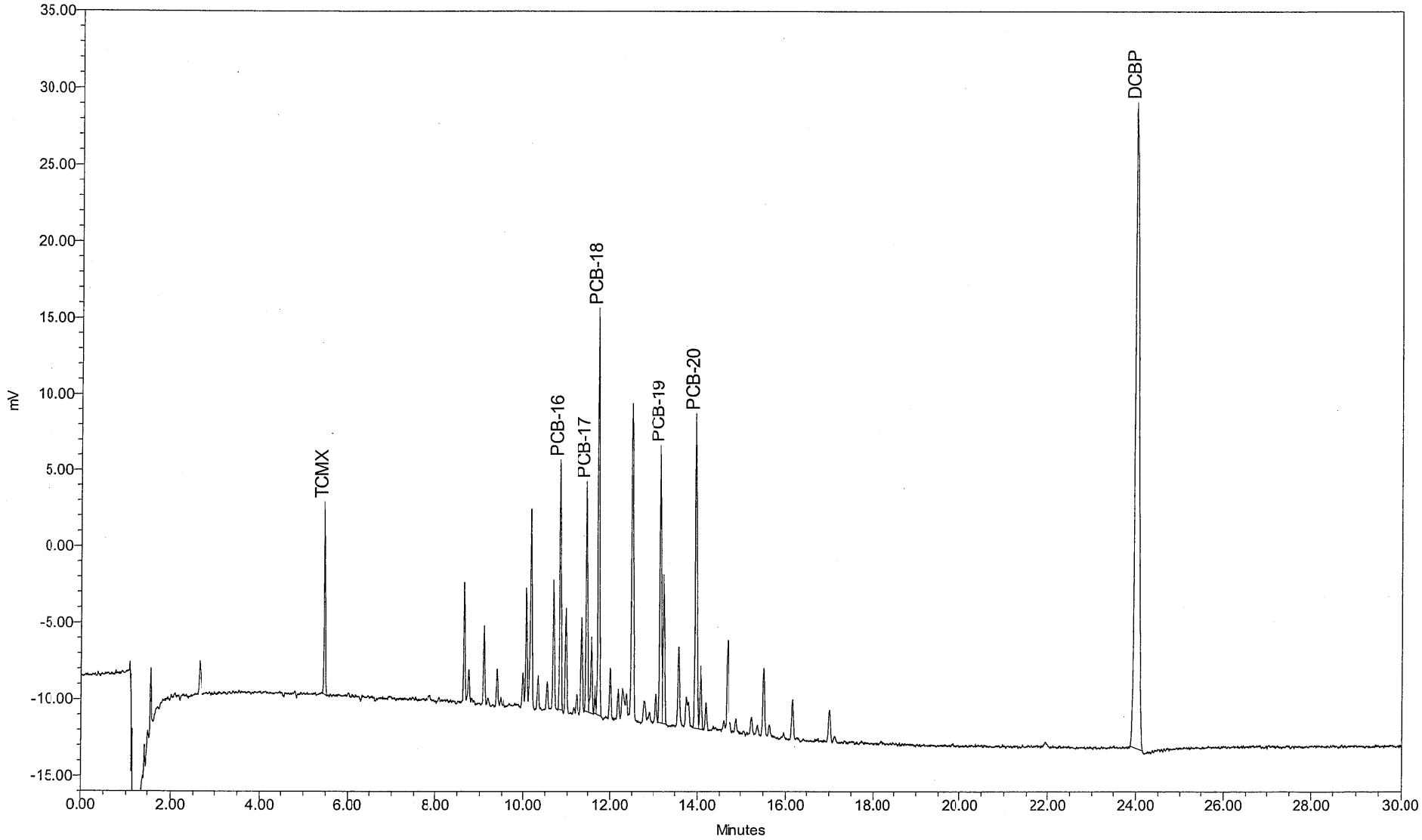
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS480725	**Sample Amount:**	1
Sample ID:	A1248 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 12:22:14	**Processing Method:**	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

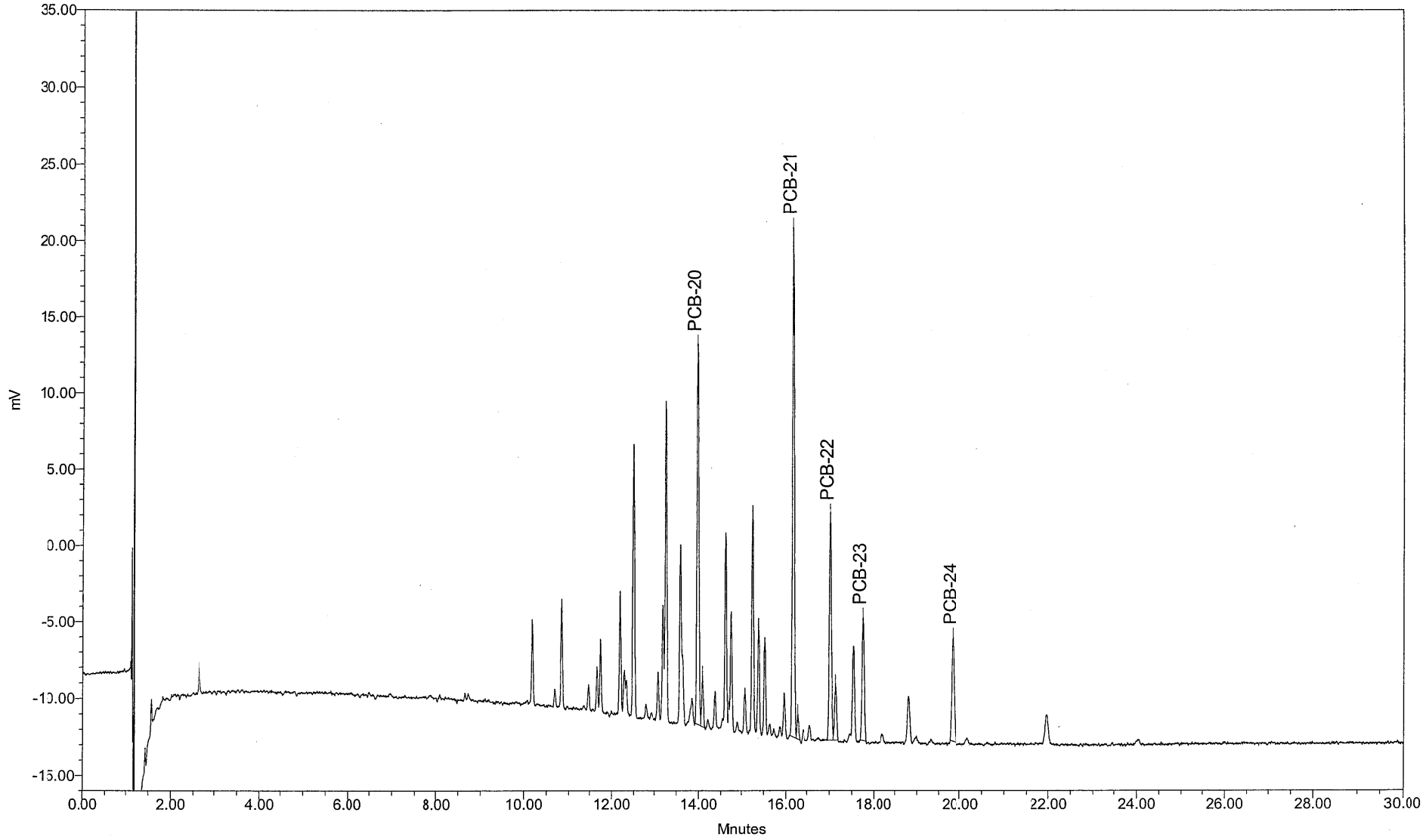
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS540725	Sample Amount:	1
Sample ID:	A1254 500 PPB	Dilution:	1
Date Acquired:	07/26/1999 12:58:21	Processing Method:	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS500725	**Sample Amount:**	1
Sample ID:	A1260 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 13:34:27	**Processing Method:**	GC7_8082_060899

ATTACHMENT E
RETENTION TIME WINDOWS

Northeast Analytical Inc 11/01/99

Retention Time Window Study
for Aroclors (PCB) by GC/ECD
EPA Method 8082

Instrument: GC 7
Column: DB-1

Analyte	PEAK	Standard 1 500 PPB R.T. Min	Standard 2 500 PPB R.T. Min	Standard 3 500 PPB R.T. Min	STD. DEV Min	%RSD	Window +/- Min.
		CS__0919	CS__1003	CS__1011			
Aroclor 1016	6	6.902	6.922	6.876	0.0231	0.33	0.069
	7	7.260	7.228	7.232	0.0174	0.24	0.052
	8	7.852	7.818	7.823	0.0184	0.23	0.055
	9	8.051	8.018	8.022	0.0180	0.22	0.054
	10	8.185	8.151	8.155	0.0186	0.23	0.056
Aroclor 1221	1	4.212	4.199	4.190	0.0111	0.26	0.033
	2	5.294	5.277	5.269	0.0128	0.24	0.038
	3	5.787	5.775	5.765	0.0110	0.19	0.033
	4	5.962	5.951	5.941	0.0105	0.18	0.032
	5	6.072	6.062	6.051	0.0105	0.17	0.032
Aroclor 1232	5	6.080	6.050	6.059	0.0154	0.25	0.046
	7	7.258	7.227	7.237	0.0158	0.22	0.047
	8	7.852	7.819	7.829	0.0169	0.22	0.051
	9	8.050	8.018	8.028	0.0164	0.20	0.049
	10	8.184	8.152	8.163	0.0163	0.20	0.049
Aroclor 1242	6	6.894	6.927	6.872	0.0277	0.40	0.083
	7	7.251	7.234	7.228	0.0119	0.16	0.036
	8	7.844	7.826	7.820	0.0125	0.16	0.037
	9	8.043	8.025	8.020	0.0121	0.15	0.036
	10	8.178	8.159	8.155	0.0123	0.15	0.037
Aroclor 1248	11	8.724	8.689	8.700	0.0179	0.21	0.054
	12	9.352	9.313	9.324	0.0201	0.22	0.060
	13	9.965	9.927	9.938	0.0196	0.20	0.059
	14	10.122	10.082	10.094	0.0205	0.20	0.062
	15	10.511	10.470	10.480	0.0214	0.20	0.064
Arolcor 1254	16	10.795	10.773	10.767	0.0147	0.14	0.044
	17	11.431	11.409	11.403	0.0147	0.13	0.044
	18	11.703	11.680	11.673	0.0157	0.13	0.047
	19	13.139	13.113	13.108	0.0166	0.13	0.050
	20	13.931	13.907	13.902	0.0155	0.11	0.047
Arolcor 1260	20	13.942	13.896	13.911	0.0235	0.17	0.070
	21	16.125	16.081	16.093	0.0227	0.14	0.068
	22	16.985	17.049	16.943	0.0534	0.31	0.160
	23	17.717	17.665	17.675	0.0276	0.16	0.083
	24	19.799	19.732	19.750	0.0347	0.18	0.104
TCMX (SURROGATE)	Surr.	5.445	5.429	5.425	0.0106	0.19	0.032
DCB (SURROGATE)	Surr.	23.984	23.91	23.91	0.0439	0.18	0.132

ATTACHMENT F
QUALITY CONTROL REQUIRMENTS
SUMMARY TABLE

Summary Table GEHR8082

Polychlorinated Biphenyls - SW-846 Method 8082
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Sulfuric Acid Cleanup, Sulfur Cleanup, Florisil Cleanup	All samples for PCB only.	Not applicable.	Not applicable.
Initial Calibration	• Established initially and when CCC fails criteria. • At 5 concentration levels for Aroclors -1221, -1242, and -1254 and surrogate compounds (TCMX and DCBP). The 5 concentration levels are to be 20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, and 1000 ng/mL for each Aroclor. The surrogate compounds are to be combined with the Aroclor 1254 standards at concentrations of 2 ng/mL, 5 ng/mL, 8 ng/mL, 10 ng/mL and 20 ng/mL (TCMX) and 20 ng/mL, 50 ng/mL, 80 ng/mL, 100 ng/mL, and 200 ng/mL (DCB). • One standard calibration for each of the remaining Aroclor mixtures (1016, 1232, 1248, and 1260), at the reporting limit. If any one of these Aroclors is detected in a sample, the sample must be reanalyzed under a 5-point calibration for the detected Aroclor(s) for quantitation.	• %RSD≤20% among calibration factors (CFs) AND correlation coefficient ≥ 0.99 for each Aroclor mixture and surrogate (to be quantitated using linear-fit calibration curve not forced through zero). • Calibration factors are to be calculated using the total area for 5 peaks for each Aroclor. (Refer to SOP GEHR8082 Section 8.3.4 for selection of peaks.) • Each Aroclor must display distinctive pattern.	• Reanalyze the initial calibration curve and/or evaluate/correct instrument malfunction to obtain initial calibration which meets criteria. • Sample results above highest standard concentration require dilution and reanalysis. • If Aroclors-1016, -1232, -1248, and/or -1260 is detected in a project sample, the instrument must be calibrated using 5 concentration levels (20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, and 1000 ng/mL) for the detected Aroclor(s) and the sample reanalyzed. Same acceptance criteria that applied to 5-point calibration for Aroclors -1221, -1242, and -1254 will apply to these Aroclors.

Summary Table GEHR8082

Polychlorinated Biphenyls - SW-846 Method 8082
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Continuing Calibration Check (CCC) Standard	• CCC for each Aroclors -1221, -1242, and -1254 at the beginning of the daily sequence (when >24-hour break in continuous analysis), unless initial calibration is performed. • If <24 hours break, CCCs will be alternated among Aroclors -1221, -1242, and -1254 after each analysis of 10 samples. • All CCCs must contain TCMX and DCB. • If analytical run is being performed for quantitation of Aroclors-1016, -1232, -1248, and/or -1260 (refer to initial calibration), CCCs for Aroclor(s) to be quantitated must be analyzed at the same frequency required for Aroclors -1221, -1242, and -1254. • Analytical sequence must end with analysis of CCCs for each Aroclors-1221, -1242, and -1254 (and/or other Aroclors if to be quantitated).	• ≤15% Drift based on "true" concentration for each Aroclor and surrogate when quantitated as a sample. • RT of each peak used for identification of the Aroclor must be within RT window (reset daily at the beginning of the sequence for the 24-hour day). • All samples must be bracketed by CCCs for Aroclors -1221, -1242, and -1254 (and/or other Aroclors if to be quantitated) that meet all criteria stated above.	• Correct system, if necessary, and recalibrate. Criteria must be met before sample analysis may begin. Samples that are not bracketed by compliant CCCs must be reanalyzed. • If a failed CCC returns to acceptable calibration later in the sequence, samples following the acceptable CCC will be reported; and samples between the failed CCC and subsequent compliant CCC will be reanalyzed.
Retention Time (RT) Windows	1. Established at ± 3 × std. dev. of RT of three standard analyses over 72-hour period. Must establish whenever a new column is installed. (Default RT window is ±0.08 minutes - Refer to SOP GEHR8082 Section 8.4 for additional guidance.) 2. RT windows are recentered daily based on RT of each of the peaks used for Aroclor identification in the first CCC of the day. (Refer to SOP GEHR8082 Section 8.5.4 for guidance on setting daily RT windows for Aroclors not analyzed as part of initial CCC.)	• RT of CCC peaks must be within established windows in the CCCs analyzed throughout day. • Recentering windows is permitted only once per 24 hours.	Adjust system, reestablish RT windows, and recalibrate.
Retention Time (RT) Shift	Each CCC analysis: RT of the peaks chosen for the identification of the Aroclors in the CCC are evaluated against the first CCC of the day.	Each quantitation peak for each Aroclor and each surrogate peak should be within window established.	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate.

Summary Table GEHR8082

Polychlorinated Biphenyls - SW-846 Method 8082
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Method Blank	• One per extraction batch of ≤20 samples of the same matrix per day. • Must be analyzed on each instrument used to analyze associated samples. • Must undergo all sample preparative procedures.	• Concentration does not exceed the reporting limit of any Aroclor. Not applicable if positive results were not reported for any associated samples. • Must meet surrogate criteria.	1. Reanalyze blank to determine if instrument contamination was the cause. If the method blank is still non-compliant, then follow 2 below. 2. Reextract and reanalyze all associated samples.
QC Reference Standard - Laboratory Control Sample (LCS)	One per extraction batch of ≤20 samples per matrix per day. The LCS must be from a second source and contain Arcolor 1242 at a concentration of 500 ng/mL at the instrument.	• % Recovery of Aroclor 1242 within project limits of 60-140%. • Must meet surrogate criteria.	Reanalyze LCS. If still out, reextract and reanalyze all associated samples. (Exception: If LCS recovery is high and no associated positives, then address in Case Narrative and no further action needed.)
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	At this time, the GE Hudson River Design Support Sediment Sampling and Analysis Program does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, one MS/MSD pair per extraction batch of ≤20 samples per matrix per day. The MS/MSD samples must be spiked with Arcolor 1242 at a concentration of 20,000 ng/mL at the instrument (note: this will require dilution).	• Aroclor 1242 % Recoveries within 60-140% (when MS/MSD spike concentration is greater than 4× the unspiked sample amount). • RPD within 40% (when MS/MSD spike concentration is greater than 4× the unspiked sample amount). • Must meet surrogate criteria (unless also outside of criteria in unspiked sample).	1. If recoveries for the spiked Aroclor are not within 60-140% or the RPD is >40%, check for documentable errors (*e.g.*, calculations and spike preparation). 2. Check unspiked sample results and surrogate recoveries for indications of matrix effects. 3. If no errors are found, and the associated LCS is within 60-140%, then sample matrix effects are the most likely cause. Note in Case Narrative.

Summary Table GEHR8082

Polychlorinated Biphenyls - SW-846 Method 8082
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Surrogates	• TCMX and DCB are added to all standards, blanks, samples, and QC samples at a concentration of 10 ng/mL TCMX and 100 ng/mL DCB at instrument level. • Calibrated as a target compound in the Aroclor 1254 initial calibration standards.	% Recovery of at least one surrogate within 60-140% for samples analyzed at an extract dilution factor of 5 or less.	If both recoveries are not within limits: 1. Check to be sure that there are no errors in calculations and surrogate solutions. Also, check instrument performance. 2. If no problem is found, reextract and reanalyze the sample. 3. If the reanalysis is within limits and holding time, then report only the reanalysis. 4. If the reanalysis is within limits, but out of holding time, then report both sets of data. 5. If the reanalysis is still out of limits, then report both sets of data. 6. No reanalysis is required if the sample was chosen for the MS/MSD analysis and the MS and/or MSD are also outside limits.
Qualitative/Quantitative Issues	If Aroclors-1016, -1232, -1248, and/or -1260 are detected in a project sample analyzed under a single-point calibration for the detected Aroclor, the sample must be reanalyzed under a 5-point calibration for the detected Aroclor(s).	All positive results for Aroclors must be quantitated using a 5-point linear-fit calibration curve and must be bracketed by compliant CCCs containing the detected Aroclor.	If Aroclors-1016, -1232, -1248, and/or -1260 are detected in a project sample, the instrument must be calibrated using 5 concentration levels for the detected Aroclor(s) and the sample reanalyzed. Same acceptance criteria that applied to initial calibration and CCC analysis for Aroclors -1221, -1242, and -1254 will apply to these Aroclors.
	If instrument level of any Aroclor in a sample exceeds the instrument level of that Aroclor in the highest level standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed.	The instrument level of all Aroclors must be within the calibration range for all samples.	Dilute the sample to bring the level of the highest concentration of Aroclors within the calibration range.

APPENDIX 6

STANDARD OPERATING PROCEDURE (SOP) GEHR3545

1.0 TITLE

General Electric (GE) Hudson River Design Support Sediment Sampling and Analysis Program Standard Operating Procedure for the extraction and cleanup of sediment/solid samples for Polychlorinated Biphenyl (PCB) analysis using the pressurized fluid extraction technique as per SW-846 Method 3545 for subsequent analysis by SW-846 Method 8082.

(Acknowledgement: This SOP is based substantially on internal method SOPs provided by Northeast Analytical, Inc. of Schenectady, N.Y.)

2.0 PURPOSE

The purpose of this SOP is to provide to the chemist the procedures required to perform extractions of PCBs, in sediment/solid samples, using the pressurized fluid extraction technique and to perform the subsequent extract volume reduction and cleanup for the GE Hudson River Design Support Sediment Sampling and Analysis Program.

3.0 SCOPE

The following procedure is utilized by the project laboratories for the extraction and cleanup of PCBs from sediment/solid samples using the pressurized fluid extraction method for subsequent analysis by SW-846 Method 8082.

4.0 COMMENTS

The soxhlet technique may be used in place of the pressurized fluid extraction at the discretion of the supervising chemist.

5.0 SAFETY

The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and protective exam gloves must be worn when handling glassware and samples. Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. The chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them. All solvents should be handled within a lab fume hood.

6.0 REQUIREMENTS

The chemist must have an understanding of the methods and requirements of USEPA-SW- 846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition. Methods 3545, 3500B, 3620B, 3660B, 3665A. An approved instructor must also certify the chemist to perform the procedure.

7.0 EQUIPMENT

7.1 Cell Body: ASE 200™ (Accelerated Solvent Extractor) Dionex, 22ML #048821, 33 mL #048822 (or equivalent).

7.2 Cell caps: Dionex #049450 (or equivalent).

7.3 Steel Rod: Used to compresses sample in the cell.

7.4 Hydromatrix (Pre-cleaned and suitable for use): Varian #0019-8004 (or equivalent).

7.5 Metal spatula.

7.6 Mixing Tray: Used to mix sample prior to weighing sample.

7.7 Analytical Balance: Mettler AG-204 (or equivalent) used to determine sample mass.

7.8 Cellulose Filter: Prevents the frits of the cell end pieces from being clogged during ASE extraction.

7.9 Sodium Sulfate: Anhydrous (12-60 Mesh), washed with Hexane and baked overnight at 180°C. Used for the laboratory method blank.

7.10 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208 (or equivalent).

7.11 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090 (or equivalent).

7.12 Turbo Vap Evaporator: Zymark #ZW640-3 (or equivalent).

7.13 Turbo Vap Evaporator concentrator tubes: Zymark 250 mL (or equivalent), 0.5 mL endpoint.

7.14 1:1 Hexane/Acetone: 50%/50% by volume solvent mixture prepared in the lab.

7.15 Zymark Turbo Vap LV (or equivalent).

7.16 60 mL VOA vials.

7.17 Vials: glass, 8 dram & 4 dram (with Polyseal sealed cap) (20 mL & 10 mL) capacity, for sample extracts.

7.18 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

7.19 Centrifuge: International Equipment Co., Model CL (or equivalent).

7.20 Wrist Shaker: Burrell wrist action shaker, Model 75 and 88 (or equivalent).

7.21 Florisil: 10% deactivated, solvent washed with 1:1 hexane/ether, baked at 130°C for 16 hours. Deactivated with D.I. water. EM Science #FX0282-1 (or equivalent).

7.22 TBA Reagent: Tetrabutylammonium Hydrogen-Sulfite Reagent (prepared in the laboratory).

7.23 Mercury: Triple distilled Mercury Refining Co, Albany, NY #328502 (or equivalent).

7.24 Sulfuric Acid: H_2SO_4 (concentrated) Mallinkrodt #2468 #UN1830 (or equivalent).

7.25 Pipettes: S/P Disposable Serological Borosilicate Pipettes.

1. 1 mL × 1/10 #P4650-11X (or equivalent)
2. 5 mL × 1/10 #P4650-15 (or equivalent)
3. 10 mL × 1/10 #P4650-110 (or equivalent)

Kimble Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

7.26 Beakers: Assorted Pyrex: 250 mL, 600 mL, and 1000 mL.

8.0 PROCEDURES

8.1 Sample Preparation

8.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, these problems should be brought to the attention of the supervisor and/or quality assurance manager for guidance and then documented in the extraction logbook.

8.1.2 If the sample is a sediment and contains a water layer, decant and discard the layer as aqueous PCB waste. Mix the sample thoroughly and discard any foreign objects such as sticks, rocks, leaves, twigs, or pebbles. **Note:** however that the sample may be composed entirely of rock, concrete or some other solid material in which case the entire sample is treated as the solid.

8.2 Sample Extraction

8.2.1 Set up one 250-mL glass beaker or 4-oz. jar for each sample. Pick the first sample, label a beaker with the sample number, and tare the beaker. Using a metal spatula, add 10 g to 11 g of the wet sample to the beaker. Samples that are observed to be very wet will require additional mass of sample such that the project sensitivity requirements are met. The moisture content of the sample as determined in Section 8.2.2 should be evaluated so that a larger wet-weight sample can be obtained to provide a dry amount of solids to meet the project sensitivity requirements. The amount taken must consider the size limitations of the ASE extraction cell. The laboratory should target a wet-weight amount of 15 g for very wet samples. Record the weight in the PCB solid extraction logbook to the nearest tenth of a gram. Use the washed and baked sodium sulfate as the sample for the method blank and Laboratory Control Sample (LCS). Record the weight in the sample mass book.

NOTE: ALL SAMPLE CONTAINERS ARE TO BE RETURNED TO THE APPROPRIATE REFRIGERATOR. FOR ALL EMPTY SAMPLE CONTAINERS, SEE THE LABORATORY'S INTERNAL CHEMICAL HYGIENE PLAN FOR PROPER DISPOSAL.

8.2.2 The PCB concentration is to be determined on a dry-weight basis and therefore, the percent total solids must be determined. Weigh approximately 5 grams of the previously homogenized sample in a previously weighed, tarred aluminum-weighing pan. Record the weight of the sample and the tare weight of the pan in the percent total solids log. Place the sample in a drying oven at 100 to 110 degrees Celsius for at least 8 hours. Record the time placed in the oven and the oven temperature in the percent total solids log. Remove the samples from the drying oven and allow to cool in a desiccator. Weigh the pan and sample.

Calculate the percent solids by:

$$\frac{\{(\text{wt. of pan + dried sample}) - (\text{wt.of pan})\}}{(\text{wt. of wet sample})} \times 100\%$$

8.2.3 Before the sample is added to the cell, the sample must be dried. The sample is dried by adding pre-cleaned Hydromatrix. The amount of this drying agent being used depends on how much water is in the sample. The more water present in the sample, the more drying agent will be needed to dry the sample. Mix the sample and drying agent thoroughly with a metal spatula.

8.2.4 The cell size to be used during the extraction will be determined by the final volume of the sample after the drying agent has been added. **Note:** sometimes the sample will have to be separated into two cells for the extraction if to much drying agent has been added.

8.2.5 Select the appropriate cell body size for each sample. Assemble one cell end cap to the cell body. Place 3 cellulose filters into the open end of the cell and push it down to the cell end cap using the black ASE push rod.

8.2.6 Label cells with the sample number. Label the corresponding 60-mL VOA vials on the base of the vial.

8.2.7 Place the cell into a clean mixing pan. Add the dried extract to the cell using the metal spatula to guide the sample into the cell. Any sample that fell outside of the cell will be collected in the mixing tray. Remove the cell from the mixing tray and added the sample that is in the mixing tray to the cell. Compact the sample in the cell, using the steel rod, while the sample is being added. **Note**: rinse the steel rod with acetone and dichloromethane before using on a different sample or placing it in the storage drawer.

8.2.8 Add surrogate and matrix spike solution at this point. The final extract volume concentration of the surrogate compounds tetrachloro-*meta*-xylene (TCMX) and decachlorobiphenyl (DCB) should be 10 ng/mL and

100 ng/mL, respectively. At this time, the GE Hudson River Design Support Sediment Sampling and Analysis Program does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, the final extract volume concentration for the spiked Aroclor (Aroclor-1242) in the matrix spike and matrix spike duplicate sample should be 20,000 ng/mL (**Note:** this spike concentration will require a sample dilution to be performed). The final extract volume concentration of the LCS should be 500 ng/mL.

8.2.9 Assemble the top cell end cap to the cell, hand tighten. Place the first cell to be extracted in position 1 on the cell tray (top tray) and the 60-mL VOA vial in position 1 on the vial tray (bottom tray). The cells and 60-mL VOA vials for each sample must be in the same numerical position on the two trays.

8.2.10 Solvent used for PCB extraction is 1:1 hexane/acetone

8.2.11 Select the appropriate method or schedule for PCB extraction and start the ASE. Recommended ASE extraction conditions for PCB in Sediment are provided in Attachment 4.

8.2.12 When the extraction program is complete, transfer the hexane layer (top layer) using a 10-mL pipette into a pre-rinsed turbo tube or 60-mL VOA vial

if using Turbo Vap LV. Leaving only the water layer in the 60-mL VOA vial. Leave the 10-mL pipette in the turbo tube.

8.2.13 Rinse the 60-mL VOA vial using 5 pipettes of hexane. Hand shake for 30 seconds. Allow the two layers to separate, and pipette the hexane layer, using the same 10-mL pipette, into the turbo tube. Repeat this step 1 more time for a total of 2 hexane extractions on the water layer.

8.2.14 Rinse the 10-mL pipette with two pipettes of hexane on the outside of the 10-mL pipette that was in contact with the sample extract and two pipettes of hexane through the 10-mL pipette and collect into the turbo tube.

8.2.15 All glassware must be rinsed with technical grade (tech)-acetone or a "for rinsing-only" labeled solvent, and dried in the hood before other cleaning steps.

8.3 Solvent Reduction: TurboVap Evaporator System

8.3.1 The Turbo Vap evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus. The turbovap uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract which allows fractional reduction of the solvents without loss of higher boiling point analytes.

8.3.2 Turn the unit on and allow to heat up to the specified temperature for individual solvent use.

8.3.3 As a precaution the TurboVap system regulators should be checked to assure that no residual gas pressure remains within the system and that the gas cylinder valve and gas pressure regulators are both off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty turbo tube into the water bath and close the lid. Make sure that the nitrogen gas cylinder valve is turned off and slowly turn on the gas pressure regulator. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Proceed to 8.3.4. Make sure to wipe down all surfaces with hexane before concentration samples.

8.3.4 Place the turbo tube containing the samples into the TurboVap and close the lid. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on.

Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction.

8.3.5 Turbo Vap – LV low volume unit: Turn the unit on and allow it to heat up to 38 degrees Celsius. As a precaution the Turbo Vap LV regulator should be checked to assure no residual gas remains in the system. Residual gas may cause splashing and cross contamination of the samples. To resolve this place a vial into the vial in to the turbo vap and close the lif. Press the start button and proceed to turn the gas regulator knob counter-clockwise until the regular reads zero. Place the 60-ml VOA vials into the turbo vap. Press the button to turn on the appropriate row of stations that are being used. The press the start button and adjust the regulator until the samples begin to swirl. Check the sample every few minutes and adjust the gas to keep the samples swirling.

8.3.6 The process for solvent (hexane/acetone) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown to dryness and PCB loss may occur. Immediately notify a supervisor if an extract is blown to dryness.

8.3.7 Concentrate the solvent to approximately 1.0 mL. Remove the samples from the TurboVap and place in the rack. The remaining solvent will consist largely of hexane since the acetone component is fractionally removed at a faster rate than hexane; however, a solvent exchange with hexane should be completed 3 times to ensure the acetone has been entirely removed. **Note**: Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing

before the 1.0-mL point is achieved. Samples that stop reducing should be removed as soon as possible.

8.3.8 Quantitatively transfer the sample extract with a pasteur pipette into an appropriate volumetric flask (25 mL for soil extracts). Rinse the turbo tube or vial with 3 pasteur pipettes of hexane, then transfer the hexane rinse to the volumetric. Repeat the hexane rinse two more times for a total of three hexane rinses of the turbo tube. After the sample has been transferred, rinse the pasteur pipette with 0.5 mL of hexane into the volumetric flask. Add hexane to the volumetric meniscus mark.

Invert the volumetric flask at least three times to mix completely. Decant the contents into a pre-labeled 8-dram vial.

8.3.9 All dirty glassware must be rinsed with tech-acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

8.4 Sample Extract Cleanup

8.4.1 Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances which must be removed before accurate chromatographic analysis can be performed.

8.4.2 Sulfuric acid, sulfur removal and Florisil® clean-ups should be performed on every sample. The sequence and number of replicates of cleanup steps performed are recorded by the sample preparation chemist on the sample tracking log sheet. Sample extract cleanups are performed on set volume extracts. The set volume is 25 mL for sediment/solid samples.

8.4.3 Sulfuric Acid Wash

8.4.3.1 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds, which are co-extracted with the PCB residues.

8.4.3.2 Chill the sample to approximately 0°C. Add 5.0 mL of concentrated H_2SO_4 and shake for 30 seconds by hand, centrifuge for approximately 1 minute, transfer approximately 20 mL of the hexane upper layer to an 8-dram vial.

8.4.3.3 Repeat 8.4.3.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. **Note**: it is entirely possible that all colored material will not be removed from the extract.

8.4.4 Elemental Sulfur Clean-up

8.4.4.1 Elemental sulfur is soluble in the extract solvents used for sediment and soil samples. It is commonly found in many sediment/soil samples, decaying organic material, and some industrial wastes.

Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak.

8.4.4.2 Two techniques exist for the elimination of elemental sulfur in PCB extracts. Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure.

Tetrabutylammonium sulfite causes the least amount of degradation to a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

8.4.5 Removal of Sulfur Using Mercury

8.4.5.1 Mercury is a highly toxic metal. All operations involving mercury should be performed within a hood. Prior to using mercury, the chemist should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet for mercury.

8.4.5.2 Add 1-3 drops of mercury to the sample extracts, cap, and place on the wrist shaker for 30 minutes. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

8.4.5.3 Remove the sample extracts from the wrist shaker and place in the centrifuge at a setting and duration appropriate to spin down the solids.

8.4.5.4 Transfer the sample extract to a clean 8-dram vial.

8.4.5.5 The precipitated sulfur can be removed from the extract by performing a sulfuric acid clean-up or a Florisil® slurry.

8.4.6 Removal of Sulfur using TBA Sulfite

8.4.6.1 The TBA procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water-soluble.

8.4.6.2 Add 2.0 mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 0.65 g of sodium sulfite crystals to the extract and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more aliquots (approximately 0.65 g) to the extract and observe.

8.4.6.3 Place the samples on the wrist shaker for 45 minutes observing at 15-minute intervals to make sure that the sodium sulfite is not consumed. Add 5 mL organic free water and shake for 10-15 minutes.

8.4.6.4 Place the samples into the centrifuge and spin at a setting and duration appropriate to spin down the solids.

8.4.6.5 Transfer the hexane layer to a new 8-dram vial and cap.

8.4.7 Florisil® Adsorption (Slurry)

8.4.7.1 The Florisil® slurry removes co-extracted polar compounds, residual water, and residual acid and is recommended as the final cleanup step before the extract is submitted for GC analysis.

8.4.7.2 Add approximately 3 grams of tested and approved 10% deactivated Florisil® to each vial containing the sample extract.

8.4.7.3 Vigorously shake the vial for approximately 1 minute by hand or on the wrist shaker.

8.4.7.4 Place the vial(s) into the centrifuge at a setting and duration appropriate to spin down the solids.

8.4.7.5 Transfer the extract to a clean 8-dram vial.

8.5 Extract Screening and Dilution

8.5.1 Screening of PCB extracts by GC to determine the approximate concentration before final analysis is highly recommended. If possible, prior site history and estimates of sample concentration will be provided by field personnel and may be used to determine what, if any, extract dilution is necessary.

8.5.2 The supervising chemist is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the original sample extract into a vial containing the correct amount of "make up" volume of hexane. Dilutions must be recorded in the instrument logbook or in the data system.

8.5.3 Perform the dilution using an appropriate disposable volumetric pipette to transfer the extract and for the make-up volume of hexane. Make sure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with the solvent.

8.5.4 Transfer 1 mL of the extract to a labeled 1.5-mL GC autosampler vial. Record the sample data and submit with the sample extracts to the GC analyst.

9.0 QUALITY CONTROL

9.1 This section outlines the necessary quality control samples that need to be instituted at the time of sample extraction. The data from these quality control samples is maintained to document the quality of the data generated.

9.2 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation steps (including clean-up steps). For sediment/solid samples, a laboratory sodium sulfate blank is processed.

9.3 At this time, the GE Hudson River Design Support Sediment Sampling and Analysis Program does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, a matrix spike for Aroclor-1242 is to be analyzed at a rate of 1 matrix spike per every 20 samples at a concentration of 20,000 ng/mL in the extract (**Note:** this spike concentration will require a sample dilution to be performed). Also a matrix spike duplicate sample is to be analyzed at a rate of 1 per every 20 samples.

9.4 A QC reference check standard (LCS) is also prepared and analyzed for Aroclor-1242 at a concentration of 500 ng/mL in the extract. For sediment/solid samples, sodium sulfate is used.

9.5 Surrogate compounds are added to each sample, matrix spike, matrix spike duplicates, method blank, and QC reference check standard (LCS) at time of extraction. The surrogate compounds TCMX and DCB are to be added for final extract concentrations of 10 ng/mL and 100 ng/mL, respectively.

10.0 REFERENCES

1. U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

2. "Guide to Environmental Analytical Methods", Third Edition, Genium Publishing Corporation, 1996.

11.0 ATTACHMENTS

1. ASE Methods

2. ASE control panel keypad.

3. ASE cell cleanup procedure.

4. Recommended ASE Extraction Conditions for PCB in Sediment

ATTACHMENT 1

ASE METHODS

METHOD #	ANALYTE OF INTEREST	MATRIX	REQUIRED SOLVENT *	AMOUNT OF SAMPLE
1	PCB	WIPE	1	WIPE
2	PET I.D.	SOIL	1	10 g
2	8270	SOIL	3	30 g
3	**PCB**	**SOIL**	**2**	**10 g**
4	NONE	NONE	2	NONE
5	**PCB (RUSH)**	**SOIL**	**2**	**10 g**

*REQUIRED SOLVENT CHART

1 - HEXANE
2 - 1:1 HEXANE / ACETONE
3 - 1:1 DICHLOROMETHANE / ACETONE

ATTACHMENT 2
CONTROL PANEL KEYPAD

* TRAY	Tray is in free spin for manual turning.
TRAY *	Tray drive mechanisms are engaged and cannot be moved manually.
RINSE	Starts a manual rinse cycle.
* START	System is idle.
START *	system is currently running a method or schedule.
ABORT	Interrupts current run. Continue with abort function to terminate ASE run.
MENU	Displays a list of available screens.

* - LIGHT IS ON

ATTACHMENT 3
ASE cell cleanup procedure

Remove the end caps of ASE cells. Using a metal spatula designated for cell clean up, push the extracted sample out of the cell into a garbage can. Wash the interior and exterior of the cell and cell end caps with soap and water (use the brush designated for ASE use only). Dry the cell parts with a paper towel and reassemble the cell.

Run the washed cells on the ASE (use a new 60-mL VOA vial for each cell) using method 7 for 22 mL cells, 8 for 33 mL cells and 1:1 dichloromethane/acetone as the solvent.

Note: After the cells has been used 20 times or if the frits become clogged, the cell end caps should be taken apart and sonicated for 10 minutes in acetone and 10 minutes in dichloromethane.

ATTACHMENT 4
Recommended ASE Extraction Conditions for PCB in Sediment

The following instrument conditions will be utilized for extraction of sediment samples by accelerated solvent extraction for PCB. These conditions may need to be optimized, as needed, according to the instrument manufacturer's recommendations. Once conditions are established, the same procedures should be performed on all samples.

Recommended extraction conditions for Dionex ASE200

Oven Temperature: 150°C
Pressure: 1750 psi
Static time: 7 minutes (Instrument will automatically perform a 7-minute pre-heat equilibration cycle)
Flush volume: 60% of cell volume
Nitrogen Purge: 180 seconds at 150 psi
Static Cycles: 3

APPENDIX 7

STANDARD OPERATING PROCEDURE (SOP) GEHR3540C

1.0 TITLE General Electric (GE) Hudson River Design Support Sediment Sampling and Analysis Program Standard Operating Procedure for the extraction and cleanup of sediment/solid samples for Polychlorinated Biphenyl (PCB) analysis using the Soxhlet extraction technique by SW-846 Method 3540C for subsequent analysis by SW-846 Method 8082.

(Acknowledgement: This SOP is based substantially on internal method SOPs provided by Northeast Analytical, Inc. of Schenectady, N.Y.)

2.0 PURPOSE The purpose of this SOP is to provide to the chemist the procedures required to perform extractions of PCBs, in sediment/solid sample, using the soxhlet extraction technique and to perform the subsequent extract volume reduction and cleanup for the GE Hudson River Design Support Sediment Sampling and Analysis Program.

3.0 SCOPE The following procedure is utilized by the project laboratories for the extraction and cleanup of PCBs from sediment/solid samples using the soxhlet extraction method for analysis by SW-846 Method 8082.

4.0 COMMENTS The automated solvent extraction may be used in place of the soxhlet extraction at the discretion of the supervising chemist. Time restraints (*i.e.* requested turn around time) may render this method inapplicable, as it requires 18 +/-2 hours of extraction reflux time.

5.0 SAFETY The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples.

Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. The chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them. All equipment and solvents should be handled within a lab fume hood.

6.0 REQUIREMENTS The chemist must have an understanding of the methods and requirements of USEPA-SW- 846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition. Methods 3540C, 3500B, 3620B, 3665A, 3660B. An approved instructor must also certify the chemist to perform the procedure.

7.0 EQUIPMENT

7.1 Water Cooled Condenser: Pyrex 45/50 #3840-MCO or equivalent.

7.2 250mL Round Bottom Flask: Pyrex #4100 or equivalent.

7.3 Soxhlet Repetitive Flushing (reflux) Unit: 45/50 Pyrex #3740-M or equivalent.

7.4 Heating Mantle: Type "VF" laboratory heating mantle #HM0250VF1. (or equivalent)

7.5 Heating Mantle Controller: Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

7.6 Analytical Balance: Mettler AG-204 (or equivalent) used to determine sample mass.

7.7 Cellulose Extraction Thimble: Contains sample during soxhlet extraction.

7.8 Sodium Sulfate: Anhydrous (12-60 Mesh), washed with hexane and baked overnight. Used for the laboratory method blank.

7.9 Boiling Chips: Chemware PTFE Boiling Stones P#0919120 (or equivalent)

7.10 Chiller: Pump driven water circulating cooling system cool flow #75 NESLABS Instruments, Inc. (or equivalent)

7.11 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208 (or equivalent).

7.12 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090 (or equivalent).

7.13 TurboVap Evaporator: Zymark #ZW640-3 (or equivalent).

7.14 TurboVap Evaporator concentrator tubes: Zymark 250 mL (or equivalent), 0.5 mL endpoint.

7.15 Beakers: Assorted Pyrex: 250 mL, 600 mL, and 1000 mL, used for liquid containment and pipette storage.

7.16 1:1 Hexane/Acetone: 50%/50% by volume solvent mixture prepared in the lab.

7.17 Vials: glass, 8 dram & 4 dram (with Polyseal sealed cap) (20 mL & 10 mL) capacity, for sample extracts.

7.18 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

7.19 Centrifuge: International Equipment Co., Model CL (or equivalent).

7.20 Wrist Shaker: Burrell wrist action shaker, Model 75 and 88 (or equivalent).

7.21 Florisil®: 10% deactivated.

7.22 TBA Reagent: Tetrabutylammonium Hydrogen-Sulfite Reagent (prepared in the laboratory).

7.23 Mercury: Triple distilled Mercury Waste Solutions, Inc, (or equivalent).

7.24 Sulfuric Acid: H_2SO_4 (concentrated) Mallinkrodt #2468 #UN1830 (or equivalent).

7.25 Pipettes: S/P Disposable Serological Borosilicate Pipettes.

1. 1 mL × 1/10
2. 5 mL × 1/10
3. 10 mL × 1/10

Fisher Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

7.26 4 oz. Jars: Industrial Glassware

8.0 PROCEDURES

8.1 Sample Preparation

8.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, these problems should be brought to the attention of the supervisor and/or quality assurance manager for guidance to proceed and then documented in the extraction logbook.

8.1.2 If the sample is sediment and contains a water layer, decant and discard the layer as aqueous PCB waste. Mix the sample thoroughly and discard any foreign objects such as sticks, rocks or leaves. **Note:** however that the sample may be composed entirely of rock, concrete or some other solid material in which case the entire sample is treated as the solid.

8.2 Sample Extraction

8.2.1 Fill a Pyrex pan with ice cubes and cold water about 1/2 inch deep. As the samples are weighed out, place the beakers or 4-oz. jars in the Pyrex pan to chill for at least 15 minutes prior to the drying step.

8.2.2 Rinse all extraction thimbles with hexane to remove extraneous material. Place thimble into a 100-mL beaker and allow to dry.

8.2.3 Set up one 250-mL glass beaker or 4-oz. jar for each sample. Using the first sample, label a beaker with the sample number, and tare the beaker. Using a metal spatula, add 10 g to 11 g of the wet sample to the beaker. Samples that are observed to be very wet will require additional mass of sample such that the project sensitivity requirements are met. The moisture content of the sample as determined in Section 8.2.4 should be evaluated so that a larger wet-weight sample can be obtained to provide a dry amount of solids to meet the project sensitivity requirements. The amount taken must consider the size limitations of the Soxhlet thimble. The laboratory should target a wet-weight amount of 15 g for very wet samples. Record the weight in the PCB

solid extraction logbook to the nearest tenth of a gram. At this point, a sample for percent total solids may also be taken (see 8.2.4). Place the beaker in the ice bath to chill.

8.2.4 The PCB concentration is to be determined on a dry weight basis and therefore, the percent total solid must be determined. Weigh approximately 5 grams of the previously homogenized sample in a previously weighed, aluminum weighing pan. Record the weight of the pan and the weight of the (pan and sample) in the percent total solids log. Place the sample in a drying oven at 100 to 110°C for at least 8 hours. Record the time placed in the oven and the oven temperature in the percent total solids log. Remove the samples from the drying oven and allow to cool in a desiccator. Weigh the pan and sample.

Calculate the percent solids by:

$$\frac{\{(\text{wt. of pan + dried sample}) - (\text{wt.of pan})\}}{(\text{wt. of wet sample})} \times 100\%$$

NOTE: ALL SAMPLE CONTAINERS ARE TO BE RETURNED TO THE APPROPRIATE REFRIDGERATOR. FOR ALL EMPTY SAMPLE CONTAINERS, SEE THE LABORATORY'S INTERNAL CHEMICAL HYGIENE PLAN FOR PROPER DISPOSAL.

8.2.5 After the sample has been sufficiently chilled, add approximately 10 g of a 1:1 mix of Magnesium Sulfate/Sodium Sulfate to the sample and mix well with a metal spatula. If the sample has not dried after a few minutes, another 10 g may be added. Once the sample is well-dried and free flowing, transfer the sample to a pre-rinsed extraction thimble. Repeat with remaining samples. Set empty mixing beaker and stirring utensil aside for later rinsing into soxhlet extractor to complete sample transfer. Be careful not to add too much drying agent to the sample, if too much is added, the sample may not fit completely in the thimble. In this case the sample will have to be split into two different soxhlets.

8.2.6 Add 200 mL of a 1:1 mixture of hexane/acetone to a 250-mL round bottom flask. Add several boiling chips. Place a soxhlet extractor on top of the round bottom flask. Label the round bottom with the sample number. Place the corresponding thimble into the soxhlet extractor. Rinse corresponding beaker & metal spatula with a few pipettes of hexane. Transfer into thimble. Repeat this step twice more with the same sample, and then repeat all preceding steps with remaining samples. After all samples have been processed, add the specified surrogate and matrix spikes required directly into thimble. The final extract volume concentrations of the surrogate compounds tetrachloro-*meta*-xylene (TCMX) and decachlorobiphenyl (DCB) should be 10 ng/mL and 100 ng/mL, respectively. At this time, the GE Hudson River Design Support Sediment Sampling and Analysis Program does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, the final extract volume

concentration for the spiked Aroclor (Aroclor-1242) in the matrix spike and matrix spike duplicate sample should be 20,000 ng/mL (**Note:** this spike concentration will require a sample dilution to be performed). The final extract volume concentration of the laboratory control sample (LCS) should be 500 ng/mL.

8.2.7 Rinse the inside and the outside connecting joints of the condenser units that will be used to condense the extraction solvent during the soxhlet extraction of the sample. Turn on chiller to cool the condensers.

8.2.8 Place the round bottom flask with attached soxhlet extractor onto a heating mantle and attach condenser unit. Turn corresponding thermostats on to a temperature that will achieve 4-6 solvent cycles per hour. At this time double check soxhlets for any cracks or chips which may leak solvent. Once the solvent begins to boil, a flushing action of once every two to three minutes should be achieved.

8.2.9 The samples should be extracted overnight for a minimum of 16 hours. Once the sample has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature. Turn off the chiller and once cool, rinse the inside of the condenser with several pipette volumes of hexane. Disengage the soxhlet and condenser unit and rinse the joint off as well into the soxhlet.

8.2.10 Move soxhlet units into a chemical fume hood and flush the remaining solvent from the soxhlet extractor by tipping the soxhlet. Using a pair of

long-handled tweezers, pull the thimbles out of the soxhlets one at a time and allow them to drip dry by balancing the thimbles on the tops of the soxhlets. Once dry; remove the thimbles to a Pyrex drying pan for total solvent evaporation.

8.2.11 Rinse the soxhlet with several pipettefull of hexane and tip again to drain into the round bottom. Set the soxhlet aside at this time. Procure the same number of TurboTubes as there are samples. Using an individual TurboTube stand, label a TurboTube with the corresponding sample ID number and place in the holder. Pour the contents of the round bottom into the TurboTube, using a pipette and Hexane to rinse the last drops out of the mouth of the round bottom. Rinse the round bottom with several pipettefull of hexane, swirl gently, and decant into same TurboTube. Repeat this step twice for same sample then repeat all preceding steps for all other samples.

8.2.12 All glassware must be rinsed with technical grade (tech)-Acetone or a "for rinsing-only" labeled solvent, and dried in the hood before other cleaning steps.

8.3 Solvent Reduction: TurboVap Evaporator System

8.3.1 The TurboVap evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus. The TurboVap uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent

extract, which allows fractional reduction of the solvents without loss of higher boiling point analytes.

8.3.2 Turn the unit on and allow to heat up to the specified temperature for individual solvent use.

8.3.3 As a precaution the TurboVap system regulators should be checked to assure that no residual gas pressure remains within the system and that gas pressure regulators is off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty TurboTube into the water bath and close the lid. Make sure that the nitrogen gas pressure regulator is turned off. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Proceed to 8.3.4. Make sure to wipe down all surfaces with Hexane before concentrating samples.

8.3.4 Place the TurboTube containing the samples into the TurboVap and close the lid. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction.

8.3.5 The process for solvent (Hexane/Acetone) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown

to dryness and PCB loss may occur. Immediately notify a supervisor if an extract is blown to dryness.

8.3.6 Concentrate the solvent to approximately 5.0 mL. Remove the samples from the TurboVap and place in the rack. **Note:** Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing before the 5.0 mL point is achieved. Samples, which stop reducing, should be removed as soon as possible.

8.3.7 Quantitatively transfer the sample extract with a Pasteur pipette into an appropriate volumetric flask (25 mL for soil extracts). Rinse the TurboTube with 3 Pasteur pipettes of hexane, and then transfer the hexane rinse to the volumetric. Repeat the hexane rinse two more times for a total of three Hexane rinses of the TurboTube. After the sample has been transferred, rinse the Pasteur pipette with 0.5 mL of hexane into the volumetric flask. Add hexane to the volumetric meniscus mark. Invert the volumetric flask at least three times to mix completely. Decant the contents into a pre-labeled 8-dram vial.

8.3.8 All dirty glassware must be rinsed with tech-Acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

8.4 Sample Extract Cleanup

Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances which must be removed before accurate chromatographic analysis can be performed.

Sulfuric acid, sulfur removal and Florisil® clean-ups should be performed on every sample. The sample preparation chemist in the extraction logbook records the sequence and number of repeats of cleanup steps performed.

Sample extract cleanups are performed on set volume extracts. The set volume is 25 mL for sediment/solid samples.

8.4.1 Sulfuric Acid Wash

8.4.2 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds that are co-extracted with the PCB residues.

8.4.3 Chill the sample to approximately 0°C. Add 5.0 mL of concentrated H_2S0_4 and shake for 30 seconds by hand, centrifuge for approximately 1 minute, transfer approximately 20 mLs of the Hexane upper layer to an 8-dram vial.

8.4.4 Repeat 8.4.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. **Note:** it is entirely possible that all colored material will not be removed from the extract.

8.5 Elemental Sulfur Clean-up

8.5.1 Elemental sulfur is soluble in the extract solvents used for sediment and soil samples. It is commonly found sediment/soil samples, decaying organic material and some industrial wastes. Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak.

8.5.2 Two techniques exist for the elimination of elemental sulfur in PCB extracts. Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

8.6 Removal of Sulfur Using Mercury

Note: Mercury is a highly toxic metal. All operations involving mercury should be performed within a hood. Prior to using mercury, the chemist should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet MSDS.

8.6.1 Add 1-3 drops of mercury to the sample extracts, cap, and place on the wrist shaker for 30 minutes. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

8.6.2 Remove the sample extracts from the wrist shaker and place in the centrifuge at a setting and duration appropriate to spin down the solids.

8.6.3 Transfer the sample extract to a new 8-dram vial.

8.6.4 The precipitated sulfur can be removed from the extract by performing a sulfuric acid clean-up or Florisil® slurry (discussed in 8.8.0).

8.7 Removal of Sulfur using TBA Sulfite

8.7.1 The TBA procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water-soluble.

8.7.2 Add 2.0 mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 0.65 g of sodium sulfite crystals to the extract and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more aliquots (approximately 0.65 g) to extract and observe.

8.7.3 Place the samples on the wrist shaker for 45 minutes observing at 15-minute intervals to make sure that the sodium sulfite is not consumed. Add 5 mL organic free water and shake for ten minutes.

8.7.4 Place the samples into the centrifuge at a setting and duration appropriate to spin down the solids.

8.7.5 Transfer the hexane layer to a new 8-dram vial and cap.

8.8 Florisil® Adsorption (Slurry)

8.8.1 The Florisil® slurry removes co-extracted polar compounds, residual water, and residual acid and is recommended as the final cleanup step before the extract is submitted for GC analysis.

8.8.2 Add approximately 3 grams of tested and approved 10% deactivated Florisil® to each vial containing the sample extract.

8.8.3 Vigorously shake the vial for approximately 1 minute by hand or on the wrist shaker.

8.8.4 Place the vial(s) into the centrifugeat a setting and duration appropriate to spin down the solids.

8.8.5 Transfer the extract to a clean 8-dram vial.

8.9 Extract Screening and Dilution:

8.9.1 Screening PCB extracts by GC to determine the approximate concentration before final analysis is highly recommended. If possible, prior site history and estimates of sample concentration will be provided by the field personnel and may be used to determine what, if any, extract dilution is necessary.

8.9.2 The supervising chemist is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the original sample extract into a vial containing the correct amount of "make up" volume of hexane. Dilutions must be recorded in the instrument logbook or in the data system.

8.9.3 Perform the dilution using appropriate disposable volumetric pipettes to transfer the extract and to add the make-up volume of hexane. Make sure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with the solvent.

8.9.4 Transfer 1 mL of the extract to a labeled 1.5-mL GC autosampler vial. Record the screening dilution along with the extract volume, the sample mass, and the percent total solids. Submit the information with the sample extracts to the GC analyst.

9.0 QUALITY CONTROL

9.1 This section outlines the necessary quality control samples that need to be instituted at the time of sample extraction. The data from these quality control samples is maintained to document the quality of the data generated.

9.2 9.2 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation steps (including clean-up steps). For sediment/solid samples, a laboratory sodium sulfate blank is processed.

9.3 At this time, the GE Hudson River Design Support Sediment Sampling and Analysis Program does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, a matrix spike for Aroclor-1242 is to be analyzed at a rate of 1 matrix spike per every 20 samples at a concentration of 20,000 ng/mL in the extract (**Note:** this spike concentration will require a sample dilution to be performed). Also a matrix spike duplicate sample is to be analyzed at a rate of 1 per every 20 samples.

9.4 A QC reference check standard (Laboratory Control Sample [LCS]) is also prepared and analyzed for Aroclor-1242 at a concentration of 500 ng/mL in the extract. For sediment/solid samples, sodium sulfate is used.

9.5 Surrogate compounds are added to each sample, matrix spike, matrix spike duplicates, duplicate, method blank, and QC reference check standard LCS at time of extraction. The surrogate compounds TCMX and DCB are to be added for final extract concentrations of 10 ng/mL and 100 ng/mL, respectively.

10.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

10.1 Pollution Prevention: see laboratory's internal SOPs

10.2 Waste Management: see laboratory's internal SOPs

11.0 REFERENCES

1. U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

2. "Guide to Environmental Analytical Methods", Third Edition, Genium Publishing Corporation, 1996.

12.0 ATTACHMENTS

1. Method Outline

ATTACHMENT 1
PCBs IN SOIL/SEDIMENT
OUTLINE FOR SOXHLET EXTRACTION

1. PREPARE SAMPLE FOR EXTRACTION
2. RINSE EXTRACTION THIMBLES
3. WEIGH SAMPLE AND RECORD WEIGHT
4. DRY SAMPLES
5. ADD SAMPLE TO THIMBLES
6. SET UP SOXHLET EXTRACTOR APPARATUS
7. ADD SURROGATES, MATRIX SPIKE, AND LABORATORY CONTROL SAMPLE SPIKE
8. EXTRACT SAMPLE FOR APPROXIMATELY 16 HOURS
9. BREAKDOWN SOXHLET EXTRACTOR APPARATUS
10. TRANSFER SOLVENT TO TURBOTUBE
11. SOLVENT REDUCTION, USING THE ZYMARK TURBOVAP EVAPORATION SYSTEM
12. TRANSFER AND SET VOLUME
13. EXTRACT CLEANUP (ACID, MERCURY OR TBA, AND FLORISIL)
14. EXTRACT DILUTION
15. GC SCREENING/ ANALYSIS

APPENDIX 8

STANDARD OPERATING PROCEDURE (SOP) GEHR680

GENERAL ELECTRIC (GE) HUDSON RIVER DESIGN SUPPORT

SEDIMENT SAMPLING AND ANALYSIS PROGRAM

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF PCBs IN SEDIMENT BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY BY EPA METHOD 680

Revision No.: 1

July 16, 2002

INDEX

1. SCOPE AND APPLICATION

1.1. This method provides procedures for mass spectrometric determination of polychlorinated biphenyls (PCBs) in sediment for the GE Hudson River Design Support Sediment Sampling and Analysis Program (SSAP). This method is applicable to samples containing PCBs as single congeners. PCBs are identified and measured as isomer groups (*i.e.,* by level of chlorination). The existence of 209 possible PCB congeners makes impractical the listing of the Chemical Abstracts Service Registry Number (CASRN) for each potential method analyte. Because PCBs are identified and measured as isomer groups, the non-specific CASRN for each level of chlorination is used to describe method analytes.

Analyte(s)	Formula	CASRN
PCBs		
Monochlorobiphenyls	$C_{12}H_9Cl$	27323-18-8
Dichlorobiphenyls	$C_{12}H_8Cl_2$	25512-42-9
Trichlorobiphenyls	$C_{12}H_7Cl_3$	25323-68-6
Tetrachlorobiphenyls	$C_{12}H_6Cl_4$	26914-33-0
Pentachlorobiphenyls	$C_{12}H_5Cl_5$	25429-29-2
Hexachlorobiphenyls	$C_{12}H_4Cl_6$	26601-64-9
Heptachlorobiphenyls	$C_{12}H_3Cl_7$	28655-71-2
Octachlorobiphenyls	$C_{12}H_2Cl_8$	31472-83-0
Nonachlorobiphenyls	$C_{12}HCl_9$	53742-07-7
Decachlorobiphenyls	$C_{12}Cl_{10}$	2051-24-3

1.2 A Method Detection Limit (MDL) study will be performed on a representative instrument in accordance with the procedures described in 40 CFR Part 136, Appendix B prior to analysis of sediment samples for the SSAP. A clean sodium sulfate will be used as the matrix for this MDL study. Detection limits vary among method analytes and with sample matrix, sample preparation procedures, condition of the GC/MS system, type of data acquisition, and individual samples. Detection limits for individual PCB congeners increase with increasing number of chlorine atoms, with the detection limit for decachlorobiphenyl being about 2 times higher than that of a monochlorobiphenyl. The detection limit for total PCBs will depend on the number of individual PCB congeners present. SIM data acquisition procedures reduce the detection limit for PCBs by at least a factor of three.

2. SUMMARY OF METHOD

In general, samples are extracted with a pesticide-grade solvent. The extracts are further processed by concentrating or diluting, depending on the PCB concentration, and carried through a series of cleanup techniques. The sample is then analyzed by injecting the extract onto a gas chromatographic system and the PCBs detected by a mass spectrometer.

This SOP provides detailed instructions for gas chromatographic/mass spectrometer conditions, calibration, and analysis of PCBs by gas chromatography/mass spectrometry (GC/MS). Sediment extraction procedures are covered in separate standard operating procedures. It is expected that the extracts generated for analysis by SOP GEHR8082 will be used for analysis by this method (GEHR680) to provide paired total PCB results by both methods for the same extract.

Sample extract components are separated with capillary column gas chromatography (GC) and identified and measured with low resolution, electron ionization mass spectrometry (MS). An interfaced data system (DS) to control data acquisition and to store, retrieve, and manipulate mass spectral data is essential. Selected-ion-monitoring (SIM) data are to be acquired.

A Varian Saturn Ion Trap GC/MS will be used by Northeast Analytical, Inc. (NEA) to perform this analysis. Varian uses a proprietary field-modulated Wave-Board technology to selectively trap only those ions of interest. Background ions are not stored. This allows for a much cleaner spectrum and a considerable increase in sensitivity since the trap's capacity is dedicated to these ions of interest. Additionally, the selected storage mass range (Method 680 requires scanning ions across 5 mass ranges) is time programmable so that many different target analytes can be selectively stored relative to the background matrix. Varian refers to this mode of operation as Selected Ion Scanning (SIS) mode. SIS is Varian's term for Selected Ion Monitoring (SIM) common to most other mass spectrometers. SIS allows the Saturn Ion Trap to store many more masses than traditional SIM techniques without a corresponding loss of sensitivity. The more common term SIM (versus SIS) will be used throughout SOP for ease of reference.

Two surrogate compounds are added to each sample before sample preparation; these compounds are tetrachloro-*meta*-xylene (TCMX) and decachlorobiphenyl (DCB). Two internal standards, chrysene-d_{12} and phenanthrene-d_{10}, are added to each sample extract before GC/MS analysis and are used to calibrate MS response. Each concentration measurement is based on an integrated ion abundance of one characteristic ion.

PCBs are identified and measured as isomer groups or homologs (*i.e.*, by level of chlorination). A concentration is measured for each PCB isomer group total; total PCB concentration in each sample extract is obtained by summing isomer group concentrations.

Nine selected PCB congeners are used as calibration standards, and one internal standard, chrysene-$d_{12,}$ is used to calibrate MS response to PCBs, unless sample conditions require the use of the second internal standard, phenanthrene-d_{10}.

3. DEFINITIONS

3.1 CONCENTRATION CALIBRATION SOLUTION (CAL) -- A solution of method analytes used to calibrate the mass spectrometer response.

3.2 CONGENER NUMBER -- Throughout this method, individual PCBs are described with the number assigned by Ballschmiter and Zell (2). (This number is also used to describe PCB congeners in catalogs produced by Ultra Scientific, Hope, RI.)

3.3 INTERNAL STANDARD -- A pure compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

3.4 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the GC/MS with respect to a defined set of method criteria.

3.5 METHOD BLANK -- An aliquot of reagent water or neutral solid reference material that is treated as a sample. It is exposed to all glassware and apparatus, and all method solvents, reagents, internal standards, and surrogate compounds are used. The extract is concentrated to the final volume used for samples and is analyzed the same as a sample extract.

3.6 LABORATORY SPIKE DUPLICATE SAMPLE-- One aliquot (LSD) of a sample is analyzed before fortification with any method analytes. In the laboratory, a known quantity of method analytes (LSA) is added to two independent aliquots of the same sample, and final analyte concentrations (LF1 and LF2) are measured with the same analytical procedures used to measure LSD. These analyses are more commonly referred to as matrix spike (MS) and matrix spike duplicate (MSD) samples. MS/MSD analyses are not required by US EPA for the GE Hudson River SSAP.

3.7 LABORATORY SURROGATE SPIKE

3.7.1 Measured Value (LS1) -- Surrogate compound concentration measured with the same procedures used to measure sample components.

3.7.2 Theoretical Value (LS2) -- The concentration of surrogate compound added to a sample aliquot before extraction. This value is determined from standard gravimetric and volumetric techniques used during sample fortification.

3.8 METHOD DETECTION LIMIT (MDL) -- A statistically determined value (1) indicating the minimum concentration of an analyte that can be identified and measured in a sample matrix with 99% confidence that the analyte concentration is greater than zero. This value varies with the precision of the replicate measurements used for the calculation.

3.9 PERFORMANCE EVALUATION SAMPLE -- A sample containing known concentrations of method analytes that has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte concentrations are unknown to the analyst.

3.10 QUALITY CONTROL (QC) CHECK OR LABORATORY CONTROL SAMPLE (LCS) -- A sample containing known concentrations of analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze environmental samples containing the same or similar analytes. Analyte concentrations are known by the analyst.

3.11 SURROGATE COMPOUND -- A compound not expected to be found in the sample is added to a sample aliquot before extraction and is measured with the same procedures used to measure sample components. Associated with the surrogate compound are two values, laboratory surrogate spike - measured value (LS1) and laboratory surrogate spike - theoretical value (LS2). The purpose of a surrogate compound is to monitor method performance with each sample.

4. INTERFERENCES

4.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment. Method blanks are analyzed routinely to demonstrate that these materials are free of interferences under the analytical conditions used for samples.

4.2 To minimize interferences, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Than wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry. Heating in a muffle furnace at 450°C for a few hours may be used as a further cleaning technique, but does not have to be performed provided that method blanks demonstrate glassware cleanliness. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent. Volumetric glassware should not be heated in a muffle furnace.

4.3 For PCBs, interference can be caused by the presence of much greater quantities of other sample components that overload the capillary column; additional sample extract preparation procedures must then be used to eliminate interferences (refer to the applicable extraction SOPs for extract cleanup procedures). Capillary column GC retention time and the compound-specific characteristics of mass spectra eliminate many interferences that formerly were of concern with PCB determinations with electron capture detection. The approach and identification criteria used in this method for PCBs eliminate interference by most chlorinated compounds other than other PCBs. With the isomer group approach, coeluting PCBs that contain the same number of chlorines are identified and measured together. Therefore, coeluting PCBs are a problem only if they contain a different number of chlorine atoms. This interference problem is obviated by rigorous application of the identification criteria described in this method.

5. SAFETY

5.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

5.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. The analyst should minimize manipulation of sample extracts outside of a fume hood.

5.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions of handling applicable solvents and chemicals used to process samples. The analyst should refer to the project laboratory's internal chemical hygiene plan for further safety information.

5.4 Samples remaining after analysis should be disposed of through the project laboratory's internal disposal plan. Refer to the project laboratory's internal standard operating procedures for disposal of laboratory waste.

6. APPARATUS AND EQUIPMENT

6.1 COMPUTERIZED GC/MS

The specific GC and MS operating parameter to be used are summarized on Table 1.

6.1.1 The GC must be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. Splitting injections is not recommended.

6.1.2 SIM mass spectral data are obtained with electron ionization at a nominal electron energy of 70 eV. To ensure sufficient precision of mass spectral data, the required MS scan rate must allow acquisition of at least five full-range mass spectra or five data points for each monitored ion while a sample component elutes from the GC. The MS must produce a mass spectrum meeting all criteria for $\leq$ 20 ng of decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet.

6.1.3 An interfaced data system (DS) is required to acquire, store, reduce, and output mass spectral data. The DS must be capable of searching a data file for specific ions and plotting ion abundances versus time or spectrum number to produce selected ion current profiles (SICPs) and extracted ion current profiles (EICPs). Also required is the capability to obtain chromatographic peak areas between specified times or spectrum numbers in SICPs or EICPs. Total data acquisition time per cycle should be $\geq$ 0.5 s and must not exceed 1.5 s.

6.1.4 SIM – For SIM data acquisition, the DS must be equipped with software capable of acquiring data for multiple groups of ions, and the DS must allow automated and rapid changes of the set of ions being monitored. The SIM program must be capable of acquiring data for five groups (or mass ranges) each consisting of $\leq$ 27 ions each. The times spent monitoring ions during sample analyses must be the same as the times used when calibration solutions were analyzed.

6.2 GC COLUMN – A 30 m $\times$ 0.25 mm ID fused silica capillary column coated with a 0.25 μm film, Durabond-XLB, Agilent Technologies is required. Operating conditions known to produce acceptable results with this column are shown in Table 1. Separation of PCB calibration congeners with a DB-XLB column and those operating conditions is shown in Figure 1. Figure 2 shows a chromatogram of the PCB Window Defining Mixture used to determine retention time windows for the five ion groups for SIM data acquisitions.

6.3 MISCELLANEOUS EQUIPMENT

6.3.1 Volumetric flasks -- 2-mL, 5-mL, 10-mL, 25-mL, and 50-mL with ground glass stoppers.

6.3.2 Microsyringes -- various standard sizes 9.

6.3.3 Analytical Balance -- capable of accurately weighing to 0.0001 g.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 SOLVENTS -- High purity, distilled-in-glass hexane and methylene chloride. For precise injections with splitless injectors and capillary columns, all samples and standards should be contained in the same solvent. Effects of minor variations in solvent composition (*i.e.,* small percentage of another solvent remaining in hexane extracts) are minimized with the use of internal standards. (External standard calibration is not acceptable.)

7.2 SODIUM SULFATE - ACS, granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.

7.3 MS PERFORMANCE CHECK SOLUTION - Prepare a 10 ng/μL solution of decafluorotriphenylphosphine (DFTPP) in an appropriate solvent.

7.4 INTERNAL STANDARDS - Chrysene-d_{12} and phenanthrene-d_{10} are used an internal standards. They are added to each sample extract just before analysis and are contained in all calibration/performance check solutions and quality control samples.

7.5 SURROGATE COMPOUNDS – TCMX and DCB are added to every sample before extraction and are included in every calibration/performance check solution and quality control samples.

7.6 PCB CONCENTRATION CALIBRATION CONGENERS - The nine individual PCB congeners listed on Table 2 are used as concentration calibration compounds for PCB determinations. One isomer at each level of chlorination is used as the concentration calibration standard for all other isomers at that level of chlorination, except that decachlorobiphenyl (Cl_{10}) is used for both Cl_9 and Cl_{10} isomer groups. The basis for selection of these calibration congeners has been reported (6).

7.7 PCB RETENTION TIME CONGENERS FOR SIM DATA ACQUISITION -- Knowledge of the retention time of certain congeners is necessary to determine when to acquire data with each ion set. Two concentration calibration congeners also serve as retention time congeners; the first eluting Cl_1-PCB indicates the time when data acquisition must have been initiated for ion set #1, and the Cl_{10}-PCB indicates when all PCBs have eluted. A PCB Window Defining Mixture Standard (AccuStandard, Inc., catalog item C-WDM or equivalent) is analyzed at a concentration of 2.5ug/mL for each PCB congener. The PCB Window Defining Mixture Standard contains the first and last eluting PCB congener for each Homolog group. The following four congeners are used from this standard to define the five retention time segments for the five Ion Set Groups: BZ#104, BZ#77, BZ#202, and BZ#189. (See Sect. 9.2.3.1.3 for Ion Set Segments).

7.8 PCB SOLUTIONS

7.8.1 Stock Solutions of PCB Calibration Congeners -- Prepare a stock solution of each of the nine PCB concentration calibration congeners at a concentration of 1 μg/μL in hexane. Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C if solutions are not to be used right away. Solutions are stable indefinitely if solvent evaporation is prevented. CAUTION: Each time a vial containing small volumes of solutions is warmed to room temperature and opened, a small volume of solvent in the vial headspace evaporates, significantly affecting concentration. Solutions should be stored with the smallest possible volume of headspace, and opening vials should be minimized.

7.8.2 PCB Primary Dilution Standard -- Take aliquots of the stock solutions of the nine PCB concentration calibration congeners and mix together-in the proportions of one part of each solution of the Cl_1 (#1), Cl_2 (#5), and Cl_3 (#29) congeners, two parts of each solution of the Cl_4 (#50), Cl_5 (#87), and Cl_6 (#154) congeners, three parts of each solution of the Cl_7 (#188) and Cl_8 (#200) congeners, and five parts of the Cl_{10} (#209) congener solution. This will provide a primary dilution standard solution of the composition shown on Table 3. Calculate the concentration in μg/μL; use three significant figures. Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C. Mark the meniscus on the vial wall to monitor solution volume during storage; solutions are stable indefinitely if solvent evaporation in prevented.

7.9 INTERNAL STANDARD (IS) SOLUTION

7.9.1 IS solution (for SIM CALs) – Phenanthrene-d_{10} and chrysene-d_{12} at a concentration of 40 ng/μL (ppm). A stock standard is prepared by transferring 1 mL of 1000 ng/μL phenanthrene-d_{10} and 0.5 mL of 2000 ng/μL chrysene-d_{12} to 25 mL hexane to provide a 40 ng/μL (ppm) solution.

7.10 CAL FOR SIM DATA ACQUISITION -- One set of six solutions is needed for PCB determinations. Appropriate concentrations of SIM CALs are given on Table 4a and 4b. Solutions are prepared by diluting appropriate primary dilution standards and adding an appropriate volume of IS solution #2. Four (4) μL of IS solution (7.9.1) will be added to 200 μL of extract to provide phenanthrene-d_{10} and chrysene-d_{12} at a concentration of 0.80 μg/μL (ppm) in the extract. The CAL6 level is prepared by using 600 μL of primary dilution standard plus 400 μL of Hexane. This gives a concentration for decachlorobiphenyl of 15.0 ug/mL. The GC/MS calibration standard is prepared by taking 200 μL of this standard and spiking with four (4) μL of internal standard. Only decachlorobiphenyl will be calibrated from this sixth standard, leaving all analytes as a five-point calibration.

7.11 Calculate the concentration (two significant figures if <100 and three significant figures if >100 ng/μL) of each component in each solution. Note: Concentrations presented in tables are only approximate.

7.12 LABORATORY PERFORMANCE CHECK SOLUTION - The Medium CAL is used as the laboratory performance check solution (LPC) to verify response factors and to demonstrate adequate GC resolution and MS performance.

7.13 PCB Window Defining Mixture Standard – This standard is used as purchased at 2.5ug/mL per congener. It is analyzed by full scan to provide a check on retention time for the four PCB congeners used to established retention time segments for SIM data acquisition.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Sample collection, preservation, and storage of sediment samples is addressed in the Design Support Sediment Sampling Analysis Program Field Sampling Plan (FSP) and Quality Assurance Project Plan (QAPP).

9. CALIBRATION

Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of continuing calibration checks. After initial calibration is successfully performed, a continuing calibration check is required at the beginning and end of each 12-h period during which analyses are performed.

9.1 DATA ACQUISITION -- SIM data acquisition is to be used.

9.1.1 SIM data acquisition will provide an increase in sensitivity from full-range data acquisition by at least a factor of three for PCB determinations.

9.2. INITIAL CALIBRATION

9.2.1 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer with any necessary modifications to meet requirements defined in this SOP.

9.2.2 Inject a 2-μL aliquot of the 10 ng/μL DFTPP solution and acquire a mass spectrum that includes data for m/z 45-450. If the spectrum does not meet all criteria (Table 5), the MS must be hardware tuned to most all criteria before proceeding with calibration.

9.2.3 SIM Calibration – Inject a 2-μL aliquot of the Medium CAL. Acquire at least five data points for each ion during elution of each GC peak. Total cycle time should be ≥ 0.5 s and <1.5 s. CAUTION: When acquiring SIM data, GC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times; if not, ions will not be monitored at the appropriate times.

9.2.3.1 SIM Calibration for PCB determinations

9.2.3.1.1 Data will be acquired with the five ion sets (≤ 27 ions each) shown on Tables 6a and 6b.

9.2.3.1.2 The time (scan number) for initiation of data acquisition with each ion set must be carefully determined from the retention times (scan numbers) of the retention time congeners. Approximate relative retention times of calibration congeners and approximate relative retention time windows for PCB isomer groups are shown on Table 7. (Also see Figure 1 and Figure 2.)

9.2.3.1.3 SIM data acquisition with five ion sets. Begin data acquisition with Ion Set #1 before elution of PCB congener #1, the first eluting Cl_1-PCB. Stop acquisition with Ion Set #1 and begin acquisition with Ion Set #2 just (approximately 10 seconds) before elution of PCB congener #104, the first eluting Cl_5-PCB. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 just (approximately 10 s) after elution of PCB congener #77, the last eluting Cl_4-PCB. Stop acquisition with Ion Set #3 and begin acquisition with ion Set #4 just (approximately 10 s) before elution of PCB congener #202, the first eluting Cl_8-PCB. Stop acquisition with Ion Set #4 and begin acquisition with Ion Set #5 just (approximately 10 s) after elution of PCB congener #189, the last eluting Cl_7-PCB, stop acquisition of Ion Set #5 after Cl_{10}-PCB elution.

9.2.4 Performance Criteria

9.2.4.1 SIM PCB Data

9.2.4.1.1 GC separation -- Baseline separation of PCB congener #87 from congeners #154 and #77, which may coelute.

9.2.4.1.2 MS sensitivity -- Signal/noise ratio of $\geq$ 5 for m/z 499 of PCB congener #209, Cl_{10}-PCB, and for m/z 241 of chrysene-d_{12}.

9.2.4.1.3 MS calibration -- Abundance of $\geq$ 70% and $\leq$ 95% of m/z 500 relative to m/z 498 for congener #209, Cl_{10}-PCB.

9.2.5 Replicate Analyses of CALs -- If all performance criteria are met, analyze one 2-uL aliquot of each of the other four CALs.

9.2.6 Response Factor Calculation

9.2.6.1 Calculate five response factors (RFs) for each PCB calibration congener and surrogate compound relative to both ISs (see Sect. 12.4.2), phenanthrene-d_{10} and chrysene-d_{12}.

$$RF = A_x Q_{is} / A_{is} Q_x$$

where:

A_x = integrated ion abundance of quantitation ion for a PCB calibration congener or a surrogate compound,

A_{is} = integrated ion abundance of m/z 240, the quantitation ion when chrysene-d_{12} is used as the internal standard or m/z 188, the quantitation ion when phenanthrene-d_{10} is used as the internal standard,

Q_{is} = injected quantity of chrysene-d_{12} or phenanthrene-d_{10},

Q_x = injected quantity of PCB calibration congener or surrogate compound.

RF is a unitless number, units used to express quantities must be equivalent.

9.2.7 Response Factor Reproducibility -- For each PCB calibration congener and surrogate compound, calculate the mean RF from analyses of each of the five CALs. When the RSD exceeds 20%, analyze additional aliquots of appropriate CALs to obtain an acceptable RSD of RFs over

the entire concentration range, or take action to improve GC/MS performance.

9.2.8 SIM Analyte Retention Time Reproducibility

9.2.8.1 PCB determinations - Absolute retention times of PCB congeners #77, #104, #202, and #189 should not vary by more than ±10 s from one analysis to the next. (Retention time reproducibility is not as critical for congeners #1 and #209 as for the other four congeners, which are used to determine when ion sets are changed.)

9.2.9 Record a spectrum of each CAL component.

9.3 CONTINUING CALIBRATION CHECK

9.3.1 With the following procedures, verify initial calibration at the beginning and end of each 12-h period during which analyses are to be performed.

9.3.2 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer.

9.3.3 Analyze a 2-μL aliquot of the DFTPP solution and ensure acceptable MS calibration and performance (Table 5).

9.3.4 Inject a 2-μL aliquot of the Medium CAL and analyze with the same conditions used during Initial Calibration.

9.3.5 Demonstrate acceptable performance for criteria described in Sect. 9.2.4.

9.3.6 Determine that neither the area measured for m/z 240 for chrysene-d_{12} nor that for m/z 188 for phenanthrene-d_{10} has decreased by more than 30% from the area measured in the most recent previous analysis of a calibration solution or by more than 50% from the mean area measured during initial calibration.

9.3.7 Response Factor Reproducibility -- For an acceptable Continuing Calibration Check, the measured RF for each analyte/surrogate compound must be within ±20% of the mean value calculated (Sect. 9.2.6) during Initial Calibration. If not, remedial action must be taken; recalibration may be necessary.

9.3.8 SIM Analyte Retention Time Reproducibility -- Demonstrate and document acceptable (Sect. 9.2.8) reproducibility of absolute retention

times of appropriate PCB retention time congeners by analysis of the PCB Window defining mixture in full scan mode.

9.3.9 Remedial actions must be taken if criteria are not met; possible remedies are:

9.3.9.1 Check and adjust GC and/or MS operating conditions.

9.3.9.2 Clean or replace injector liner.

9.3.9.3 Flush column with solvent according to manufacturers instructions.

9.3.9.4 Break off a short portion (approximately 0.33 m) of the column; check column performance by analysis of performance check solution.

9.3.9.5 Replace GC column; performance of all initial calibration procedures is then required.

9.3.9.6 Adjust MS for greater or lesser resolution.

9.3.9.7 Calibrate MS mass scale.

9.3.9.8 Prepare and analyze new concentration calibration/performance check solution.

9.3.9.9 Prepare new concentration calibration curve(s).

10. QUALITY CONTROL

The QC sample extracts (method blank and laboratory control sample) associated with the sediment sample extracts will be performed at a frequency of one method blank and one laboratory control sample (LCS) per 20 sample extracts. As many field sediment sample extracts originating from multiple laboratories and analysis extraction batches will be selected for Method 680 analysis, a representative method blank and LCS extract that has passed GEHR8082 acceptance criteria will be selected to be run with up to 20 sediment sample extracts for this analysis. Sediment sample extracts for Method 680 analysis will be selected from SOP GEHR8082 analysis batches where the method blank and LCS passed SOP GEHR8082 criteria. If this is not always possible, then the method and LCS that failed SOP GEHR8082 criteria will also be run by Method 680 (SOP GEHR680).

10.1 Method Blank – The extracts for this analysis will be the same extracts as those generated for the analysis of total PCBs as Aroclors by SOP GEHR8082.

10.1.1 A method blank must contain the same amount of surrogate compounds and internal standards that is added to each sample.

10.1.2 Analyze a method blank before any samples are analyzed.

10.1.3 An acceptable method blank contains no method analyte at a concentration greater than its reporting limit (RL) for the PCB homologue and contains no additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte at its RL. If the method blank that was extracted along with a batch of samples is contaminated, the entire batch of samples must be reanalyzed.

10.1.4 Corrective action for unacceptable method blank -- Check solvents, reagents, apparatus and glassware to locate and eliminate the source of contamination before any samples are extracted and analyzed. Purify or discard contaminated reagents and solvents.

10.2 CALIBRATION - Included among initial and continuing calibration procedures are numerous quality control checks to ensure that valid data are acquired (see Sect. 9). Continuing calibration checks are accomplished with results from analysis of the medium-level calibration solution and the PCB Window Defining Mixture to monitor criteria times for the five (5) ion sets.

10.2.1 If some criteria are not met for a Continuing Calibration Check after a 12-h period during which samples were analyzed, those samples must be reanalyzed. Those criteria are: GC performance (Sect. 9.2.4), MS calibration as indicated by DFTPP spectrum (Sect. 9.2.2), and MS sensitivity as indicated by area of internal standards (Sect. 9.3.6).

10.2.2 When other criteria in Sect. 9.2 are not met, results for affected analytes must be labeled as suspect to alert the data user of the observed problem. Included among those criteria are: response factor check for each PCB calibration congener and retention time reproducibility for SIM data acquisition.

10.3 LABORATORY PERFORMANCE CHECK SOLUTION -- In this method, the medium-level concentration calibration solution also serves the purpose of a laboratory performance check solution.

10.4 LABORATORY SURROGATE SPIKE

10.4.1 Measure the concentration of both surrogate compounds in every sample and blank.

10.4.2 Acceptance limits for surrogate compounds will be 60-140% recovery for sediment extracts.

10.5 LABORATORY CONTROL SAMPLE -- A QC reference check standard (LCS) is also prepared and analyzed for Aroclor-1242 at a concentration of 500 ng/mL in the extract. For sediment/solid samples, sodium sulfate is used for the QC reference check standard (LCS). Calculate the percent recovery for the Total PCB Aroclor spike and compare to the project limits of 60-140%. If the percent recovery for the QC reference check standard (LCS) is out of criteria, the analysis is out of the control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be reanalyzed (Exception: If the LCS recovery is high and there were no associated positive results, then address the issue in the Case Narrative and no further action is needed).

10.6 MS/MSD SAMPLES -- At this time, the GE Hudson River Design Support Sediment Sampling and Analysis Program does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, a matrix spike for Aroclor-1242 is to be analyzed at a rate of 1 matrix spike per every 20 samples at a concentration of 20,000 ng/mL in the extract (**Note:** this spike concentration will require a sample dilution to be performed). The result by GEHR680 will be reported as a Total PCB. Also a matrix spike duplicate sample is to be analyzed at a rate of 1 per every 20 samples.

10.6.1 If requested, analyze one unspiked and two spiked samples. Calculate the percent recovery based on Aroclor concentration of both samples as follows:

A = concentration of spiked sample
B = concentration of unspiked sample (background)
T = known true value of the spike

Percent Recovery (p) = 100 (A-B) %/T

Compare the percent recovery calculated with the project limits of 60-140%. If the total PCB concentrations of the matrix spikes are *greater* than four times the calculated sample amount, then the quality control limits should be applied. If the total PCB concentrations of the matrix spikes are *less* than four times the sample, then there are no established limits applicable. If the percent recovery falls outside of the acceptance range for the total PCB used as the spiking analyte, then the matrix spike recovery failed the acceptance criteria. Check for documentable errors (*e.g.,* calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated QC reference check standard

(Laboratory Control Sample [LCS]) is within 60-140%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

A relative percent difference (RPD) must also be calculated on the matrix spike set recoveries. This is calculated as follows:

A = % recovery of matrix spike sample
B = % recovery of matrix spike duplicate sample

RPD = [(A-B)/{(A+B)/2}] x 100
where (A-B) *is taken as an absolute value*

If the total PCB concentrations of the matrix spike set are *greater* than four times the calculated sample amount, then an RPD of 40% or less is acceptable. If the total PCB concentrations of the matrix spike set are *less* than four times the calculated sample amount than there are no established limits applicable to the RPD. If the criterion is not met, check for documentable errors (*e.g.,* calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated LCS is within 60-140%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

11. PROCEDURES

11.1 Sediment Samples – The extracts for this analysis will be the same extracts as those generated for the analysis of total PCBs as Aroclors by SOP GEHR8082.

11.2 GC/MS ANALYSIS

11.2.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature, if necessary. Add an appropriate volume of the appropriate internal standard stock solution.

11.2.1.1 Internal standard concentration for SIM data acquisition = 4 μL of 40 ng/μL solution (of each chrysene-d_{12} and phenenthrene-d_{10}) added to 200 μL of extract for a concentration of 0.80 ng/μL.

11.2.2 Inject a 2-μL aliquot of the blank/sample extract into the GC operated under conditions used to produce acceptable results during calibration.

11.2.3 Acquire mass spectral data with SIM conditions. Use the same data acquisition time and MS operating conditions previously used to determine response factors.

11.2.4 Examine data for saturated ions in mass spectra of target compounds, if saturation occurred, dilute and reanalyze the extract after the quantity of the internal standards is adjusted appropriately. In addition, any individual PCB analyte amount that exceeds the high level calibration standard of the calibration curve will require dilution and re-analysis of the extract to place that analyte within the calibration range.

11.2.5 For each internal standard, determine that the area measured in the sample extract has not decreased by >30% from the area measured during the most recent previous analysis of a calibration solution or by >50% from the mean area measured during initial calibration. If either criterion is not met, remedial action must be taken to improve sensitivity, and the sample extract must be reanalyzed.

11.3 IDENTIFICATION PROCEDURES

11.3.1 Using the ions shown on Tables 6a-6b for PCBs examine ion current profiles (ICPs) to locate internal standards, surrogate compounds, and PCBs for each isomer group. Use the RRT window data on Table 7 as guidelines for location of PCB isomers. (A reverse search software routine can be used to locate compounds of concern.)

11.3.2 SIM Data -- Obtain appropriate selected ion current profiles (SICPs) for IS quantitation and confirmation ions for the quantitation and confirmation ions for each PCB isomer group.

11.3.3 PCB Analytes

11.3.3.1 For all PCB candidates, confirm the presence of an (M-70)$^-$ ion cluster by examining ICPs or spectra for at least one of the most intense ions in the appropriate ion cluster.

11.3.3.2 For Cl_3-Cl_7 isomer groups, examine ICPs or spectra for intense $(M+70)^+$ ions that would indicate a coeluting PCB containing two additional chlorines. (GC retention time data show that this is not a potential problem for other PCB isomer groups.) If this interference occurs, a correction can be made. Obtain and record the area for the appropriate ion (Table 9) for the candidate PCB isomer group. Use the information in Table 10 to correct the measured abundance of M+. For example, if a Cl_7-PCB and a Cl_5-PCB candidate coelute, the Cl_7-PCB will contribute to the ion measured for m/z 326 and m/z 324, the quantitation and confirmation ions, respectively, for a Cl_5-PCB. Obtain and record the area for m/z 322 (the lowest mass ion in the $(M+-70)^+$ ion cluster of a Cl_5-PCB

fragment produced by a Cl_7-PCB). To determine the m/z 326 and m/z 324 areas produced by the Cl_5-PCB, calculate the Cl_7-PCB contribution to each and subtract it from the measured area. In this example, 164% of the area measured for m/z 322 should be subtracted from the area measured for m/z 324, and 108% of the m/z 322 area should be subtracted from the area measured for m/z 326 (Table 10).

11.3.3.3 For Cl_2-Cl_8-PCB candidates, examine ICPs or spectra for intense $(M+35)^+$ ions that would indicate a coeluting PCB containing one additional chlorine. This coelution causes interferences because of the natural abundance of ^{13}C. (This interference will be small and can be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of another PCB containing one more chlorine.) To correct for this interference, obtain and record the area for the appropriate ion (Table 11) from the $(M-1)^+$ ion cluster, and subtract 13.5% of the area measured for the $(M-1)^+$ ion from the measured area of the quantitation ion. For example, for Cl_5–PCB candidates, obtain and record the area for m/z 325; subtract 13.5% of that area from the measured area of m/z 326.

11.3.4 All Analytes -- Use ICP data to calculate the ratio of the measured peak areas of the quantitation ion and confirmation ion(s), and compare to the acceptable ratio (Table 9). If acceptable ratios are not obtained, a coeluting or partially coeluting compound may be interfering. Examination of data from several scans may provide information that will allow application of additional background corrections to improve the ion ratio.

11.4 IDENTIFICATION CRITERIA

11.4.1 Internal Standards

11.4.1.1 Chrysene-d_{12} -- the abundance of m/z 241 relative to m/z 240 must be $\geq$ 15% and $\leq$ 25%, and these ions must maximize simultaneously. The area measured for m/z 240 must be within 30% of the area measured during the most recent calibration.

11.4.1.2 Phenanthrene-d_{10} -- the abundance of m/z 189 relative to m/z 188 must be $\geq$ 10% and $\leq$ 22%, and these ions must maximize simultaneously. The area measured for m/z 188 must be within 30% of the area measured during the most recent acceptable calibration.

11.4.1.3 Retention time must be within ±10 s of that observed during the most recent acceptable calibration.

11.4.2 SIM Data for PCBs

11.4.2.1 Absolute retention times of surrogate compounds must be within ±10 s of that measured during the last previous continuing calibration check.

11.4.2.2 Quantitation and confirmation ions for each PCB isomer group must maximize within ±1 scan of each other.

11.4.2.3 The integrated ion current for each quantitation and confirmation ion must be at least three times background noise and must not have saturated the detector.

11.4.2.4 For each PCB isomer group candidate, the ratio of the quantitation ion area to the confirmation ion area must be within limits shown on Table 9; at least one ion in the $(M-70)^+$ ion cluster most be present.

12. CALCULATIONS

12.1 From appropriate ICPs of quantitation ions, obtain and record the spectrum number of the chromatographic peak apex and the area of the entire chromatographic peak.

12.2 GC/MS Analytes Detected Above the Initial Low Level Calibration Standard Concentration

Any individual PCB analyte amount in a sample or QC sample above the initial low-level calibration standard concentration will be reported as such with no associated flags. Any individual PCB analyte amount that exceeds the high level calibration standard of the calibration curve will require dilution and re-analysis of the extract to place that analyte within the calibration range.

12.3 GC/MS Analytes Detected Below the Initial Low Level Calibration Standard Concentration

As stated in Section 1.2, a Method Detection Limit (MDL) will be performed in accordance with procedures set forth in 40CFR Part 136, Appendix B. Any individual PCB analyte amount in a sample or QC sample that is above the established MDL but below the initial low level calibration standard concentration will be reported and appropriately flagged with a "J" flag. A "J" flag signifies that the analyte amount was below the initial low level calibration standard concentration but above the determined MDL for the analyte.

12.4 GC/MS Analytes Detected Below the MDL

Any individual PCB analyte amount in a sample or QC sample that is below the established MDL for that analyte or not present will be reported as not detected (ND). The associated MDL concentration value for that analyte will be reported to provide information on the analyte reporting limit.

12.5 PCB Homolog Group Amounts

For each PCB Homolog Group all reportable (both non-flagged and "J" flagged) PCB analytes associated with a given chlorination level (i.e. All dichlorobiphenyls) will be summed and a total provided. No flagging of Homolog Group concentrations will occur. This will provide 10 PCB sub-totals from monochlorobiphenyl to decachlorobiphenyl. If for a given Homolog there are no reportable analytes to report or sum, then a not detected (ND) will be reported. The associated analyte MDL concentration value for that chlorination level will be reported as the Homolog reporting limit.

12.6 Total PCB Amount

The Total PCB amount for a sample or QC sample will be provided by summation of the Homolog Group amounts. No flagging of the Total PCB amount will occur. If all 10 Homolog Groups are reported as not detected (ND), then the Total PCB amount will be reported as not detected (ND). For this reporting condition (i.e. Total PCB amount = ND), the single highest reporting limit from the 10 Homolog groups (highest PCB analyte MDL from MDL study) will be used and will provide the reporting limit for the Total PCB amount.

12.7 All sediment results will be reported on a dry-weight basis using the moisture determined during the GEHR8082 analysis for total PCBs as Aroclors.

12.8 For PCBs, sum the areas for all isomers identified at each level of chlorination (*e.g.*, sum all quantitation ion areas for Cl_4-PCBs).

12.9 Calculate the concentration of each surrogate compound and PCB isomer group using the formula:

$$C_x = (A_x \cdot Q_{is})/(A_{is} \cdot RF \cdot W \cdot D)$$

where:

C_x = concentration (micrograms per kilogram or micrograms per liter) of surrogate compound or a PCB isomer group,

A_x = the area of the quantitation ion for each surrogate compound or the sum of quantitation ion areas for all PCB isomers at a particular level of chlorination,

A_{is} = the area of the internal standard quantitation ion, m/z 240 for chrysene-d_{12} or m/z 188 for phenanthrene-d_{10},

Q_{is} = quantity (micrograms) of internal standard added to the extract before GC/MS analysis,

RF = calculated response factor for the surrogate compound or the PCB calibration compound for the isomer group (level of chlorination), and

W = weight (kilograms) of sample extracted.

D = (100 - % moisture)/100

12.4.1 Use the average RF calculated during Initial Calibration.

12.4.2 For PCBs, use the RF relative to chrysene-d_{12} unless an interference makes the use of the RF relative to phenanthrene-d_{10} necessary.

12.10 Report calculated values to two significant figures.

12.11 When samples of known composition or fortified samples are analyzed, calculate the percent method bias using the equation:

$$B = 100 (C_s - C_t)/ C_t$$

where:

C_s = measured concentration (in micrograms per kilogram or micrograms per liter) and

C_t = theoretical concentration (*i.e.*, the quantity added to the sample aliquot/weight or volume of sample aliquot).

Note: The bias value retains a positive or negative sign.

13. AUTOMATED IDENTIFICATION AND MEASUREMENT

Automated identification and measurement software for PCBs will be used to assist in handling and reducing the data.

14. REFERENCES

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4. “OSHA Safety and Health Standards, General Industry”, 29 CPR 1910, Occupational Safety and Health Administration, OSHA 2206, Revised January 1976.

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7. Rote, J. W. and W. J. Morris, “Use of Isotopic Abundance Ratios in Identification of Polychlorinated Biphenyls by Mass Spectrometry", J. Assoc. Offic. Anal. Chem. 56 (l), 188, 1973.

Table 1. Recommended GC and MS Operating Parameters

Mass Spectrometer Parameters:

Varian Model Saturn 2000 Ion Trap Mass Spectrometer

Ion Trap Temperature: 200°C
Emission Current: 70 microamps
Scan Time: 0.700 seconds
Ionization Mode: EI AGC
Ion Technique: SIS (Selected Ion scanning, which is Varian's term for SIM)

Gas Chromatograph Parameters:

Varian Model 3800 Gas Chromatograph

Injector Model 1079 (Temperature Programmable):

Coolant: Enabled
Initial Temperature: 50°C
Initial Hold Time: 1.00 minute
Final Temperature: 250°C
Temperature Ramp: 150°C/minute
Final Hold Time: 50 minutes
1079 Valve at 0.0 minutes: split state: on split ratio: 50
1079 valve at 0.50 minutes: split state: off split ratio: off
1079 valve at 3.00 minutes: split state: on split ratio: 50
Constant column flow: 1.0mL/min
Pulsed Pressure: On
Pulse Pressure: 24.0 psi
Pulse Pressure Duration: 0.75 minutes

Oven Temperature Profile:

Initial Temperature: 80°C
Initial Hold Time: 1.00 minute
First Temperature Ramp: 80 °C to 160°C at 30°C/minute, hold 1 minute
Second Temperature Ramp: 160°C to 310°C at 3°C/minute, hold 5.30 minutes

Table 1. Recommended GC and MS Operating Parameters (Cont.)

Sample Injection Parameters:

Syringe Size: 10uL
Solvent Flush: Yes, solvent A then B
Syringe Wash: 20 seconds
Solvent plug size: 0.3uL
Upper Air Gap: Yes
Lower Air Gap: Yes
Injection Rate: 0.5uL/sec
Extract Injection Volume: 2.0uL

Table 2. PCB Congeners Used as Calibration Standards

PCB Isomer Group	Congener Number [a]	Chlorine Substitution
Concentration Calibration Standard		
Monochlorobiphenyl	1	2
Dichlorobiphenyl	5	2, 3
Trichlorobiphenyl	29	2, 4, 5
Tetrachlorobiphenyl	50	2, 2', 4, 6
Pentachlorobiphenyl	87	2, 2', 3, 4, 5'
Hexachlorobiphenyl	154	2, 2', 4, 4', 5, 6'
Heptachlorobiphenyl	188	2, 2', 3, 4', 5, 6, 6'
Octachlorobiphenyl	200	2, 2', 3, 3', 4, 5', 6, 6'
Nonachlorobiphenyl[b]	-	---
Decachlorobiphenyl	209	2, 2', 3, 3', 4, 4', 5, 5', 6, 6'
Retention Time Calibration Standards		
Tetrachlorobiphenyl	77	3, 3', 4, 4'
Pentachlorobiphenyl	104	2, 2', 4, 6, 6'
Heptachlorobiphenyl	189	2, 3, 3′ 4, 4′, 5, 5′
Octachlorobiphenyl	202	2, 2′, 3, 3′, 5, 5′, 6, 6′

[a] Numbered according to the system of Ballschmiter and Zell (2).
[b] Decachlorobiphenyl is used as the calibration congener for both nona- and decachlorobiphenyl isomer groups.

Table 3. Scheme for Preparation of PCB Primary Dilution Standards

PCB Cong.	Isomer Group	Stock Sol. Conc. mg/mL	Proportion for Primary Dil. Sol.	Primary Dil. Std. Conc. ng/μL
#1	Cl_1	1.0	1 part	50
#5	Cl_2	1.0	1 part	50
#29	Cl_3	1.0	1 part	50
#50	Cl_4	1.0	2 parts	100
#87	Cl_5	1.0	2 parts	100
#154	Cl_6	1.0	2 parts	100
#188	Cl_7	1.0	3 parts	150
#200	Cl_8	1.0	3 parts	150
#209	Cl_{10}	1.0	5 parts	250
			Total 20 parts	

Table 4a. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for PCB Determinations

Concentration (ng/μL)

Compound	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6
Cal. Congeners						-
Cl_1 (#1)	0.05	0.5	1	2	5	-
Cl_2 (#5)	0.05	0.5	1	2	5	-
Cl_3 (#29)	0.05	0.5	1	2	5	-
Cl_4 (#50)	0.10	1.0	2	4	10	-
Cl_5 (#87)	0.10	1	2	4	10	-
Cl_6 (#154)	0.10	1	2	4	10	-
Cl_7 (#188)	0.15	1.5	3	6	15	-
Cl_8 (#200)	0.15	1.5	3	6	15	-
Cl_{10} (#209)	0.25	2.5	5	10	-	15
Internal Standards						
Chrysene-d_{12}	0.80	0.80	0.80	0.80	0.80	0.80
Phenanthrene-d_{10}	0.80	0.80	0.80	0.80	0.80	0.80
Surrogate Compounds						
TCMX	0.05	0.5	1	2	5	-
DCB	0.05	0.5	1	2	5	-

Table 4b. Retention Time Calibration Standards
Concentration (ng/μL)

Compound	CAL 1
Pentachlorobiphenyl (#014)	2.50
Tetrachlorobiphenyl (#77)	2.50
Octachlorobiphenyl (#202)	2.50
Heptachlorobiphenyl (#189)	2.50

Table 5. Criteria for DFTPP Spectrum

m/z	Relative Abundance
127	40-60%
197	<1%
198	100% (Base Peak)
199	5-9%
275	10-30%
365	>1%
441	Present and <m/z 443
442	>40%
443	17-23% of m/z 442

Table 6a. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Sets of ≤27 Ions Each

Ion Set	Isomer Group/ IS/Surrogate	Quant. Ion	Confirm Ions	M-70 Ions	M+70 Ions	M+35 Ions	Ion Measured[a] for Correction	
1	Cl_1	188	190	152, 153[b]	256, 258	222, 224	-	-
	Cl_2	222	224	152, 153, 186, 188[c]	290, 292, 294	256, 258	-	221
	Cl_3	256	258	186, 188	-	290, 292, 294	-	225
	Cl_4	292	290, 294	220, 222	-	-	-	-
	Phenanthrene-d_{10}	188	189	-	-	-	-	-
2	Cl_3	256	258	188, 188	324, 326, 328	290, 292, 294	254	255
	Cl_4	292	290, 294	220, 222	360, 362	324, 326, 328	288	289
	Cl_5	326	324, 328	254, 256, 258	-	360, 362	-	323
	Cl_6	360	358, 362	288, 290, 292	-	-	-	-
3	Cl_5	326	324, 328	254, 256	392, 394, 396, 398	360, 362	322	323
	Cl_6	360	358, 362	288, 290	-	392, 394, 396, 398	-	357
	Cl_7	394	392, 396	322, 324, 326	-	-	-	-
4	Cl_6	360	358, 362	288, 290	426, 428, 430, 432	392, 394, 396	356	357
	Cl_7	394	392, 396, 398	322, 324	-	428, 430, 432	-	391
	Cl_8	430	428, 432	356, 358, 360	-	462, 464, 466	-	425
	Cl_9	464	460, 462, 466	390, 392, 394	-	-	-	-
	Chrysene-d_{12}	240	241	-	-	-	-	-

Table 6a. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Sets of ≤27 Ions Each (Cont.)

Ion Set	Isomer Group/ IS/Surrogate	Quant. Ion	Confirm Ions	M-70 Ions	M+70 Ions	M+35 Ions	Ion Measured[a] for Correction	
5	Cl_8	430	426, 428, 432	356, 358, 360	494, 496, 498, 500	462, 464, 466	-	425
	Cl_9	464	460, 462, 466	390, 392, 394	-	496, 498, 500	-	-
	Cl_{10}	498	494, 496, 500	424, 426, 428, 430	-	-	-	-

[a]See Tables 9-10.
[b]Cl_1-PCBs lose HCl.
[c]Some Cl_2-PCBs lose Cl_2 and some lose HCl.

Table 6b. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤27 Ions

Ion Set #1[a]	Ion Set #2[b]	Ion Set #3[c]	Ion Set #4[d]	Ion Set #5[e]
152	186	247	240	356
153	188	249	241	358
186	220	254	288	360
187	222	256	290	390
188	254	288	322	392
189	255	290	324	394
190	256	322	326	424
220	258	323	356	425
221	288	324	357	426
222	289	326	358	428
224	290	328	360	430
255	292	357	362	432
256	294	358	390	462
258	323	360	391	464
290	324	362	392	466
292	326	392	394	496
294	328	394	396	498
	358	396	398	499
	360	398	425	500
	362		426	502
			428	
			430	
			432	
			460	
			462	
			464	
			466	

Table 6b. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤27 Ions (Cont.)

Scan Range #1	Scan Range #2	Scan Range #3	Scan Range #4	Scan Range #5
145m/z to 330m/z	179m/z to 398m/z	240m/z to 428m/z	233m/z to 520m/z	349m/z to 532m/z
SIS Ion Preparation	**SIS Ion Preparation**	**SIS Ion Preparation**	**SIS Ion Preparation**	**SIS Ion Preparation**
Mass Range 1: 150mz/ to 155m/z	Mass Range 1: 184mz/ to 226m/z	Mass Range 1: 244mz/ to 260m/z	Mass Range 1: 236mz/ to 296m/z	Mass Range 1: 350mz/ to 366m/z
Mass Range 2: 180mz/ to 195m/z	Mass Range 2: 250mz/ to 263m/z	Mass Range 2: 284mz/ to 294m/z	Mass Range 2: 316mz/ to 368m/z	Mass Range 2: 384mz/ to 400m/z
Mass Range 3: 215mz/ to 260m/z	Mass Range 3: 283mz/ to 300m/z	Mass Range 3: 318mz/ to 332m/z	Mass Range 3: 385mz/ to 404m/z	Mass Range 3: 418mz/ to 438m/z
Mass Range 4: 285mz/ to 300m/z	Mass Range 4: 320mz/ to 332m/z	Mass Range 4: 388mz/ to 404m/z	Mass Range 4: 422mz/ to 438m/z	Mass Range 4: 456mz/ to 472m/z
Mass Range 5: not used	Mass Range 5: 355m/z to 368m/z	Mass Range 5: not used	Mass Range 5: 455m/z to 506m/z	Mass Range 5: 490m/z to 508m/z
R.T. Window (minutes)	**R.T. Window (minutes)**	**R.T. Window (minutes)**	**R.T. Window (minutes)**	**R.T. Window (minutes)**
5.00 to 17.21	17.21 to 25.01	25.01 to 30.25	30.25 to 36.35	36.35 to 54.67
Total number of Ions	**Total number of Ions**	**Total number of Ions**	**Total number of Ions**	**Total number of Ions**
17	20	19	27	20

[a] Ions to identify and measure Cl_1 – Cl_4 PCBs and phenanthrene-d_{10}.

[b] Ions to identify and measure Cl_3– Cl_6 PCBs.

[c] Ions to identify and measure Cl_5 – Cl_7 PCBs.

[d] Ions to identify and measure Cl_6 – Cl_9 PCBs and chrysene-d_{12}.

[e] Ions to identify and measure Cl_8 – Cl_{10} PCBs.

Table 7. Retention Time Data for PCB Isomer Groups and Calibration Congeners

Isomer Group	Approximate RRT Range[a]	Cal. Cong. Number	Cal. Cong. RRT[a]
Monochlorobiphenyls	0.23-0.28	1	0.23
Dichlorobiphenyls	0.29-0.43	5	0.34
Trichlorobiphenyls	0.36-0.60	29	0.45
Tetrachlorobiphenyls	0.44-0.77	50	0.47
Pentachlorobiphenyls	0.55-0.93	87	0.73
Hexachlorobiphenyls	0.65-1.07	154	0.74
Heptachlorobiphenyls	0.81-1.13	188	0.81
Octachlorobiphenyls	0.95-1.18	200	0.97
Nonachlorobiphenyls	1.11-1.22	-	-
Decachlorobiphenyls	1.26	209	1.26

[a] Retention time relative to chrysene-d_{12} with a 30 m $\times$ 0.25 mm ID DB-XLB fused silica capillary column and the GC conditions set forth in Table 1.

Table 8. Known Relative Abundances of Ions in PCB Molecular Ion Clusters[a]

m/z	Relative Intensity
Monochlorobiphenyls	
188	100.00
189	13.50
190	33.40
192	4.41
Dichlorobiphenyls	
222	100.00
223	13.50
224	66.00
225	8.82
226	11.20
227	1.44
Trichlorobiphenyls	
256	100.00
257	13.50
258	98.60
259	13.20
260	32.70
261	4.31
262	3.73
263	0.47
Tetrachlorobiphenyls	
290	76.20
291	10.30
292	100.00
293	13.40
294	49.40
295	6.57
296	11.00
297	1.43
298	0.95
Pentachlorobiphenyls	
324	61.00
325	8.26
326	100.00
327	13.50
328	65.70
329	8.78
330	21.70
331	2.86
332	3.62
333	0.47
334	0.25
Hexachlorobiphenyls	
358	50.90
359	6.89
360	100.00
361	13.50
362	82.00
363	11.00
364	36.00
365	4.77
366	8.92
367	1.17
368	1.20
369	0.15
Heptachlorobiphenyls	
392	43.70
393	5.91
394	100.00
395	13.50
396	98.30
397	13.20
398	53.80
399	7.16
400	17.70
401	2.34
402	3.52
403	0.46
404	0.40
Octachlorobiphenyl	
426	33.40
427	4.51
428	87.30
429	11.80
430	100.00
431	13.40
432	65.6
433	8.76
434	26.90
435	3.57
436	7.10
437	0.93
438	1.18
439	0.15
440	0.11
Nonachlorobiphenyls	
460	26.00
461	3.51
462	76.40
463	10.30
464	100.00
465	13.40
466	76.40
467	10.20
468	37.60
469	5.00
470	12.40
471	1.63
472	2.72
473	0.35
474	0.39
Decachlorobiphenyl	
494	20.80
495	2.81
496	68.00
497	9.17
498	100.00
499	13.4
500	87.30
501	11.70
502	50.00
503	6.67
504	19.70
505	2.61
506	5.40
507	0.71
508	1.02
509	0.13

[a] Source: Rote and Morris (7)

Table 9. Quantitation, Confirmation, and Interference Check Ions for PCBs, Internal Standards, and Surrogate Compounds

Analyte/ Internal Std.	Nom. MW	Quant. Ion	Confirm. Ion	Expected Ratio[a]	Accept Ratio[a]	M-70 Confirm. Ion	Interference Check Ions M+70	Interference Check Ions M+35
PCB Isomer Group								
Cl_1	188	188	190	3.0	2.5-3.5	152[b]	256	222
Cl_2	222	222	224	1.5	1.3-1.7	152	292	256
Cl_3	256	256	258	1.0	0.8-1.2	186	326	290
Cl_4	290	292	290	1.3	1.1-1.5	220	360	326
Cl_5	324	326	324	1.6	1.4-1.8	254	394	360
Cl_6	358	360	362	1.2	1.0-1.4	288	430	394
Cl_7	392	394	396	1.0	0.9-1.2	322	464	430
Cl_8	426	430	428	1.1	0.9-1.3	356	498	464
Cl_9	460	464	466	1.3	1.1-1.5	390	-	498
Cl_{10}	494	498	500	1.1	0.9-1.3	424	-	-
Internal standards								
Chrysene-d_{12}	240	240	241	5.1	4.3-5.9	-	-	-
Phenanthrene-d_{10}	188	188	189	6.6	6.0-7.2	-	-	-
Surrogate compounds								
TCMX	242	244	242	1.3	1.1-1.5	-	-	-
DCB	494	498	500	1.1	0.9-1.3	424	-	-

[a] Ratio of quantitation ion to confirmation ion.

[b] Monochlorobiphenyls lose HCl to produce an ion at m/z 152.

Table 10. Correction for Interference of PCB Containing Two Additional Chlorines

Candidate Isomer Group	Quant. Ion	Confirm. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from	
				Quant. Ion Area	Confirm. Ion Area
Trichlorobiphenyls	256	258	254	99%	33%
Tetrachlorobiphenyls	292	290	288	65%	131%
Pentachlorobiphenyls	326	324	322	108%	164%
Hexachlorobiphenyls	360	362	356	161%	71%
Heptachlorobiphenyls	394	396	390	225%	123%

Table 11. Correction for Interference of PCB Containing One Additional Chlorine

Candidate Isomer Group	Quant. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from Quant. Ion Area
Dichlorobiphenyls	222	221	13.5%
Trichlorobiphenyls	256	255	13.5%
Tetrachlorobiphenyls	292	289	17.4%
Pentachlorobiphenyls	326	323	22.0%
Hexachlorobiphenyls	360	357	26.5%
Heptachlorobiphenyls	394	391	30.9%
Octachlorobiphenyls	430	425	40.0%

Figure 1. Merged Ion Current Profile of PCB Calibration Congeners

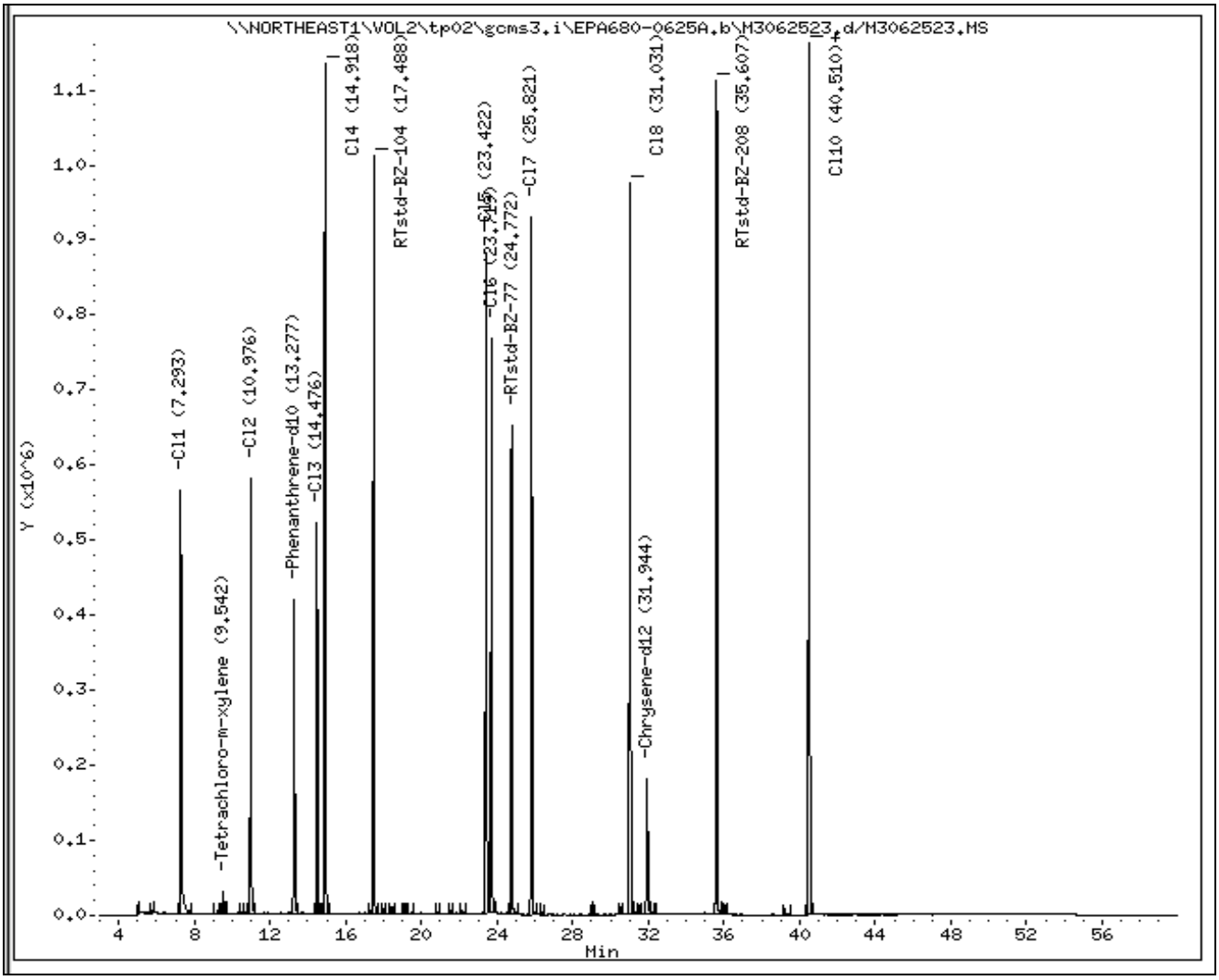
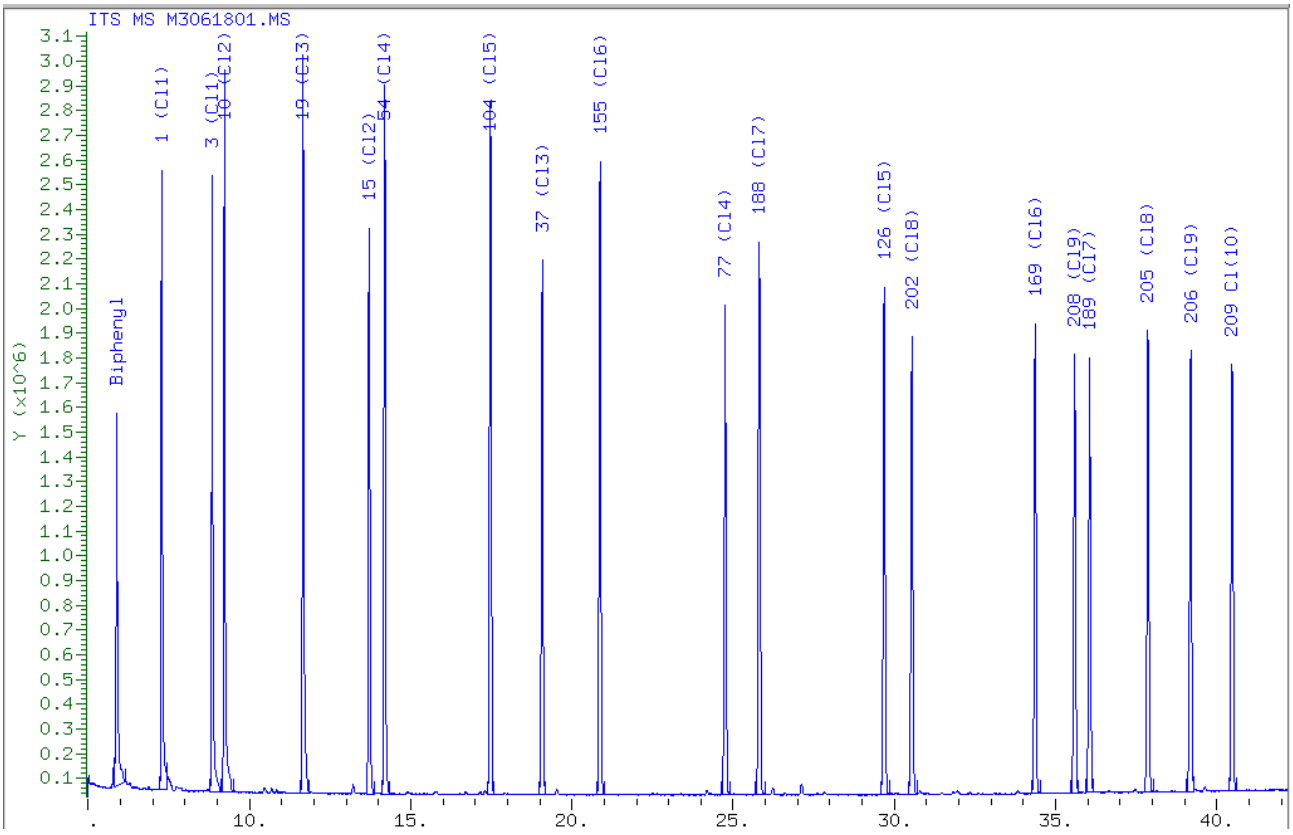


Figure 2: Total Ion Chromatogram of PCB Window Defining Mixture Standard



APPENDIX 9

OBJECTIVE

This Standard Operating Procedure (SOP) describes the requirements for the data packages that will be generated as part of the Hudson River Design Support Sediment Sampling and Analysis Program. This SOP applies to the contractor(s) involved in analytical data generation and reporting. All data packages generated for the Hudson River Design Support Sediment Sampling and Analysis Program must be provided in an Adobe Acrobat (.PDF) file format. The laboratory will be notified of the samples that will undergo data validation. For these samples, the laboratory will be required to generate hard copy data packages as well as the Adobe Acrobat (.PDF) file format.

SECTION A-9 DATA PACKAGE DELIVERABLES

The following sections describe in detail the types of data packages designed for the Hudson River Design Support Sediment Sampling and Analysis Program. These details are provided to allow several participating laboratories to produce data packages that are similar in format, order of presentation, and content. The data packages detailed in Section A-9.1 have been developed based on deliverables specified in the US EPA Contract Laboratory Program Statement of Work (CLP SOW). The CLP SOW has additional details concerning data packages that are specific to the CLP analyses. The most recent Statement of Work should be referenced for details concerning CLP-style data packages. Note: the summary forms provided in these data packages should be in similar format and content to the Contract Laboratory Program (CLP) forms listed (as references) next to the form title. These CLP forms references are only provided as guidance on content and format and should be modified by the laboratory to meet specific method requirements. Section A-9.2 provides details concerning specific contents of the data deliverables described in Section A-9.1.

The data package deliverables are categorized into two distinct levels as follows:

Level A - Case Narrative, analytical results, and Chain-of-Custody Records for the sample delivery group (SDG).

Level B - Fully documented data package.

The Level A data package is a basic "results-only" style of data package that includes a cover letter, SDG narrative, field Chain-of-Custody Records, analytical results summaries, and a glossary of qualifier codes. The Level B package resembles the information required by the CLP SOW. This type of package includes all information provided in Level A package but also includes summary forms for quality control procedures and all sample and quality control raw data to support the results reported.

A-9.1 Data Package Contents and Order of Presentation

The laboratory will be required to submit supporting documentation for the reported analytical results. The supporting documentation and the analytical results will be reported in one of two data package delivery categories. The categories are defined below. The data package deliverables must be submitted in the order in which the deliverables appear in the text. The laboratory need not include the documentation for any fraction not required for an SDG.

A-9.1.1 General Format for Level B Deliverables

For some analyses, Level B Sample Data Package deliverables may be requested. A Level A Data Package will also be required with the Level B package as a summary package.

The Level B Sample Data Package shall include data for analyses of all samples in one SDG, including field samples, reanalyses, secondary dilutions, blanks, laboratory control samples, matrix spikes, matrix spike duplicates, and/or laboratory duplicates. The complete Sample Data Package is divided into the units as described below. Units for each analytical fraction have been detailed. If the analysis of that fraction was not required for samples in the SDG, the fraction-specific unit is not a required deliverable. The Sample Data Package must be complete before submission and must be consecutively paginated. The Sample Data Package will be arranged in the following order:

A) Cover Letter/Letter of Transmittal signed by the laboratory manager.

B) Title Page

C) Table of Contents

D) Sample Delivery Group (SDG) Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: laboratory name; SDG number; GE sample identifications; laboratory sample numbers; and detailed documentation of any quality control, sample, shipment, and/or analytical problems encountered in processing (preparing and analyzing) the samples reported in the data package. A glossary of qualifier codes used in the SDG must also be provided.

The laboratory must also include any technical and administrative problems encountered, corrective actions taken and method of resolution, and an explanation of all flagged edits (i.e., exhibit edits) on quantitation reports.

Additionally, the SDG Narrative must be signed and dated by the laboratory manager.

E) Field and Internal (Laboratory) Chain-of-Custody Records and Sample Receipt Documentation Log

Copies of both the external and internal Chain-of-Custody Records for all samples within the SDG must be included in the deliverables. A description of the condition and temperature of the samples upon laboratory receipt (*i.e.*, custody seal condition, container status) must be provided for each Chain-of-Custody Record/sample cooler.

F) GC/MS Volatile Organic Data.

1. Quality Control (QC) Summary.

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II VOA).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III VOA).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III VOA).

d. Method Blank Summary (modified CLP SOW288 Form IV VOA) -- arranged in chronological order by date of analysis of the blank, by instrument.

e. GC/MS Tuning and Mass Calibration Summary (modified CLP SOW288 Form V VOA) -- arranged in chronological order, by instrument.

f. Internal Standard Area and Retention Time Summary (modified CLP SOW288 Form VIII VOA) -- arranged in chronological order, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for volatile samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Target Compound Results (modified CLP SOW288 Form I VOA).

b. Reconstructed total ion chromatogram (RIC) and quantitation reports.

c. Copies of raw spectra and copies of background-subtracted mass spectra of each target compound identified in the sample and corresponding background-subtracted target compound standard mass spectra.

d. Exhibit work sheet (including example calculations showing how sample results are calculated using the initial calibration and sample responses for at least one sample).

3. Standards Data

a. Initial Calibration Data (modified CLP SOW288 Form VI VOA and associated volatile standard RICs and quantitation reports) -- for all initial calibrations associated with analyses in the SDG, in chronological order, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

b. Continuing Calibration Data (modified CLP SOW288 Form VII VOA and associated volatile standard RICs and quantitation reports) -- for all continuing calibrations associated with analyses in the SDG, in chronological order, by instrument.

4. Raw QC Data

a. For each GC/MS tuning and mass calibration (in chronological order, by instrument):

1. Bromofluorobenzene (BFB) bar graph spectrum.

2. BFB mass listing.

b. Method/Storage Blank Data - in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

iii. Copies of raw spectra and copies of background-subtracted mass spectra of each target compounds identified in the blank and corresponding background-subtracted target compound standard mass spectra.

c. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

d. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

e. Matrix Spike Duplicate Data:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

G) GC/MS Semivolatile Organic Data

1. QC Summary

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II SV).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III SV).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III SV).

d. Method Blank Summary (modified CLP SOW288 Form IV SV) -- arranged in chronological order by date of analysis of the blank, by instrument.

e. GC/MS Tuning and Mass Calibration Summary (modified CLP SOW288 Form V SV) -- arranged in chronological order, by instrument.

f. Internal Standard Area and Retention Time Summary (modified CLP SOW288 Form VIII SV-1, SV-2) -- arranged in chronological order, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries, followed by the raw data for semivolatile samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

b. RIC and quantitation report.

c. Copies of raw spectra and copies of background-subtracted mass spectra of each target compound identified in the sample and corresponding background-subtracted target compound standard mass spectra.

d. UV traces from Gel Permeation Chromatography (GPC) chromatograms cleanup (if performed).

e. Exhibit work sheet (including example calculations showing how sample results are calculated using the initial calibration and sample responses for at least one sample).

3. Standards Data

   a. Initial Calibration Data (modified CLP SOW288 Form VI SV-1, SV-2 and associated semivolatile standard RICs and quantitation reports) -- for all initial calibrations associated with analyses in the SDG, in chronological order, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

   b. Continuing Calibration Data (modified CLP SOW288 Form VII SV-1, SV-2 and associated semivolatile standard RICs and quantitation reports) -- for all continuing calibrations associated with analyses in the SDG, in chronological order, by instrument.

4. Raw QC Data

   a. For each GC/MS tuning and mass calibration (in chronological order, by instrument):

      i. Decafluorotriphenylphosphine (DFTPP) bar graph spectrum.

      ii. DFTPP mass listing.

   b. Blank Data -- in chronological order, by instrument:

      i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

iii. Copies of raw spectra and copies of background-subtracted mass spectra of each target compounds identified in the blank and corresponding background-subtracted target compound standard mass spectra.

c. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

d. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

e. Matrix Spike Duplicate Data

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

H) GC Organochlorine Pesticide Data

1. QC Summary

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II PEST).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III PEST).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III PEST).

d. Method Blank Summary (modified CLP SOW288 Form IV PEST) -- arranged in chronological order by date of analysis of the blank, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for organochlorine pesticide samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary (modified CLP SOW288 Form I PEST).

b. Copies of organochlorine pesticide chromatograms.

c. Copies of organochlorine pesticide chromatograms from second GC column confirmation (if performed).

d. GC integration reports or data system printouts.

e. Exhibit work sheet (including example calculation showing how sample results are calculated using initial calibration standard and sample responses for at least one sample).

f. UV traces from GPC cleanup (if performed).

g. If organochlorine pesticides are confirmed by GC/MS, the laboratory must submit copies of raw spectra and copies of background-subtracted mass spectra of target compounds that are identified in the sample and corresponding background-subtracted target compound standard mass spectra. For multi-component pesticides confirmed by GC/MS, the laboratory will submit mass spectra of three major peaks of multi-component compounds from samples and standards.

3. Standards Data

a. Analytical Sequence Form -- in chronological order, by GC column, by instrument for all samples and quality control analyses.

b. Initial Calibration Data (Initial Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], organochlorine pesticide standard chromatograms, and integration reports) -- for each initial calibration associated with SDG in chronological order, by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

c. Continuing Calibration Data (Continuing Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], organochlorine pesticide standard chromatograms, and integration reports) -- for each continuing calibration associated with SDG in chronological order, by GC column, by instrument following the associated initial calibrations.

d. 4,4′-DDT and Endrin Breakdown Data (Percent Breakdown Summary Form, organochlorine pesticide chromatograms and integration reports) -- for each standard associated with SDG in chronological order by GC column, by instrument.

4. Raw QC Data

a. Blank Data -- in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

b. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

c. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

d. Matrix Spike Duplicate Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

e. UV traces from GPC cleanup (if performed).

i. UV traces for the initial calibration standards and blanks. Compound names shall be written over the peaks or printed over the peaks, or retention times shall be written over the peaks, and a separate table listing compounds and retention times shall be provided.

ii. Chromatographs and data system reports for all standards used to quantify compounds in the GPC blanks.

iii. Chromatographs and data system reports for the GPC calibration check solution and all standards used to quantify compounds in the GPC calibration check solution.

f. Raw Florisil® data, arranged in chronological order.

i. Chromatographs and data system reports for the analysis of the Florisil® cartridge performance check.

ii. Chromatographs and data system reports for the standards used to quantify compounds in the Florisil® cartridge performance check analysis (*i.e.*, INDA, INDB, and the 2,4,5-trichlorophenol standards).

I) GC Polychlorinated Biphenyl (PCB) Data

1. QC Summary

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II PEST).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III PEST).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III PEST).

d. Method Blank Summary (modified CLP SOW288 Form IV PEST) -- arranged in chronological order by date of analysis of the blank, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for PCB samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary (modified CLP SOW288 Form I PEST).

b. Copies of PCB chromatograms.

c. Copies of PCB chromatograms from second GC column confirmation (if performed).

d. GC integration reports or data system printouts. The integration reports or data system printouts must include all peaks not just the peaks corresponding to the target analytes.

e. Exhibit work sheets (including example calibration showing how sample results are calculated using initial calibration and sample responses for at least one sample).

f. UV traces from GPC (if performed).

g. If PCBs are confirmed by GC/MS, then the laboratory must submit copies of raw spectra and background-subtracted mass spectra of target compounds that are identified in the sample and corresponding background-subtracted target compound standard mass spectra. The laboratory will submit mass spectra of three major peaks of multi-component compounds from samples and standards for each PCB result confirmed by GC/MS.

3. Standards Data

a. Analytical Sequence Form -- in chronological order, by GC column, by instrument for all samples and quality control analyses.

b. Initial Calibration Data -- Initial Calibration Summary Form (inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.), PCB standard chromatograms, and integration reports for each initial calibration associated with SDG in chronological order, by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

c. Continuing Calibration Data -- Continuing Calibration Summary Form (inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.), PCB standard chromatograms, and integration reports for each continuing calibration associated with SDG in chronological order, by GC column, by instrument following the associated initial calibration.

4. Raw QC data

a. Blank Data -- in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

b. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

c. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

d. Matrix Spike Duplicate Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

e. UV traces from GPC cleanup (if performed).

i. UV traces for the initial calibration standards and blanks. Compound names shall be written or printed over the peaks, or retention times shall be written over the peaks, and a

separate table listing compounds and retention times shall be provided.

ii. Chromatographs and data system reports for all standards used to quantify compounds in the GPC blanks.

iii. Chromatographs and data system reports for the GPC calibration check solution and all standards used to quantify compounds in the GPC calibration check solution (or used to assess the Aroclor pattern).

f. Raw Florisil® data, arranged in chronological order:

i. Chromatographs and data system reports for the analysis of the Florisil® cartridge performance check.

ii. Chromatographs and data system reports for the standards used to quantify compounds in the Florisil® cartridge performance check analysis (*i.e.*, INDA, INDB, and the 2,4,5-trichlorophenol standards).

J) GC Herbicide Data

1. QC Summary

a. Surrogate Percent Recovery Summary ("CLP SOW288-like" Form II PEST).

b. Matrix Spike/Matrix Spike Duplicate Summary ("CLP SOW288-like" Form III PEST).

c. Laboratory Control Sample Summary ("CLP SOW288-like" Form III PEST).

d. Method Blank Summary ("CLP SOW288-like" Form IV PEST) -- arranged in chronological order by date of analysis of the blank, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for herbicide samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary ("CLP SOW288-like" Form I PEST).

b. Copies of herbicide chromatograms.

c. Copies of herbicide chromatograms from second GC column confirmation (if performed).

d. GC integration reports or data system printouts.

e. Exhibit work sheets (including example calculation showing how sample results are calculated using initial calibration and sample responses for at least one sample).

f. UV traces from GPC (if performed).

g. If herbicides are confirmed by GC/MS, the laboratory must submit copies of raw spectra and copies of background-subtracted mass spectra of target compounds that are identified in the sample and corresponding background-subtracted target compound standard mass spectra.

3. Standards Data

a. Analytical Sequence Form -- in chronological order, by GC column, by instrument for all samples and quality control analyses.

b. Initial Calibration Data (Initial Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], herbicide standard chromatograms, and integration reports) -- for each initial calibration associated with SDG in chronological order, by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

c. Continuing Calibration Data (Continuing Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], herbicide standard chromatograms, and integration reports) -- for each continuing calibration associated with SDG in chronological order, by GC column, by instrument following the associated initial calibrations.

4. Raw QC Data

a. Blank Data -- in chronological order, by instrument:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

b. Laboratory Control Sample Data:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

c. Matrix Spike Data:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

d. Matrix Spike Duplicate Data:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

e. UV traces from GPC cleanup (if performed).

i. UV traces for the initial calibration standards and blanks. Compound names shall be written or printed over the peaks, or retention times shall be written over the peaks and a separate table listing compounds and retention times shall be provided.

ii. Chromatographs and data system reports for all standards used to quantify compounds in the GPC blanks.

iii. Chromatographs and data system reports for the GPC calibration check solution and all standards used to quantify compounds in the GPC calibration check solution (or used to assess the Aroclor pattern).

K) GC/MS Dioxin/Furan Data

1. Quality Control (QC) Summary

a. Matrix Spike/Matrix Spike Duplicate Summary.

b. Ongoing Precision and Recovery (ORP) Summary.

c. Method Blank Analysis Summary.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for dioxin/furan samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary.

For each sample including peak retention times, ion ratios, reported concentrations, Estimated Detection Limit (EDL) designation, and internal standard recoveries.

b. Calculation of Toxicity Equivalence.

c. Dioxin/Furan Review Worksheet and Quantitation Report. The quantitation reports must include all information required to reproduce reported positive results and EDL results.

d. Extracted Ion Current Profile (EICP) Chromatograms.

e. Second Column Confirmation Data (if necessary; will include A-9.1.1.K, Section 2, items a, b, c, and d).

f. Exhibit work sheets (including example calibration showing how sample results are calculated using initial calibration and sample responses for at least one sample. The calculations should cover positive results and EDL results).

3. Standards Data

a. Mass spectrometer performance standard data for each calibration associated with the SDG, in chronological order by GC column, by instrument.

b. Window-defining mix and isotope ratio data for each calibration associated with the SDG, in chronological order by GC column, by instrument. The retention time windows must be summarized for reference.

c. Isomer Specificity Test Standard Summary and raw data in chronological order by GC column, by instrument.

d. Initial Calibration Data (Initial Calibration Summary Form, quantitation report, and EICP Chromatograms) for each initial calibration associated with the SDG, in chronological order by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

e. Continuing Calibration Data (Continuing Calibration Summary Form, quantitation report, and EICP Chromatograms) for each continuing calibration associated with the SDG, in chronological order, by GC column, by instrument.

4. Raw QC Data

a. Blank Data -- in chronological order, by instrument:

i. Analytical Results Summary.

For each blank including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

b. OPR Standard Data:

i. Analytical Results Summary.

For each OPR standard including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

c. Matrix Spike Data:

i. Analytical Results Summary.

For each matrix spike including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

d. Matrix Spike Duplicate Data:

i. Analytical Results Summary.

For each matrix spike duplicate including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

5. GC/MS Instrument Run Logs.

L) Inorganic Data for ICP or ICP/MS

1. Cover Page for the Inorganic Analyses Data Package.

2. Sample Results Summaries (modified CLP SOW390 Form I-INs) -- for all samples in the SDG, arranged in increasing alphanumeric order by GE sample identification.

3. Quality Control and Quarterly Verification of Instrument Parameters Summaries:

a. Initial and Continuing Calibration Verification summaries (modified CLP SOW390 Form II [PART 1]-INs).

b. Detection Limit Standards summaries (if performed, modified CLP SOW390 Form II [PART 2]-INs).

c. Blanks summaries (modified CLP SOW390 Form III-INs).

d. ICP Interference Check Sample summaries (modified CLP SOW390 Form IV-INs).

e. Matrix Spike/Matrix Spike Duplicate Sample Recovery summary (modified CLP SOW390 Form V [PART 1]-IN).

f. Post-Digest Spike Sample Recovery forms (modified CLP SOW390 Form V [PART 2]-IN).

g. Duplicates summary (modified CLP SOW390 Form VI-IN).

h. Laboratory Control Sample summary (modified CLP SOW390 Form VII-IN)

i. Method of Standard Addition Results summary (modified CLP SOW390 Form VIII-IN).

j. ICP Serial Dilution summary (modified CLP SOW390 Form IX-IN).

k. Method Detection Limits (MDL) and Reporting Limits (modified CLP SOW390 Form X-IN).

l. ICP Interelement Correction Factors (if performed, modified CLP SOW390 Form XI [PART 1]-IN).

m. ICP Linear Ranges (if performed, modified CLP SOW390 Form XII-INs).

n. Preparation Logs (modified CLP SOW390 Form XIII-INs).

o. Analytical Run Logs (modified CLP SOW390 Form XIV-INs).

4. ICP/MS Data Package will also include the following additional forms. The forms for ICP analysis listed A-9.1.1.K Sections 1-3 are also required using the SOW1091-LCIN protocol.

a. Linear Range Standard Summary (if performed, modified CLP For IV-LCIN).

b. ICP and ICP/MS Interference Check Sample (modified CLP Form VI-LCIN).

c. ICP/MS Tuning and Response Factor Criteria (modified CLP Form XIV-LCIN).

d. ICP/MS Internal Standards Summary (modified Form XV-LCIN).

5. Raw Data

For each reported value, the contracted laboratories will provide all raw data used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, and all sample analysis results. This statement does not apply to the Quarterly Verifications Parameters submitted as part of each data package (Section A-9.1.1.L, items 3k-3m). Raw data must contain all instrument readouts used for the sample results. Each exposure or instrumental reading must be provided, including those readouts that may fall below the MDL. All AA and ICP instruments must provide a legible hard copy of the direct real-time instrument readout (*i.e.,* strip charts, printer tapes, etc.). A photocopy of the instrument's direct sequential readout must be included. A hard copy of the instrument's direct instrument readout for cyanide must be included if the instrumentation has the capability.

The order of raw data in the data package shall be ICP-AES, ICP/MS, flame AA, furnace AA, mercury, and cyanide. All flame and furnace AA data will be grouped by element.

M) Wet Chemistry/Conventionals Data

The wet chemistry data will be arranged in the following order by individual parameter requested for the samples in the SDG.

1. Analytical Results Summaries -- for all samples in the SDG, arranged in increasing alphanumeric order by GE sample identification.

2. Quality Control Summaries

   a. Initial and Continuing Calibration Verification summaries.

   b. Blanks summaries.

   c. Spike Sample/Spike Duplicate Recovery summary.

   d. Duplicates summary.

   e. Laboratory Control Sample summary.

   f. Analytical Run Logs for instrumental analyses.

3. Raw Data

   For each reported value, the contracted laboratories will provide all raw data (instrument printouts or logbook pages) used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, as well as all sample analysis results. Raw data must contain all instrument readouts/logbooks pages used for the sample results. Each exposure or instrumental reading must be provided, including those readouts/logbook pages that may fall below the quantitation limit. A photocopy of the instrument's direct sequential readout must be included if the instrumentation has the capability.

P) Preparation Logs

1. TCLP Extraction Logs (if TCLP extraction was performed).

2. Volatile Extraction Logs (if medium-level volatile analyses were performed).

3. Semivolatile Extraction Logs.

4. Organochlorine Pesticide/PCB Extraction Logs.

5. Herbicide Extraction Logs.

6. Dioxin/Furan Extraction Logs.

7. Metals Digestion Logs.

8. Wet Chemistry Preparation Logs (by parameter).

A-9.1.3 General Format for Level A Deliverables

A Level A Data Package will be prepared concurrently with each complete Sample Data Package prepared for quality assurance review. The Level A Data Package shall contain data for all samples in one SDG. All Level A Data Packages will be arranged in the following order:

A) Cover Letter/Letter of Transmittal

B) SDG Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: laboratory name, SDG number, GE sample identifications, laboratory sample numbers, and detailed documentation of any quality control, sample, shipment, and/or analytical problems encountered in processing (preparing and analyzing) the samples reported in the data package. A glossary of qualifier codes used in the SDG must also be provided.

The laboratory must also include any technical and administrative problems encountered, and corrective actions taken. An explanation of all flagged edits (*i.e.,* exhibit edits) on quantitation reports must be included in the SDG Narrative.

Additionally, the SDG Narrative must be signed and dated by the laboratory manager.

C) Field and Internal (Laboratory) Chain-of-Custody Records and Sample Receipt Documentation Log

Copies of both the external and internal Chain-of-Custody Records for all samples within the SDG must be included in the deliverables. A description of the condition and temperature of the samples upon laboratory receipt (*i.e.*, custody seal condition, container status) must be provided for each Chain-of-Custody Record/sample cooler.

D) Analytical Results Summaries, grouped by fraction, and submitted in the same order of fractions as the Level B Deliverables.

A-9.2 Deliverables Reporting Requirements for GC/MS Volatile and Semivolatile Organic Analyses

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e*., recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any recoveries that are outside of the acceptance criteria. The raw data associated with the samples, blanks, and standards must clearly identify the GE sample identifier, the laboratory sample number, the instrument, the laboratory file number for the analysis, and the peak areas/heights and retention times that correspond to the compounds of interest observed in all analyses reported. If the requirement of a summary form is not applicable to a particular sample, standard, or blank, the requirement should still appear on the form; however, no entry will be necessary on the form for that sample, standard, or blank.

A) 1. An analysis summary of the results for all target compounds for all sample analyses, matrix spike analyses, matrix spike duplicate analyses, laboratory control sample analyses, and method/storage blank analyses must be supplied. The summary must include an entry for each target compound, date(s) and time(s) of analysis, GE sample identification, laboratory sample number, date of sample collection, sample matrix, sample weight, sample percent solids, heated or unheated purge, column type(s), column internal diameter, dilution factor, solid extract volume, solid aliquot volume,

concentration units, and sample results. For semivolatile analyses, date of sample extraction, final extract volume, injection volume, and an indication of whether the GPC cleanup was performed (yes/no) is also required. If positive results below the lowest calibration standard are reported, they must be flagged as estimated ("J") on the analysis summary. "Not-detected" results will be represented by the GE required quantitation limit and a "U" flag. If a compound was detected in a sample as well as in the method blank associated with the sample, the result must be flagged with a "B" on the summary form. Additionally, if a dilution is performed on a sample because a target compound is above the calibration range, then the positive result for the particular compound should be flagged with a "D." If the compound is still above the calibration rage after a dilution is performed on the sample, then the compound should be flagged with an "E."

2. The raw data for the sample analyses, method blank analyses, and storage blank analyses by GC/MS methodologies will include the RICs, mass spectra for all target compounds identified, and quantitation reports for the target compounds and surrogates. The raw data for the matrix spike and matrix spike duplicate analyses will include the RIC and quantitation report for the target compounds. These are required only for Level B Deliverables.

B) A surrogate percent recoveries summary for all of the reported analyses (samples, blanks, *etc*.). The surrogate recovery forms should be segregated by method (*i.e*., high-level solid samples separate from low-level solid samples). The summary form should also include the surrogate recovery limits and the laboratory should flag the compounds that do not meet the recovery limits, on the summary form.

C) A matrix spike/matrix spike duplicate concentration and percent recovery/relative percent difference summary for each matrix spike/matrix spike duplicate pair analyzed. The matrix spike/matrix spike duplicate summary form will indicate the GE identification of the unspiked sample, the MS/MSD sample, the spike concentrations, the matrix, and the concentrations of the compounds present in the unspiked sample and the MS/MSD sample. The summary form should also include the MS/MSD recovery criteria and RPD criterion. The laboratory should flag the compounds that do not meet the criteria. A similar form for the LCS must be included with the deliverables.

D) A method/storage blank summary form for each method/storage blank which identifies the samples associated with each method/storage blank. The date of analysis, time of analysis, file number, and matrix of the method/storage blank must also be reported on the summary form. Storage blanks are only required for volatiles analysis.

E) 1. A GC/MS tuning summary which summarizes the percent abundances for the mass ions of interest and the acceptance criteria for the mass ions. Additionally, the summary must include a list of the sample and QC sample analyses (sample names, file numbers, and dates and times of analysis) associated with the GC/MS tune. The summary should indicate the instrument identification, date and time of analysis, column type, diameter of the column, and the type of purge (heated or unheated for volatiles) used to analyze the samples.

2. The raw data for the GC/MS tuning summary, consisting of a summary of the mass ion abundances and a mass spectral representation of the tuning peak.

F) 1. For the internal standard calibration method, an initial calibration summary for each initial calibration performed, summarizing all of the relative response factors for each calibration standard, the average relative response factor, and the relative standard deviation among the relative response factors. If a calibration curve equation is utilized, the laboratory must summarize the curve equation and the coefficient of determination. Additionally, the summary should indicate the compounds that must meet a minimum relative response factor or a maximum relative standard deviation criterion and the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the file identifications of the analyses, the dates and times of calibration commencement and completion, column type, diameter of the column, and the type of purge (heated or unheated for volatiles) used to analyze the samples.

2. The raw data for the initial calibration, consisting of the reconstructed ion chromatogram and the raw quantitation report for each calibration standard. This is a requirement for the Level B Deliverables only.

G) 1. For the internal standard calibration method, a continuing calibration summary for each continuing calibration standard analyzed, summarizing the average relative response factors of the initial calibration associated with the continuing calibration standard, the relative response factors of the continuing calibration standard, and the percent differences between the

average relative response factors of the initial calibration and the relative response factors of the continuing calibration. If calibration curve equations are utilized the laboratory must summarize the true concentration, observed concentration, and the percent drift. Additionally, the summary must indicate the compounds that are subject to a minimum relative response factor criterion, the compounds that are subject to a maximum percent difference criterion, and the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the date of the initial calibration, the date and time of analysis, column type, diameter of the column, and the type of purge (heated or unheated for volatiles) used to analyze the samples.

2. The raw data for the continuing calibration, consisting of the reconstructed ion chromatogram and the raw quantitation report for each calibration standard. This is a requirement only for the Level B Deliverables.

H) An internal standard area counts summary, containing a summary of the area counts and retention times for the internal standards for a continuing calibration. The summary must indicate the acceptance windows for the internal standard retention times and area counts. This summary must supply a comparison of the continuing calibration internal standards to the mid-level initial calibration internal standards. Additionally, the summary must include a listing of the internal standard retention times and area counts for all of the samples, method blanks, matrix spikes, and matrix spike duplicates associated with the continuing calibration standard.

I) A copy of all of the extraction log information for semivolatiles is required. At a minimum, the extraction information must include the date the extraction was

started, the date the extraction was completed, the initial sample weight or volume, final extraction volume, laboratory sample number, the amount and concentration of surrogate spike added, and the amount and concentration of matrix spike solution added. Additionally, the extraction log should indicate if a cleanup procedure was performed on the sample. If a medium-level extraction was performed for the volatiles analysis, all extraction logs for this analysis will be required. For volatile organics analyses that require weighing sample aliquots in the field, copies of the field measurement documentation will be included in this section.

A-9.3 Deliverables Reporting Requirements for Organochlorine Pesticide, PCB, and Herbicide Analysis

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (i.e., recovery ranges, relative percent difference limits, etc.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any recoveries that are outside of the acceptance criteria. The raw data associated with the samples, blanks, and standards must clearly identify the GE sample identification, the laboratory sample number, the instrument, the laboratory file number for the analysis, and the peak areas/heights and retention times that correspond to the compounds of interest observed in all analyses reported. If the requirement of a summary form is not applicable to a particular sample, standard or blank, the requirement should still appear on the form; however, no entry will be necessary on the form for that requirement.

A) 1. An analysis summary of the concentrations of all target compounds for all sample analyses, matrix spike analyses, matrix spike duplicate analyses, and blank analyses. The blank analyses must consist of all of the extraction

(method) blank analyses, injection blank analyses, and any blanks associated with cleanup procedures. The summary must include dates and times of analysis, GE sample identifications, laboratory sample numbers, dates of sample collection, date of sample receipt, dates of sample extraction, sample matrices, sample weights or volumes, sample percent solids, column types, column internal diameters, dilution factors, initial extract volumes/weights, final extract volumes, concentration units, the type of cleanup performed, and sample results. If positive results below the lowest calibration standard are reported, they must be flagged as estimated ("J") on the analysis summary. "Not-detected" results will be represented by the GE required quantitation limit and a "U" flag. If a compound was detected in a sample as well as in the method blank associated with the sample, the result must be flagged with a "B" on the summary form. Additionally, if a dilution is performed on a sample because a target compound is above the calibration range then the positive result for the particular compound should be flagged with a "D." If the compound is still above the calibration range after a dilution is performed on the sample, then the positive result for the compound should be flagged with an "E."

2. The raw data for the sample analyses, matrix spike analyses, matrix spike duplicate analyses, and blank analyses, consisting of the chromatograms indicating the surrogate peaks and target compound peaks and quantitation reports for the target compounds and surrogates. This is a requirement only for the Level B Deliverables.

B) A surrogate percent recovery summary for all of the reported analyses (samples, blanks, *etc*.). The surrogate recovery forms should be segregated by matrix and

method (*i.e.*, medium-level solid samples separate from low-level solid samples). The summary form should also include the surrogate recovery limits and the laboratory should flag the compounds that do not meet the recovery limits on the summary form.

C) A matrix spike/matrix spike duplicate concentration and percent recovery/relative percent difference summary for each matrix spike/matrix spike duplicate pair analyzed. The matrix spike/matrix spike duplicate summary form will indicate the GE identification of the unspiked sample, the MS/MSD sample, the spike concentrations, the matrix, and the concentrations of the compounds present in the unspiked sample and the MS/MSD sample. The summary form should also include the MS/MSD recovery criteria and RPD criterion. The laboratory should flag the compounds that do not meet the criteria. A similar form for the LCS should be included with the deliverables.

D) A method blank summary form for each method blank, identifying the samples associated with each method blank. The date, time, lab file number, and matrix of the method blank must also be reported on the summary form.

E) Initial Calibration Data: A summary of the initial calibration retention times, mean retention time, and a retention time window for all target compounds and surrogates must be provided for all initial calibrations. A second summary of the initial calibration standard calibration factors, average calibration factors, and relative standard deviations for all target compounds and surrogates must also be provided for all initial calibrations. If a calibration curve equations is utilized the laboratory must supply the curve equation and the coefficient of determination. Both summaries should include the SDG number, instrument identification, GC column

type and diameter, date(s) of analysis, the concentration level for each initial calibration standard (as a multiplication factor of the low calibration standard), and the acceptance limit for the relative standard deviation. Copies of the pesticide, herbicide, and PCB standard chromatograms and integration reports associated with summaries should immediately follow the summary (only for the Level B Deliverables). Each initial calibration associated with the SDG must be presented in chronological order, by GC column and by instrument.

F) Continuing Calibration Data: A summary of the observed retention times, calculated compound concentrations, true concentrations, percent differences, and retention time window from the initial calibration (or from the daily retention time window update) must be provided for all continuing calibration standards. If calibration curve equations are utilized the laboratory must summarize the true concentration, observed concentration, and the percent drift. The summary should list the SDG number, GC column type and diameter, date and time of analysis, laboratory sample number, initial calibration dates, and acceptance limits. Copies of the pesticide, herbicide, and PCB standard chromatograms and integration reports associated with summaries should immediately follow the summary (only for the Level B Deliverable). Each continuing calibration associated with an SDG must be presented in chronological order, by GC column and by instrument.

G) 4,4′-DDT and Endrin Breakdown Data (organochlorine pesticides only): A summary of the observed 4,4′-DDT, endrin, and combined percent breakdowns must be presented for each breakdown check performed. (Alternatively, if this data is obtained from a continuing calibration standard rather than a specific breakdown standard, this information may be reported on the associated continuing calibration

summary form.) The summary should list the SDG number, GC column type and diameter, date and time of analysis, laboratory sample number, initial calibration dates, and acceptance limits. Copies of the pesticide/PCB standard chromatograms and integration reports associated with summaries should immediately follow the summary (only for the Level B Deliverables). Each breakdown summary associated with an SDG must be presented in chronological order, by GC column and by instrument.

H) A summary of the analytical sequence for each column and instrument used for the analysis of the project samples. The summary must contain the GC column number, the internal diameter of the column, initial calibration dates associated with the sequence, the instrument identification, the mean retention time(s) for the surrogate(s) utilized, a listing of the GE sample names, the laboratory sample numbers, dates and times of analysis, and the retention times for the surrogate(s). The summary should also indicate the retention time window for all surrogates used and any surrogate retention times that do not meet the acceptance criterion. The summary must contain all of the analyses for the samples, blanks, initial calibration standards, and continuing calibration standards associated with the sequence. All sequences will begin with an initial calibration and will terminate with a continuing calibration or breakdown check standard that meets all acceptance criteria.

I) When a GPC cleanup procedure is required for the samples, a summary for each check standard associated with the GPC calibration. The summary must contain the GPC column identification, the calibration date of the GPC column, the GC column(s) used for the analysis of the standard, the GC column internal diameter, the theoretical concentrations of the compounds in the GPC standard, the observed concentrations of the GPC standard, the percent recovery for each compound in the

GPC standard, the GE sample identification, laboratory sample number, and the date(s) of analysis for all samples associated with the GPC standard. The limits for each compound in the GPC standard should be listed on the summary form. The laboratory should flag any compound if the percent recovery was not within the control limits.

J) When a Florisil® cartridge cleanup procedure is required for the samples, a summary for each check standard associated with a Florisil® cartridge lot. The summary must contain the Florisil® cartridge lot number, the date of analysis of the Florisil® cartridge check standard, the GC column(s) used for the analysis of the standard, the GC column internal diameter(s), the theoretical concentrations of the compounds in the Florisil® cartridge check standard, the observed concentrations of the Florisil® cartridge check standard, the percent recovery for each compound in the Florisil® cartridge check standard, the GE sample identifications, the laboratory sample number, and the date(s) of analysis for all samples in the data deliverable associated with each lot of Florisil® cartridges.

K) Second column confirmation may be performed for all pesticide, PCB, and herbicide analyses when there is a positive result reported for a project sample. When the laboratory performs a dual column quantitative analysis for organochlorine pesticides, PCBs, and herbicides, a summary of the identified compounds and observed concentrations for the two columns utilized for sample analyses is required. The summary must contain the GE sample identification, the laboratory sample number, the dates and times of analysis, the instruments used for analysis, the GC columns, the GC column internal diameters, the retention time windows for each peak used to quantitate the compound, the observed retention time for each

peak used to quantitate the compound, the calculated concentration for each peak used, the mean concentration for each column for each compound identified, and the percent difference between the mean concentrations calculated for each column.

If the percent difference between the results for the analyte from the two GC columns is greater than 40% for the analysis, then the higher of the two values is reported and flagged with a "P." Finally, the "C" flag is used when the identification of a pesticide result is confirmed by GC/MS.

A-9.4 Deliverables Reporting Requirements for Dioxin/Furan Analyses

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e*., recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any recoveries that are outside of the acceptance criteria. The raw data associated with the samples, blanks, and standards must clearly identify the GE sample identifier, the laboratory sample number, the instrument, the laboratory file number for the analysis, and the peak areas/heights and retention times that correspond to the compounds of interest observed in all analyses reported. The raw data must provide all information necessary to reproduce all reported positive and EDL results. If the requirement of a summary form is not applicable to a particular sample, standard, or blank, the requirement should still appear on the form; however, no entry will be necessary on the form for that requirement.

A) 1. An analysis summary of the results for all target compounds for all sample analyses, second column confirmation analyses, matrix spike analyses, ORP

standard analyses, and method blank analyses must be supplied. The summary must include an entry for each target 2,3,7,8-substituted compound and total homologue concentrations, date(s) and time(s) of analysis, GE sample identification, laboratory sample number, date of sample collection, date of sample preparation, sample matrix, sample weight, sample percent solids, column type(s), column internal diameter(s), dilution factor, concentrated extract volume, concentration units, peak retention times, isotope ratios, and sample results. If positive results below the lowest calibration standard are reported, they must be flagged as estimated ("J") on the analysis summary. "Not-detected" results will be represented by the EDL and a "U" flag. If a compound was detected in a sample as well as in the method blank associated with the sample, the result must be flagged with a "B" on the summary form. Additionally, if a dilution is performed on a sample because a target compound is above the calibration range, then the positive result for the particular compound should be flagged with a "D". If the compound is still above the calibration rage after a dilution is performed on the sample, the positive result for the compound should be flagged with an "E".

2. The raw data for the sample analyses and method blank analyses by GC/MS methodologies, consisting of the EICP, quantitation reports for the target compounds, the associated areas or height for each peak within the established retention time window, and all other information required to reproduce all reported positive and EDL results. The raw data for the matrix spike and matrix spike duplicate analyses will include the EICP chromatogram and quantitation report for the target compounds.

B) A matrix spike concentration and percent recovery summary for each matrix spike analyzed is required. The matrix spike summary form will indicate the GE identification of the unspiked sample, the sample, the matrix, and the concentrations of the compounds present in the unspiked and spiked sample. The summary form should also include the MS recovery criteria. The laboratory should mark the compounds that do not meet the specified criteria. A similar form for the OPR standard should be included with the deliverables.

C) A method blank summary form for each method blank that identifies the samples associated with each method blank. The date of extraction, date of analysis, time of analysis, lab file number, sample weight, and matrix of the method blank must also be reported on the summary form.

D) A mass spectrometer performance summary for each mass spectrometer performance standard analyzed should identify the sample number, lab file identification, date and time of analysis, instrument identification, GC column identification, and static resolving power.

E) A window defining mix summary form for each window defining analysis should identify the sample number, lab file identification, date and time of analysis, instrument identification, and GC column identification. This form should include the retention time of the first eluting and last eluting isomer for each congener group.

F) An isomer specificity test standard summary should identify the sample number, file number, instrument ID, date and time of analysis, the GC column and instrument identification, and the percent valley determination between $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-1,2,3,4-TCDD. In addition, if second column confirmation is required,

percent valley for 2,3,7,8-TCDD and the closest isomers should be calculated and reported.

G) A summary of the analytical sequence for each column and instrument used for the analysis of the project samples. The summary must contain the GC column number, the internal diameter of the column, initial calibration dates associated with the sequence, the instrument identification, a listing of the GE sample names, the laboratory sample numbers, and dates and times of analysis. The summary must contain all of the analyses for the samples, blanks, initial calibration standards, and the continuing calibration standards associated with the sequence.

H) 1. An initial calibration summary for each initial calibration performed, summarizing all of the relative response factors for each calibration standard, the average relative response factor, and the relative standard deviation among the relative response factors. If calibration curve equations are utilized, the laboratory must supply the curve equation and coefficient of determination. Additionally, the summary should indicate maximum relative standard deviation and minimum relative response factor criteria as well as the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the dates and times of calibration commencement and completion, column type, and diameter of the column.

2. The raw data for the initial calibration, consisting of the EICPs and the raw quantitation report for each calibration standard.

I) 1. A continuing calibration summary for each continuing calibration standard analyzed, summarizing the average relative response factors of the initial calibration associated with the continuing calibration standard, the relative response factors of the continuing calibration standard, and the percent differences between the average relative response factors of the initial calibration and the relative response factors of the continuing calibration, and the isotope ratios and retention times. If calibration curve equations are utilized the laboratory must summarize the true concentration, observed concentration, and the percent drift. Additionally, the summary must indicate the compounds that are subject to a minimum relative response factor criterion, the compounds that are subject to a maximum percent difference criterion, and the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the date of the initial calibration, the date and time of analysis, column type, and diameter of the column.

2. The raw data for the continuing calibration, consisting of the EICPs and the raw quantitation report for each calibration standard.

A-9.5 Deliverables Reporting Requirements for Inorganic Analyses

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e.,* recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any quality control results that are outside the acceptance criteria. All instrument raw data printouts for the points discussed below must be provided in an orderly

fashion. This applies to all required QA/QC measurements, and instrument standardization, as well as sample analysis results. Additionally, all associated extraction, digestion, and distillation logs must be supplied. The order of the raw data in the data package shall be ICP-AES, ICP/MS, flame AA (if performed), furnace AA (if performed), and mercury. All flame and furnace AA data shall be grouped by element. All raw data shall be grouped by analysis date for all analytical results.

A) 1. A sample reference list for all samples present in an SDG. This reference list must summarize and correlate the laboratory sample number, the GE designated sample identification, and any laboratory code (*i.e.*, truncation of GE designated sample number by the laboratory) for each sample in an SDG.

2. A Table of Contents listing page numbers associated with information such as:

a. Methodology Summary

b. Case Narrative

c. Sample Results

d. Quality Control Data

e. Verification of Instrument Parameters

f. Preparation and Analysis Logs

g. Raw Data, including but not limited to:

i. ICP-AES, ICP/MS, Flame AA, GFAA, and Mercury Data

ii. Digestion Logs

iii. Confirmation Data

h. Chain-of-Custody Records

B) Analysis summaries of the concentrations of all target analytes for all sample analyses. The summary must include the GE designated sample number, the laboratory sample number, date of sample collection, date of sample receipt, sample matrix, sample percent solids, concentration units, sample results, data qualifier codes, analysis method codes, description of sample before and after analysis, and any comments relating to the sample.

C) A summary of the initial and continuing calibration verifications for each calibration performed. This summary will include the concentrations observed as well as the true value of the analyte in the initial and continuing calibrations. A percent recovery will be summarized based on the observed and true values for each analyte.

D) A summary of the Detection Limit (DL) standard analyses for both Atomic Absorption (AA) and Inductively Coupled Plasma (ICP) analyses. This summary will include the concentrations observed as well as the true value of the analyte in the DL standard. A percent recovery will be summarized based on the observed and true values for each analyte.

E) A summary of the initial and continuing laboratory blank analyses for each calibration performed. This summary will include the concentrations (positive or negative) observed of any analyte in the initial and continuing blank analyses at values greater than the MDL. The summary should also include the concentrations of any analyte observed in the laboratory preparation blank associated with each calibration sequence performed by the laboratory.

F) A summary of the ICP interference check sample analysis for each analytical sequence performed. This form will summarize the true and found values (positive, negative, or zero) of all analytes present in Solutions A and AB of the ICP interference check sample analysis. This form will also summarize the percent recoveries of the analytes/interferences present in the standards.

G) A summary of the pre-digestion matrix spike analysis. This form will summarize the percent recovery control limit for each analyte. Also, the sample result, the spike sample result, and the spike-added amount must be summarized on this form for all parameters analyzed. The laboratory-calculated percent recovery as well as the laboratory qualifier stating whether the calculated percent recovery was within control limits must also be summarized on this form.

H) A summary of the post-digestion matrix spike analysis. This form will require the same information described in item G.

I) A summary of the laboratory duplicate analysis. This form will summarize the percent differences observed between the sample and laboratory duplicate analyses. The appropriate control limits must be specified by the laboratory, and a summary of

the sample and laboratory duplicate analyses must be provided. The percent solids for the sample and the duplicate sample should be included on the summary form.

J) A summary of the Laboratory Control Sample (LCS) analysis. This form will summarize the percent recovery, control limits, and true and found values for the solid sample analyses.

K) A summary of any required Method of Standard Additions (MSA) determinations. This form will summarize the concentrations and absorbencies of all samples and analytes that require analysis by MSA. The correlation coefficient for the MSA analysis will be calculated and summarized on this form. Also, the sample concentration determined from the MSA determination will be summarized on this form.

L) A summary of the ICP Serial Dilution analyses performed by the laboratory. This summary will show the result of the initial sample analysis (in aqueous units, as observed from the raw data), the result of the five-fold serial dilution analysis, and the percent difference between the two analyses.

M) The summaries necessary for the verification of instrument parameters. These include an Method Detection Limit and Reporting Limit Summary, an ICP Interelement Correction Factor Summary (if performed) for each ICP used for analysis, and an ICP Linear Range Summary (if performed) for each ICP used for analysis.

N) The analysis log summaries. These include a Sample Preparation log that provides the sample identification; the preparation date; the sample weight (in grams) used;

and the digestion volume (in mL) used and an Analysis Run Log that provides the instrument identification, the sample identification, any dilution factors employed in the analysis, the date and time of analysis, the method of analysis, and the parameters analyzed. Additionally, the GFAA post-digestion analytical spike sample recoveries are listed on the Analysis Run Log.

A-9.6 Deliverables Reporting Requirements for Wet Chemistry/Conventionals Analysis

The laboratory will be required to submit the information detailed in Sections A-9.5 A) -C), A-9.5, E) and A-9.5, G) - J) and A-9.5-N as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e*., recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any quality control results that are outside the acceptance criteria. All instrument raw data printouts for the points discussed in the above mentioned sections must be provided in an orderly fashion. This applies to all required QA/QC measurements, and instrument standardization, as well as sample analysis results. Additionally, a direct sequential readout must be included if the instrument has the capability.

APPENDIX 10

METHOD: ASTM D422
STANDARD OPERATING PROCEDURE
FOR PARTICLE SIZE ANALYSIS OF SOILS
Applicable Matrix or Matrices: Soil, Sediment, Sludge
Standard Compound List and Reporting Limits: NA

Approvals and Signatures

Laboratory Director:	Christopher A. Ouellette	Date: 5-12-00
QA Manager:	Kim B. Watson	Date: 5-12-00
Inorganics Technical Director:	Kristine A. Dusablon	Date: 5-12-00
Geotechnical Supervisor:	Jeffrey R. McMahon	Date: 5/12/00

1.0 SCOPE AND APPLICATION

1.1 This method determines the particle size distribution in soil. Particles greater than 75um (gravels to fine sands) are determined by sieving and particles less than 75um (silts and clays) are determined by sedimentation using an hydrometer.

1.2 Minimum quantity of sample depends on subsequent analyses to be performed. Typical range is 150 to 350 grams of dry soil. Larger amounts (from 500 to 5000 grams) are specified for particle size analysis of soils with appreciable gravel component.

1.3 This preparation is amenable to samples containing sand, silt, clay and gravel.

2.0 SUMMARY OF METHOD

2.1 Soils for particle size analysis are prepared according to ASTM D421 or D2217. The soils are sieved in two steps. The particles greater than 2.00mm (retained on the No. 10 sieve) are sieved after the soil has been prepared. A portion of the soil passing the No. 10 sieve is prepared for hydrometer measurements. Seven hydrometer readings are made over a 24 hour time frame. The soil in the hydrometer is rinsed on a No. 200 (75 um) sieve and dried for sieve analysis of material less than 2.00mm (No. 10 sieve). Calculations are made to determine the percent finer of soil for each sieve and hydrometer reading. These calculations are dependent on percent solid, which is determined during the drying process, and the specific gravity that is assumed to be 2.65 (unless separate analysis is requested for specific gravity).

3.0 DEFINITIONS

N/A

4.0 INTERFERENCES

N/A

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 STL Burlington maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL Burlington also has a written environmental health and safety plan.

5.3 Please note chemicals that have the potential to be highly toxic or hazardous, the appropriate MSDS must be reviewed by the employee before handling the chemical.

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance sensitive to 0.01 grams

6.2 Mixer and dispersion cup

6.3 1000 ml sedimentation cylinder

6.4 Soil test hydrometer meeting specification E 100

6.5 Mortar and rubber tipped pestle for breaking up soil aggregates

6.6 Sieves of the following size:

3.0 in (75.00mm)	No. 20 (850.0um)
2.0 in (50.00mm)	No. 40 (425um)
1.5 in (37.50mm)	No. 60 (250.0um)
1.0 in (25.00mm)	No. 80 (180.0um)
3/4 in (19.00mm)	No. 100 (150.0um)
3/8 in (9.50mm)	No. 200 (75.0um)
No. 4 (4.75mm)	
No. 10 (2.00mm)	

6.7 Oven with temperature range of 60° C to 110° C

6.8 Thermometer accurate to 0.5° C

6.9 Timer with second hand and capable of counting up to 25 hours

6.10 Mixing utensils, metal and bristle brushes for sample recovery.

6.11 Rototap machine

7.0 REAGENTS AND STANDARDS

7.1 Sodium Hexametaphosphate (dispersion reagent)

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Typical sample of 150 to 350 grams is used for analysis. Larger amounts (from 500 to 5000 grams) are specified for particle size analysis of soils with appreciable gravel component. The sample container must remained sealed to maintain natural water content.

8.2 There are no holding time requirements.

9.0 QUALITY CONTROL

9.1 Check balance daily with Class S weight, yearly manufacturer calibration.

9.2 Oven temperature is checked daily prior to start of work.

9.3 Thermometer is checked against similar or more accurate temperature device.

9.4 Duplicate samples are recommended every 20 samples.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Sieves calibrated twice a year using the National Bureau of Standard, Certificate of Calibration, standard reference materials 1017a, 1018a and 1019a calibrated glass beads.

10.2 Hydrometers are calibrated twice a year, and checked prior to each use.

10.3 Thermometer calibrated against NIST certified thermometer.

11.0 PROCEDURE

11.1 Large Sieve (dry): The soil retained on the No. 10 sieve is used in this step. Rinse the particles on a No. 10 sieve and then place the material in an oven until dry.

Large Sieve (wet): Take the equivalent of 200 grams of dry soil (use the percent solid table). Place soil on a No. 10 sieve and wash the soil. Take the soil retained on the No. 10 sieve and place in an oven until dry.

11.1.1 Record the weights of the sieves greater than No. 10. Take the dry soil and pour into the sieve stack. Place the sieve stack on the Rototap machine and shake sample for ten minutes.

11.1.2 Weigh and record the contents of each sieve.

11.1.3 Record the maximum particle size. Determine the hardness of the particles by dropping a hammer on the particle from a height or approximately one foot. Record the hardness as hard, soft or brittle. Save the soil particles.

11.2 Hydroscopic Moisture (dry prep. only): The soil passing the No. 10 sieve is used in this step. Take a small tin, label it and record the weight. Place approximately 10 to 15 grams of soil in the tin. Place the tin in the oven at 110°C for at least 16 hours. Remove the tin and record the weight.

11.3 Hydrometer Test: The soil passing the No. 10 sieve is used in this step.

11.3.1 Sample Preparation:

- Dry Prep: Tare a 250 ml beaker. Place and record approximately 50 grams for silt or clay particles or 100 grams for same particles into the beaker. Add 125 ml of a 40g/l sodium Hexametaphosphate solution to sample and allow to soak overnight

  Wet Prep: Tare a 500 ml beaker. Place and record the dry equivalent (use the percent solid table) of approximately 50 grams for silt or clay particles into the beaker. Add 125 ml of a 40g/l sodium Hexametaphosphate solution to sample.

- Dry Prep: Rinse the sample with DI water into a dispersion cup. Fill the cup to the halfway mark with DI water and place cup on the blender. Mix sample for approximately one minute. Pour content of cup into a 1000 ml sedimentation cylinder. Rinse cup with DI water to wash all the sample into cylinder. Fill the cylinder to the 1000 ml line and cover with a sheet of paraffin wax.

  Wet Prep: Rinse the sample with DI water into a dispersion cup. Fill the cup to the halfway mark with DI water and place cup on the blender. Mix sample for approximately five minutes. Pour content of cup through a No. 10 sieve into a 1000 ml flask. Rinse cup with DI water to wash all the sample into the flask. Fill the flask to the 1000

ml line and cover the flask with a sheet of paraffin wax. Take the material on the No. 10 sieve, dry it in the oven and record the weight.

11.3.2 After preparing up to 12 flasks, begin setup for hydrometer readings. The following paperwork is needed: hydrometer data sheet, hydrometer reading table, and temperature table if conversion from Fahrenheit to Celsius is necessary. Initiate timer to indicate the elapsed time, counting up from zero. Check readings of hydrometer and temperature probe in a DI water rinse bath. Get the rubber stopper to shake flask and prepare staging and test areas.

11.3.3 Initiate timer to indicate the elapsed time. The hydrometer reading table is used to perform activities as indicated (shake, place or read) for each 1000 ml cylinder.

A reading consists of inserting the hydrometer gently into the cylinder, (after the cylinder has been shaken for 1 minute), about 20 seconds before the actual reading. Read the hydrometer to the nearest 0.0005 at the top of the meniscus. Remove the hydrometer and insert a temperature sensor into the cylinder to the depth to which the hydrometer reached. Read the temperature meter to the nearest 0.1°C and remove the temperature sensor. The hydrometers and temperature sensor are rinsed in a DI bath between each reading.

After each cylinder is read, the hydrometer reading, temperature, and time (from table) is entered on the hydrometer data sheet at the corresponding cylinder (test) number and time portion on the data sheet; deviations from the table schedule are noted on the sheet. The readings are taken at 2, 5 and 15 minute and at 30, 60, 240 and 1440 minutes.

11.4 Small Sieve: Soils from the hydrometer test are rinsed on the No. 200 sieve. The soil retained on the No. 200 sieve is placed in an oven and dried over night.

11.4.1 Record the weights of the sieves used between No. 10 and No. 200. Take the dry soil and pour into the sieve stack. Place the sieve stack on the Rototap machine and shake sample for ten minutes.

11.4.2 Weigh and record the contents of each sieve.

12.0 CALCULATIONS

12.1 Percent Solids (PS) and Hydroscopic Moisture Correction Factor (HMCF)

12.1.1 HMCF is used for air dried samples (dry prep.)

*HMCF = (pan and baked sample - pan)/(pan and dry sample -pan)*100*

12.1.2 Wet Method:

*PS = (pan and dry sample- pan)/(pan and wet sample - pan)*100*

Dry Method:

*PS = HMCF * (pan and dry sample -pan)/(pan and wet sample - pan)* 100*

12.2 Sample Used (SU):

12.2.1 Wet Method:

SU = (pan and wet sample - pan) PS*

Note: for hydrometer SU, subtract the dry weight of any material retained on the No. 10 sieve.

12.2.2 Dry Method:

*SU = ((pan and dry sample - pan) - (pan and non-soil material - pan)) * HMCF*

12.3 Sieve Analysis (Percent Finer = PF)

12.3.1 Large Sieves:

- 3 inch: PF = 100-100* (Sieve and Sample (3 inch) - Sieve (3 inch))/SU
- 2 inch: PF = PF (3 inch) - 100*(Sieve and Sample (2 inch) - Sieve (2 inch))/SU and so on through the #10 Sieve.

12.3.2 Small Sieves

- #20: PF = PF(#10) - 100*(mass passing #10/sample mass (Hyd))*(sieve and sample (#20) - sieve(#20))/sample used
- #40: PF = PF (#20) - 100*(mass passing #10/sample mass (Hyd))*(sieve and sample (#40) - sieve (#40))/sample used and so on up through #10 sieve.

12.4 Hydrometer Analysis

12.4.1 Particle size, Micron

*1000*sqrt [930*viscosity/980*(SG-1))*(effective depth/time)]*

Viscosity at sample temperature, poises

- Effective Depth, cm = 16.29-264.5*(actual Hydrometer reading - 1) above equation for effective depth based on equation found with table 2 in method, in which 16.29 = 0.5*(14.0-67.0/27.8)+10.5 and 264.5 = (10.5-2.3)/0.031
- Time, minutes = Time of hydrometer reading from beginning of sedimentation

Sqrt - square root
SG - Specific Gravity of soil
Viscosity - is the resistance of a liquid to flow

12.4.2 Percent Finer (PF):

PF = Constant(actual hydrometer reading - hydrometer correction factor - 1)*

Where:
Constant = (100,00/W)*SG/(SG-1)
W = (Total sample used *sample used for hydrometer analysis*HMCF)/Amount of total sample passing #10 sieve
Hydrometer Correction = slope*sample temperature + Intercept
Slope = ((low temp. reading -1)-(high temp. reading -1)/(low temp. - high temp.))
Intercept = (low temp. reading -1) - (low temp. * slope)

13.0 METHOD PERFORMANCE

N/A

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has

established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036; (202) 872-4477.

15.0 DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data is initially reviewed by the analyst in the lab. Following this, the data is secondarily reviewed by QC personnel before being put into its final data package form (where the data is thirdly reviewed before being sent to the client).

15.2 Data that is out of control is marked as such and slated for re-analysis. Any corrective action undertaken is documented on a corrective action form (detailing the client information, problem, investigation findings and solution). This form is kept together with the project.

16.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1 Generally, any data that is out of control is considered unusable. There are, however, cases in which laboratory supervisor will be made aware of the issue and, if the data is used, it will be thoroughly narrative noted.

17.0 WASTE MANAGEMENT

17.1 The USEPA requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and

method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

18.0 REFERENCES

18.1 Annual Book of ASTM Standards, volume 04.08 Soil and Rock (I): D 420 - D4914, Section 4, Construction edition; American Society for Testing and Materials, Philadelphia, Pa., 1994.

19.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION FORMS

APPENDIX 11

METHOD: ASTM D4318-93
STANDARD OPERATING PROCEDURE FOR
LIQUID LIMIT, PLASTIC LIMIT, AND PLASTICITY INDEX OF SOILS

Applicable Matrix or Matrices: Soil, Sediment, Sludge
Standard Compound List and Reporting Limits: NA

Approvals and Signatures

Laboratory Director:	Christopher A. Ouellette	Date: 5-12-00
QA Manager:	Kim B. Watson	Date: 5-12-00
Inorganics Technical Director:	Kristine A. Dusablon	Date: 5-12-00
Geotechnical Supervisor:	Jeffrey R. McMahon	Date: 5/12/00

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of liquid limit, plastic limit and plasticity index of soils

1.2 Minimum quantity of sample is 150 grams of soil passing the No. 40 (425 um) sieve.

1.3 There is no holding time requirement. Samples that are being prepared by the wet preparation procedure should be kept in their natural water content and will

require refrigeration.

1.4 This analysis is amenable to soils with significant amount of silts and clay particles.

2.0 SUMMARY OF METHOD

2.1 Take a representative portion of the sample, approximately 150 to 200 grams, which has passed through the No. 40 (425 um) sieve. The liquid limit is determined by spreading a portion of the soil in a brass cup and dividing the sample in two parts with a groove tool. The cup is repeatedly dropped with a standard mechanical (liquid limit) device until the sample flows together. This test is repeated several times at the same and/or different water contents. The water content of the soil when it takes 25 drops of the liquid limit device to make the sample flow together is the liquid limit. The plastic limit is determined by repeatedly pressing and rolling the soil into a 3.2 mm (1/8 inch) diameter thread, until the thread crumbles and can no longer be rolled into a ball or thread. The water content of the soil at this point is the plastic limit. The plasticity index is calculated as the difference between the liquid and plastic limits.

3.0 DEFINITIONS

N/A

4.0 INTERFERENCES

N/A

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 STL Burlington maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. Material Safety Data

Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL Burlington also has a written environmental health and safety plan.

5.3 Please note chemicals that have the potential to be highly toxic or hazardous, the appropriate MSDS must be reviewed by the employee before handling the chemical.

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance sensitive to 0.01 grams.

6.2 No. 40 (425 um) sieve.

6.3 Liquid limit device which meets the requirements of ASTM D4318

6.4 Flat grooving tool that meets the requirements of ASTM D8314.

6.5 Ground glass plate that is 12 inches square and 3/8 inch thick.

6.6 Spatulas and mixing utensils for mixing and sample recovery.

6.7 Tins for drying samples.

6.8 Storage containers to preserve moisture content.

6.9 Squirt bottles for de-ionized water.

6.10 Oven with temperature control that can maintain a constant temperature of 110 $\pm$ 5°C.

7.0 REAGENTS AND STANDARDS

N/A

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 At minimum a 150 grams of sample is used for analysis. The sample container must remained sealed to maintain natural water content.

8.2 There is no holding time requirement. Samples that are being prepared by the wet preparation procedure should be kept in their natural water content and will require refrigeration.

9.0 QUALITY CONTROL

9.1 Check the balance daily with Class S weights and yearly by factory calibration.

9.2 Calibrate the sieves biannually or as requested.

9.3 Inspect the Liquid Limit Device prior to each use for wear of the cup, of the cup hanger, of the rubber base and of the cam. Adjust the drop height prior to each use.

9.4 Check the temperature of the 110°C oven daily in the morning.

9.5 A duplicate analysis is recommended for every set of 20 samples.

10.0 CALIBRATION AND STANDARDIZATION

N/A

11.0 PROCEDURE

11.1 Soil Preparation

11.1.1 Wet preparation: This is the preferred method, because the natural water content is maintained. Samples with minimal particles greater than the 425 um should be pressed through the No 40 sieve by hand until 150 to 200 grams of soil has passed through. For samples with significant amount of particles greater than 425 um, the soils should be washed through the No. 40 sieve with de-ionized water. Excess water should be evaporated off by exposing the sample to an air current and/or excess clear water should be decanted from the sample. Avoid over drying the soil by occasionally mixing the soils. The soils should be brought to a water content by either adding or removing water, so that closure of the soil in the liquid limit device is within 25 to 35 blows based on the analyst judgement. Store the sample in a sealed container for 16 hours.

11.1.2 Dry Preparation: The sample should be allowed to dry at room

temperature. Separate the soil particles with a mortar and pestle. Take 150 to 200 grams of soil that has passed through the No. 40 sieve and add de-ionized water. Mix the soil and water until a moisture content is reached that will achieve closure of the soil in the liquid limit device with 25 to 35 blows based on the analyst judgement. Store the sample in a sealed container for 16 hours.

11.2 For the Liquid Limit spread the soil to a thickness of 10 mm at its maximum depth in the brass cup of the liquid limit device. Take care to work any air bubbles out of the sample. Divide the sample in two with the groove tool, so that there is no soil in the groove and the sides of the sample are smooth. Turn the crank of the liquid limit device at a rate of two revolutions per second until the soil flows together along a 13 mm (1/2 inch) length. Verify that premature closure has not occurred due to an air bubble. A successful test will achieve closure between 15 to 35 blows depending on the test method below. Take a representative portion of the sample and determine moisture content in accordance to ASTM D2216.

11.2.1 Multipoint Liquid Limit: Repeat the test above at a different water content by adding or evaporating water from the sample. Three test should be completed that have achieved results between 15 to 25 blows, 20 to 30 blows and 25 to 35 blows. If all the tests are below 25 blows, or if the soil keeps crumbling when it is cut, or if the soil keeps sliding in the cup, then the liquid limit cannot be determined; record the soil as non plastic without performing the plastic limit test.

11.2.2 One Point Liquid Limit: This method is successful when closure of the groove is achieved between 20 and 30 blows. Repeated tests are considered successful when closure is achieved with no more than a two drop difference. If all the tests are below 20 or greater than 30 blows, or if the soil keeps crumbling when it is cut, or if the soil keeps sliding in the cup, then the liquid limit cannot be determined; record the soil as non-plastic without performing the plastic limit test.

11.3 For the Plastic Limit, take approximately 20 grams of soil from the sample prepared for the liquid limit test. Reduce the water content by working the soil on the ground glass plate, exposing it to an air current, and/or blotting it with a paper towel. Adequate moisture content is when the soil can be rolled in ones hand with out sticking to it. Take approximately 1.5 to 2.0 grams of sample for the test. Roll the sample in an ellipsoidal form. Roll the sample between ones fingers and palm and on the glass plate to form a thread with a uniform thickness of 3.2 mm (1/8 inch) thick. The amount of hand and finger pressure will very greatly with

different soils. If a thread of uniform thickness is achieved, roll the thread into an ellipsoid again. Repeat this process until the soil cannot be rolled to a 3.2 mm thread or into an ellipsoid. When the soil reaches that state, one trial is completed. Determine the moisture content of the combined soil from three completed trials according to ASTM D2216. Repeat the plastic limit by performing three more trials as described above.

12.0 CALCULATIONS

12.1 Liquid Limit (LL)

12.1.1 Multipoint Liquid Limit: Plot the relationship between the water content (Wn) and the corresponding number of drops (N) on a semilogarithmic scale. The water content (Wn) is plotted on the X-axis with an arithmetical scale, and the number of blows (N) is plotted on the Y-axis with a logarithmic scale. Draw the best straight line through three or more points. Take the water content that corresponds with 25 drops as the liquid limit.

12.1.2 One-Point Liquid Limit:

$$LL = Wn * (N/25)^{0.121}$$

The liquid limit is the average between two trials. If the difference between the two trials is greater than one percentage point, repeat the test.

12.2 Plastic Limit (PL): The plastic limit is the average between the two water contents. The results are considered accurate if the results are within the precision range of Table 2 in ASTM D4318 (typically a difference of 2.6 or less in water content).

12.3 Plasticity Index (PI):

$$PI = LL - PL$$

If the liquid limit or plastic limits could not be determined, or the plastic limit is equal to or greater than the liquid limit, report the soil as nonplastic.

13.0 METHOD PERFORMANCE

N/A

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036; (202) 872-4477.

15.0 DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data is initially reviewed by the analyst in the lab. Following this, the data is secondarily reviewed by QC personnel before being put into its final data package form (where the data is thirdly reviewed before being sent to the client).

15.2 Data that is out of control is marked as such and slated for re-analysis. Any corrective action undertaken is documented on a corrective action form (detailing the client information, problem, investigation findings and solution). This form is kept together with the project.

16.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1 Generally, any data that is out of control is considered unusable. There are, however, cases in which laboratory supervisor will be made aware of the issue and, if the data is used, it will be thoroughly narrative noted.

17.0 WASTE MANAGEMENT

17.1 The USEPA requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

18.0 REFERENCES

18.1 Annual Book of ASTM Standards, volume 04.08 Soil and Rock (I): D 420 - D4914, Section 4, Construction edition; American Society for Testing and Materials, Philadelphia, Pa., 1994.

19.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION FORMS

N/A

APPENDIX 12

METHOD: ASTM D854
STANDARD OPERATING PROCEDURE
FOR: SPECIFIC GRAVITY
Applicable Matrix or Matrices: Soil, Sediment, Sludge
Standard Compound List and Reporting Limits: NA

Approvals and Signatures

Laboratory Director:	Christopher A. Ouellette	Date: 5-12-00
QA Manager:	Kim B. Watson	Date: 5-12-00
Inorganics Technical Director:	Kristine A. Dusablon	Date: 5-12-00
Geotechnical Supervisor:	Jeffrey R. McMahon	Date: 5/12/00

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of specific gravity of soil.

1.2 Minimum quantity of sample is 25 grams of dry soil.

1.3 There is no specified holding time.

1.4 This analysis is amenable to sand, silt and clay samples.

2.0 SUMMARY OF METHOD

2.1 Weigh out a representative portion of the sample passing the No. 10 (2.00 mm) sieve (25 to 30 grams) and record this mass. Place the sample in a calibrated volumetric flask, add enough de-ionized (DI) water to cover the sample, and allow the sample to soak overnight. Apply a vacuum to the flask for 30 minutes and periodically tap the flask to dislodge any trapped air. Fill the flask to the referenced volume with DI water. Weigh the flask\sample\water and record the weight and the temperature of the water.

3.0 DEFINITIONS

N/A

4.0 INTERFERENCES

N/A

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 STL Burlington maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL Burlington also has a written environmental health and safety plan.

5.3 Please note chemicals that have the potential to be highly toxic or hazardous, the appropriate MSDS must be reviewed by the employee before handling the chemical.

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance sensitive to 0.01 grams

6.2 No. 10 (2.00mm) sieve.

6.3 Volumetric flask, 100 mL or 500 mL.

6.4 Spatulas, brushes and mixing utensils for mixing and sample recovery.

6.5 Squirt bottles for de-ionized water.

6.6 Oven with a temperature control ranging from 60°C to 110°C.

6.7 Mortar and Pestle.

6.8 Blender and dispersion cup as specified in ASTM D422 (wet preparation method only).

6.9 Temperature measuring device accurate to $\pm$ 0.5°C.

6.10 1000 mL beaker, plastic or glass.

7.0 REAGENTS AND STANDARDS

N/A

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 At minimum a 25 grams of sample is used for analysis. The sample container must remained sealed to maintain natural water content.

9.0 QUALITY CONTROL

9.1 Check the balance daily with Class S weight and yearly by factory calibration.

9.2 Check the temperature of the 110°C oven daily in the morning.

9.3 Temperature measuring device is checked against similar or more accurate temperature measuring device.

9.4 A duplicate analysis is recommended for every set of 20 samples.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibrate the pycnometer biannually, as replaced, or as requested.

10.2 Calibrate the sieves biannually or as requested.

11.0 PROCEDURE

11.1 Flask Preparation: Pycnometer calibration: Weigh the mass of the clean and oven dried volumetric flask. Fill flask with DI water to reference volume line and weigh. Measure temperature of water in degrees Celsius.

11.2 Soil Preparation

11.1.1 Dry: Separate soil particles with mortar and pestle. Remove particles greater than 2.00 mm in size using a No.10 sieve. Tare a calibrated 100 mL volumetric flask. Add 25 grams of a representative soil sample passing the No. 10 sieve, place in the flask and record this mass. Fill flask 3/4 full with DI water and allow to sit overnight.

11.1.2 Wet Prep: Add 25 to 30 grams of the dry soil sample passing the No. 10 sieve into dispersion cup and blenderize for 5 minutes. Pour and wash (using DI water) contents of dispersion cup through No. 10 sieve into a 500 mL volumetric flask. Discard any particles retained on the No. 10 sieve.

11.2 Connect volumetric flask to a vacuum for 30 minutes. Tap flask with a rubber covered pestle to remove air bubbles.

11.3 Fill the volumetric flask to the reference line with DI water, weigh and record mass.

11.4 Measure temperature of water in flask and record.

11.5 If wet preparation was used, weigh and record the mass of 1000 mL beaker. Completely wash contents of volumetric flask into beaker using DI water. Place beaker into 110°C oven until dry. Weigh and record mass of beaker/dry sample.

12.0 CALCULATIONS

12.1 The mass of the pycnometer and water is calculated using the following equation (mass used in test = beaker & dry sample – beaker):

Ma at Tx = Mf + (Dw at Tx/(Dw at Ta) * (Ma at Ta - Mf)

where:
Dw = Density of water
Ma = Mass of pycnometer and water, g
Mf = Mass of pycnometer, g
Ta = Observed temperature of water, °C
Tx = any other desired temperature, °C

Note 1: Density of water is from Table 1 of ASTM D854 or equivalent.

12.2 The Specific Gravity of the sample is calculated using the following equation:

SG at Ta = [Mo/(Mo + (Ma - Mb)] x (Dw at Tb/Dw at Ta)

where:
SG = Specific Gravity
Mo = Mass of oven dried sample see (note 1)
Ma = Mass of pycnometer filled with DI water at Temp. a (typically 20 C)
Mb = Mass of pycnometer/sample/DI water at Temp. b (observed during step 11.4)
Ta = Temp. of water at desired reference temperature. (typically 20 C)

Note 2: If sample was not oven dried, the soil mass is multiplied by the hydroscopic moisture correction factor (see ASTM D422).

13.0 METHOD PERFORMANCE

N/A

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever

feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036; (202) 872-4477.

15.0 DATA ASSESSMENT AND CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data is initially reviewed by the analyst in the lab. Following this, the data is secondarily reviewed by QC personnel before being put into its final data package form (where the data is thirdly reviewed before being sent to the client).

15.2 Data that is out of control is marked as such and slated for re-analysis. Any corrective action undertaken is documented on a corrective action form (detailing the client information, problem, investigation findings and solution). This form is kept together with the project.

16.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1 Generally, any data that is out of control is considered unusable. There are, however, cases in which laboratory supervisor will be made aware of the issue and, if the data is used, it will be thoroughly narrative noted.

17.0 WASTE MANAGEMENT

17.1 The USEPA requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water and land by

minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

18.0 REFERENCES

18.1 Annual Book of ASTM Standards, volume 04.08 Soil and Rock (I): D 420 - D4914, Section 4, Construction edition; American Society for Testing and Materials, Philadelphia, Pa., 1994.

19.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION FORMS

N/A

APPENDIX 13

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE188_01.DOC
REVISION NUMBER: 01

STANDARD OPERATING PROCEDURE FOR BULK DENSITY DETERMINATION

MAY 26, 2002

COPY

STANDARD OPERATING PROCEDURE

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Northeast Analytical, Inc.
Issuing Section: Inorganics Laboratory
SOP Name: NE188_01.SOP
Date: 5/26/2002
Revision Number: 01

1.0 TITLE Standard operating procedure for the determination of Bulk Density.

2.0 PURPOSE To provide the SOP for the preparation and analyses of soil samples for the determination of Bulk Density.

3.0 SCOPE This method is applicable to soil, peats and soil mixtures. This procedure is based on procedures found in ASTM Method D4531-86 (1996).

4.0 COMMENTS The difference in the varying bulk density procedures is in the method in which the sample is obtained and the volumes that are used. Variation in bulk density is attributable to the relative proportion and specific gravity of solid organic and inorganic particles and to the porosity of the soil.

5.0 SAFETY

5.1 Safety glasses, lab coat or lab apron and disposable gloves must be worn when handling chemicals and samples.

5.2 Personnel should familiarize themselves with the necessary safety precautions by reading MSDS information covering any chemicals used to perform SOP.

5.3 Samples that emit undersirable odors when heated should be placed in the oven at the end of the day. The oven used for drying samples is connected to a fume hood. The hood should be operational at all times. If the hood is not working properly, contact a member of the safety committee immediately.

5.4 If samples contain known quanities of hazardous material, the dried samples and the drying dishes or cups are classified as hazardous waste and are subject to the procedures listed in SOP NE054.

6.0 REQUIREMENTS

6.1 Knowledge on the operation and calibration of the analytical balance is required.

6.2 Knowledge on the operation of the drying oven located in the Inorganics laboratory.
6.3 Knowledge on the maintenance of the portable desiccator box.

7.0 EQUIPMENT

7.1 Apparatus and Equipment. Located in the Inorganics laboratory.

7.1.1 VWR model 1370FD model drying oven. Inside the oven is a calibrated thermometer placed in a sand filled bottle. Located in the metals laboratory.

7.1.2 Analytical balance. Mettler model AG204. Located in the metals lab.

7.1.3 Aluminum drying dishes. VWR p/n 25433-008. Located in the lab storage room.

7.1.4 Plastic spoons. Located in the third floor storage room. Available at local stores.

7.1.5 Bulk Density, % Moisture and % Total Solids logbook. Located in the metals laboratory. See attachment A for an example.

7.1.6 Glass trays. Located throughout the laboratory.

7.1.7 Portable desiccator. Located in the metals laboratory.

7.2 Operation of drying oven.

7.2.1 Before drying samples, the drying oven "set temperature" knob has to be adjusted so that the temperature is between 103° and 105° C.

7.2.2 After adjusting the temperature, wait approximately 15 minutues and oper the door and read the thermometer. If the temperature is not within the specified range, repeat 6.2.1. If the oven will not stabilize, contact the inorganics manager.

7.3 Calibration of GFAA cups

7.3.1 Calculate the average volume of the GFAA cups annually.

7.3.2 Prepare 10 GFAA cups bu numbering them "1" through "10".

7.3.3 Place the cups in a vial rack and place in the drying oven for a minimum of one hour at a temperature of 103° to 105° C.

7.3.4 Each day that the cups are to be weighed, pull the desiccant material from the oven and place in the desiccator for a minimum of one hour before placing the rack and cups in the desiccator. At the end of the day the desiccant material is poured into a glass tray and placed in the drying oven at 103° to 105°C. Place the cups in the desiccator for exactly one hour.

7.3.5 Place a cup on the balance and write the cup number in the logbook. Record the weight of the cup.

7.3.6 Repeat the above process for each cup.

7.3.7 Fill each cup to the top with laboratory grade water.

7.3.8 Carefully record the weight of the cup and wter under "WETSAW" column. Subtract the weigh of the cup from the "WETSAW". Record the wter weight under the "Comments" column.

7.3.9 Calculate the average water weight and record under the "Comments column".

7.3.10 Divide the average weight of the water in each cup by the density of water (1 g/ml) to calculate the average volume of water in each cup. Record the average volume (ml) under "Comments" column.

7.3.11 Sample cups may be purchased from Perkin Elmer p/n B008-7056 or any other vendor of 2ml GFAA cups.

8.0 PROCEDURE

8.1 Sample Analysis.

8.1.1 Prepare the GFAA sample cups by writing the last three digits of the NEA sample ID on the cups, for example, the sample cup for NEA sample AB01234 would be labeled as '234'. Prepare extra sample cups with their own unique numbers.

8.1.2 Place the cups in a vial rack and place in the drying oven for a minimum of one hour at a temperature of 103° to 105°C.

8.1.3 Each day that the cups are to be weighed, pull the desiccant material from the oven and place in the desiccator for a minimum of one hour before placing the rack and cups in the desiccator. At the end of the day the desiccant material is poured into a glass tray and placed in the drying oven at 103° to 105°C. Place the cups in the desiccator for exactly one hour.

8.1.4 Set up the logbook by writing the NEA#'s under the appropriate column.

8.1.5 Access LIMs and go to 'WIN RESUTS'. Select "SAMPLE DESIGNATION" and type the NEA#'s in the white box. Select the 'TEST' template and click 'OK'.

8.1.6 Place a cup on the balance and write the cup number in the logbook. See the following table to determine what column heading and cell to use.

8.1.7 Right click and select "Take BOAT". Copy the value from the cell into the logbook. Repeat process for all the samples.

8.1.8 Using a tongue depressor or spatula, carefully place a portion of well mixed sample into the cup (do not use rocks or stones). Remove air pockets in the cup by gently tapping the cup on the counter. Fill the cups to the top.

8.1.9 Access LIMs and go to 'WIN RESULTS'. Select "SAMPLE DESIGNATION" and type the NEA#'s in the white box. Select the "TEST" template and click "OK".3

8.1.10 Place each cup on the balance. Right click and select "Take "WETSAW". Coopy the value from the cell into thelogbook. Repeat process for all the samples.

8.1.11 Place the cups in a vial rack and place in the drying oven OVERNIGHT at a temperature of 103° to 105°C.

8.1.12 Place the cups in the desiccator for exactly one hour.

8.1.13 Access LIMs and go to "WIN RESULTS". Select "SAMPLE DESIGNATION" and type the NEA#'s in the white box. Select the "TEST" template and click "OK".

8.1.14 Place a cup on the balance. See the following table to determine what column heading and cell to use.

8.1.15 Right click and select "Take DRYSAW". Copy the value from the cell into the logbook. Repeat process for all samples.

8.1.16 Enter the aver volume of the cups under "BDMCVO".

8.1.17 The results are automatically calculated.

9.0 SAMPLE COLLECTION AND STORAGE

9.1 No preservation is required.

9.2 Samples can be collected in plastic or glass bottles with Polyseal caps.

10.0 QUALITY CONTROL

10.1 Duplicates:

10.1.1 One duplicate sample is processed each day that samples are prepared or every 10 samples, which ever occurs first.

10.2 Criteria:

10.2.1 % RPD = ABS[(X1-X2)/(X1+X2)]*200.

10.3 Limits:

10.3.1 The % RPD must be less than 20 %. If not samples need to be reanalyzed.

11.0 DOCUMENTATION

11.1 In the logbook, record the temperature of the oven and the date and time that the sample cups were placed in the oven.

11.2 In the logbook, record the temperature of the oven and the date and time that the sample cups were taken out of the oven.

11.3 Copies of the LIMs sheets are to be reviewed against the logbook by the analyst and placed in the folder.

11.4

LIMS RESULT TEMPLATE "TEST" COLUMN HEADINGS AND DESCRIPTIONS

Column	Description	Column	Description	Column	Description
%SOLIDS	Percent solids	**BOATWT**	Cup or boat wt.	**WETSAW**	Cup and wet sample wt.
BULK	Bulk density	**BDMCVO**	Cup volume ml.	**MOIST**	% Moisture
D_BULK	Dup. Bulk density	**BDMCDVOL**	Cup volume ml.	**DUPBOATWT**	Dup. boat wt.
P_BULK	Precision calculation	**D_MOIST**	Dup. %Moist.	**WETDUPWT**	Dup. wet sample wt.
P_MOIST	Precision calculation	**DRYDUPWT**	Dup. dry sample wt.	**DRYSAW**	Dry sample wt.

12.0 POLLUTION PREVENTION/WASTE MANAGEMENT.

12.1 Refer to NEA168.SOP for instructions for pollution prevention.

12.2 Refer to NEA089.SOP and NEA054.SOP for instructions for disposal of waste generated during the procedures previously mentioned.

13.0 DEFINITIONS

13.1 Analytical Batch – The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. groundwater, sludge, ash, etc.)

13.2 Bulk Density – Is the measure of the weight of the soil per unit volume (g/ml), usually given on an oven dry (110º C) basis.

13.3 Matrix – The predominant material of which the sample to be analyzed is composed.

13.4 MSDS – Material safety data sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs. The thrust of the law is to have those who make, distribute, and use hazardous materials responsible for effective communication.

13.5 Relative Percent Difference (RPD) – To compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

13.6 Replicate – Repeated operation occurring within an analytical procedure. Two or more analyses for the same constituent in an extract of a single sample constitute replicate extract analyses.

13.7 RCRA – Resource Conservation and Recovery Act, PL 94-580. Found at 40 CFR 240-271. EPA has jurisdiction. Enacted November 21, 1976, and amended since. RCRA's major emphasis is the control of hazardous waste disposal. It controls all soil-waste disposal and encourages recycling and alternative energy sources.

13.8 RCRA Hazardous Waste – A material designated by RCRA as hazardous waste and assigned a number to be used in record keeping and reporting compliance.

13.9 Reagent Water – Water in which an interferent is not observed at or above the minimum quantitation limit of the parameters of interest.

13.10 Rounding Rules – If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by

13.10.1 If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number.

13.10.2 If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

13.11 Sample Delivery Group (SDG) – Unit within a single case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a case, received over a period of up to 14 calendar days (7 calendar days for 14-day data turnaround contracts). Data from all samples in an SDG are due concurrently.

14.0 REFERENCES

14.1 ASTM methods D4531-86(1996).

APPENDIX 14
(Note: SOP for Water Content is not included because the Percent Moisture will now be measured according to the procedure in the PCB Extraction SOPs.)

APPENDIX 15

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE205_01.SOP
REVISION NUMBER: 01

STANDARD OPERATING PROCEDURE FOR THE PREPARATION AND ANALYSIS OF SAMPLES FOR TOTAL ORGANIC CARBON BY US-EPA LLOYD KAHN METHOD AND TEKMAR-DOHRMANN APPLICATION NOTE TOC-011,

AUGUST 20, 2002

COPY

STANDARD OPERATING PROCEDURE

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Robert E. Wagner/Laboratory Director

Northeast Analytical, Inc.
Issuing section: Inorganics Laboratory
SOP Name: NE205_01.DOC
Date: 8/20/2002
Revision: 01

1.0 TITLE Standard Operating Procedure for the preparation and analysis of samples for Total Organic Carbon (TOC) according to Determination of Total Organic Carbon in sediment, Lloyd Kahn, U.S.E.P.A. Region II, Edison NJ 1988 and Tekmar-Dohrmann application note TOC-011.

2.0 PURPOSE

2.1 Procedures for the preparation and analyses of aqueous samples for particulate organic carbon by the use of a Boat Sampler Module are provided.

2.2 Procedures for the preparation and analyses of solid samples for total organic carbon by the use of a Boat Sampler Module are provided.

3.0 SCOPE/APPLICABLE MATRICES

3.1 Methods in this procedure are used for soils, sediments, and solids for total organic carbon.

4.0 SUMMARY OF METHOD

4.1 Principle: Depending upon the configuration, TOC can be measured by ultra-violet promoted persulfate oxidation or high-temperature combustion, followed by infrared detection. The combustion method is used for solid samples.

4.2 Organic carbon is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

4.3 The fractions of total carbon (TC) are defined as:

4.3.1 inorganic carbon (IC)-the carbonate, bicarbonate, and dissolved CO_2;

4.3.2 total organic carbon (TOC)-all carbon atoms covalently bonded in organic molecules;

4.3.3 dissolved organic carbon (DOC)-the fraction of TOC that passes through a 0.45-µm -pore-diameter filter,

4.3.4 particulate organic carbon (POC)-also referred to as non dissolved organic carbon, the fraction of TOC retained by a 0.45-µm filter.

4.4 TOC and POC in solid and sludge can be measured by utilizing the combustion-infrared method. The sample is homogenized and treated with acid and then heated to remove IC. The treated sample is placed into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide. The organic carbon is oxidized to CO_2 and H_2O. The sludge and sediment sampler combusts samples at 800^oC in an oxygen atmosphere so that solids as well as liquids can be analyzed.

4.5 The sampler consists of a magnetically coupled boat inlet system that delivers the sample to the high temperature furnace. Two ports are provided for sample introduction, a septum port for liquid injections, and a flip-top port for solid samples. The CO_2 from the oxidation of organic carbon is transported in the carrier-gas stream and is measured by means of a nondispersive infrared analyzer (NDIR).

5.0 COMMENTS

5.1 The detection limit for samples is dependent on the amount of sample analyzed.

6.0 SAMPLE STORAGE AND HANDLING

6.1 Samples are stored in the walk-in cooler.

6.2 Solid samples require no preservation prior to analysis other than storage at 4 ^oC and have a holding time of 14 days.

7.0 INTERFERENCES

7.1 Volatile organics in sediments may be lost in the decarbonation step resulting in a low bias.

7.2 Bacterial decomposition and volatilization of the organic compounds are minimized by maintaining the sample at 4^o C and analyzing within the specified holding times.

8.0 DOCUMENTATION

8.1 The following information is documented in logbooks:

8.1.1 Document maintenance or replacement of parts to the infrared analyzer in the General laboratory equipment maintenance logbook. Record problems, steps taken to repair instrument and the names of representatives of instrument vendor in General laboratory equipment maintenance logbook.

8.1.2 Document the following information during the preparation and analysis of samples in the Inorganics laboratory logbook:

8.1.2.1 The method, analysts' initials, and the dates of extraction and analyses.

8.1.2.2 The standard codes of solutions used during the course of analysis.

8.1.2.3 Record the NEA sample identification numbers, initial sample weights or volumes, post extraction dilution factors, Infrared sample area counts, boat number and any relevant comments.

9.0 SAFETY

9.1 Safety glasses, lab coat or lab apron, and disposable gloves must be worn when handling chemicals and samples.

9.2 Personnel should familiarize themselves with the necessary safety precautions by reading MSDS information covering any chemicals used to perform SOP.

9.3 Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Specifically, concentrated nitric, sulfuric, and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood and if skin contact occurs, flush with large volumes of water.

9.4 Ultra-violet radiation can cause damage to the eyes. Do not open the door to the UV persulfate module without turning the lamp off.

10.0EQUIPMENT

10.1 Apparatus and Equipment. Located in the Inorganics laboratory and Main Extraction Laboratory.

10.1.1 Dohrmann IR-I NDIR detector module. Located in the main laboratory.

10.1.2 Dohrmann sludge/sediment sampler. Dohrmann (p/n 832-222). Located in the main laboratory.

10.1.3 250 and 1000 µL Rainin autopipets. Rainin (p/n EP-250 and EP-1000).

10.1.4 250 and 1000 µL pipette tips. Rainin (p/n RT-96 and RT-200).

10.1.5 1-5 ml Eppendorf digital pipette with pipette tips. Located in the Inorganics laboratory.

10.1.6 Quartz boats. Dohrmann (p/n 899-624). Located in the main laboratory.

10.1.7 Quartz wool. Dohrmann (p/n 511-735). Located in the main laboratory.

10.1.8 Drying oven.

10.1.9 Propane tank with torch assembly. Located in the main laboratory.

10.1.10 Tweezers and steel spatula. Located in the main laboratory.

10.1.11 50, 100 and 250 µl syringe. Located in the main laboratory.

10.1.12 High purity oxygen tank with regulator. Located in the main laboratory.

10.1.13 Aluminum weighing boats. Located in the main laboratory.

10.1.14 UV-Persulfate Reaction Module. Located in the main laboratory.

10.1.15 Teflon sleeve reactor, taper joint. Dohrmann (p/n 070-627). Located in the main laboratory.

10.1.16 Lamp, Ultra-violet. Dohrmann (p/n 512-092). Located in the main laboratory.

10.1.17 High purity nitrogen tank with regulator. Located in the main laboratory.

10.1.18 20-mesh tin. Dohrmann (p/n 511-876). Located in the main laboratory and used for tin/copper scrubber.

10.1.19 Copper. Dohrmann (p/n 511-895). Located in the main laboratory and used for tin/copper scrubber.

10.1.20 Pyrex wool. Dohrmann (p/n 511-895). Located in the main laboratory and used for tin/copper scrubber.

10.1.21 Class A volumetric flasks at volumes of 10, 25, 50, 100, and 200 ml.

10.1.22 Analytical balance. The vendor is Mettler and the model number is AG204. Capable of weighing to 0.0001 grams.

10.1.23 Graduated cylinders.

10.1.24 Disposable 1, 5, and 10 ml pipettes.

10.1.25 TOC logbook.

10.1.26 Rinse bottle. Filled with laboratory grade water. Located in the Inorganics laboratory.

10.1.27 Inorganics department standard preparation logbook.

10.1.28 Gray septum. Dohrmann (p/n 517-807). Located in the main laboratory.

10.2 Reagents

10.2.1 Preparation of TOC working standard solution.

10.2.1.1 ERA p/n 516 or other suitable vendor.

10.2.1.2 Determine total ug of TOC in stock standard = {[standard conc. (mg/L)]*[dilution volume (ml)]}

10.2.1.2.1 For example, the instructions supplied with the solution stipulate that 5 ml of the vial be diluted to 1000 ml. The standard concentration stated in the 'Certificate of Analysis 'will be 72.6 mg/L. Thus, the total amount of TOC in the vial is 14,520 ug.(200X)

10.2.2 Preparation of TOC (solids) calibration standards:

10.2.2.1 Prepare 5 calibration standards ranging in concentration from approximately 70 mg/L to 12,000 mg/L.

10.2.2.2 Use the following formula to assist in preparing the calibration standards.

$$\text{Cal. Std. (mg/L)} = \frac{\{[\text{Conc. Of working std. (ug/ml)}]*\{\text{vol. of stock std. (ml)}\}]}{\{\text{Final vol. (ml)}\}}$$

10.2.2.3 Using information from the previous examples to prepare a calibration standard.

$$\frac{\{[14{,}520\ (\text{ug/ml})]*[0.05(\text{ml})]\}}{(10\ \text{ml})} = 72.6\ \text{mg/L calibration standard}$$

11.0 METHOD PERFORMANCE

11.1 Statistics for method performance are maintained by the Quality Assurance unit and are available for review.

12.0 PROCEDURE

12.1 Operation and maintenance of the Dohrmann IR-I NDIR detector module.

12.1.1 Refer to the instrument manual for specific instructions and part numbers for all components.

12.1.2 To prepare the tin/copper scrubber;

12.1.2.1 fit one end of the Pyrex scrubber tube with a cored gray septum.

12.1.2.2 Insert a tuft of Pyrex wool and then about 2 inches of tin in the other end. Secure the tin with another tuft of Pyrex wool.

12.1.2.3 Fill the remaining half of the scrubber tube with an equal amount of copper. Secure the copper with a third tuft of Pyrex wool. Insert a cored gray septum.

12.1.2.4 Each day of use, inspect the tin/copper scrubber and change the contents of the tube when one-half of the tin is discolored.

12.1.3 The detector must be on for several hours in order to achieve equilibrium. It is recommended that the detector be turned on the day before the analysis is to be performed. Power up the detector and the main unit.

12.1.4 Verify that the printer has sufficient amount of paper before starting the analysis. Reset the printer so that the number "1" will be printed for the first analysis performed for that day.

12.1.5 Select the "TOC" and the "DET" positions. For the detector, select position "3" for high concentrations, "2" for medium concentrations, and "1" for low concentrations of TOC.

12.1.6 The module will not light the green "ready" light if the baseline is above 0.05. Adjust the "zero" control until the baseline is less than 0.02. The "CALIB" light must be off during analysis.

12.2 Operation and maintenance of the Dohrmann sludge/sediment sampler.

12.2.1 Refer to the instrument manual for specific instructions and part numbers for all components.

12.2.2 A portion of sample is weighed into a quartz boat where it is acidified and dried. The boat is placed in the boat carriage of the sampler and it is moved into the combustion chamber. Gas from the combustion tube flows into the flask to the right where it passes through acidified water.

12.2.3 The gas travels to the flask to the left where excess water is removed before traveling to the detector module. The gas passes through the tin and copper scrubber and into the detector.

12.2.4 Before turning on the solid sampler, carefully examine individual components for sign of wear.

12.2.4.1 Adjust the flow of oxygen to 30 psi.

12.2.4.2 The level of acidified water in the right flask must be above the fritted sparging finger. A vigorous flow of gas emitting from the sparging finger should be easily observed, if not, check the gas lines and connections for leaks.

12.2.4.3 The water collection flask should be emptied on a daily basis.

12.2.5 Turn on the furnace unit.

12.2.6 When using the module for the first time or after a long period of inactivity, the furnace should be monitored with a voltmeter to verify that the temperature is at 800^{o}C.

12.2.6.1 Place the black (ground) probe in the "com" port.

12.2.6.2 Place the red (positive) probe in the "monitor", set the voltmeter to "volts".

12.2.6.3 The voltage reading should read "0.80", if not, place the red probe in the "adj" port.

12.2.6.4 The voltage reading should read "0.80", if not, adjust the voltage by turning the setscrew until the correct voltage is achieved.

12.2.7 If the gray septum (p/n 517-807) at either end of the combustion tube have corroded and require replacement, the furnace must be turned off before replacing the septum.

12.3 Calibration of Dohrmann sludge/sediment sampler and IR-I NDIR detector module.

12.3.1 A new calibration curve must be generated:

12.3.1.1 Every four months;

12.3.1.2 if either the ICV or CCV are outside acceptance criteria or

12.3.1.3 If the detector has been rebuilt.

12.3.2 The calibration curve is based on 'µg of carbon' versus 'area'. The calibration standards require duplicate injections. The average blank area is subtracted from the average area for each calibration standard.

12.3.3 Press ‘Reset’ on printer to reset the number log for the printer.

12.3.4 A fresh tuft of quartz wool is inserted into a quartz boat. The boat is placed inside the sediment sampler module. Hook the loop of the boat with the end of the magnetic boat carriage.

12.3.5 Remove contaminates from the boat by placing it in the furnace until the baseline has started to decrease. Pull the boat out of the furnace.

12.3.6 After the boat has cooled (approximately 30 seconds), place the boat underneath the injection port. Remove septum and inject 0.070 ml of the blank or calibration standard onto the boat. Replace septum.

12.3.7 After the baseline has stabilized, place the boat in the furnace. Press the "Start" button. After the signal has started to decrease, pull the boat out of the furnace.

12.3.8 Repeat injection of the standard until consecutive measurements are obtained that are reproducible to within $\pm$ 10%.

12.3.9 Repeat for the remaining calibration standards.

12.3.10 Every standard must be within the scale of the detector.

12.3.11 If the needle in the IR meter goes past ‘95’ or if the red error light has lit after injecting the stock standard or a sample, inject a smaller volume of the standard or prepare a smaller amount of sample and reanalyze.

12.3.12 Enter the injection number, standard label, date analyzed, injection volume, and the area printed by the printer in the TOC logbook.

12.3.13 After the calibration curve has been completed, enter the area and the ug of carbon for each standard in the appropriate fields in the TOC solids Excel spreadsheet. The slope for the calibration curve, the average area for the blank and the average area for the lowest calibration standard are entered into a formula in LIMS that converts the average area for each sample into the average ug of carbon.

12.4 Preparation of solid samples.

12.4.1 Between 1.0 and 50 mg of material can placed in a boat depending on the percent of carbon in the sample. Solid samples are analyzed once..(If Client requires triplicate analysis see NE177.SOP).

12.4.2 The concentration of the samples must be within the range of the calibration curve. If the sample concentration of the sample is outside the range of the calibration curve, repeat the analysis of the sample.

12.4.3 If the sample concentration is too high, repeat the sample preparation and analysis with a lower sample weight (minimum 1.0 mg).

12.4.4 Place each quartz boat in a numbered aluminum weigh boat.

12.4.5 Homogenize a portion of the sample.

12.4.6 Place one aluminum boat with a quartz boat on the analytical balance and tare the balance.

12.4.7 Transfer an aliquot of the sample to the quartz boat and record the NEA #, weight and the boat number in the TOC logbook.

12.4.8 Add 2 to 3 drops of 1+1 nitric acid to each sample.

12.4.9 Place the aluminum weigh boats in the oven. Remove the sample when dried (minimum of 10 minutes).

12.4.10 Place the boat in the raceway. After the baseline has stabilized, place the boat in the furnace and press the 'Start' button.

12.4.11 Copy the TOC area from the printer into the TOC logbook.

12.4.12 After each sample analysis, rinse the boat with LGR water, scrape any remaining material from the boat and place the boat in the flame of the propane torch to remove any contaminates.

12.5 Percent total solids determination**.**

12.5.1 Determine the percent total solids for each sample as described in NE090.SOP

.

12.6 Sample calculations using Microsoft Excel 4.0.

12.6.1 The calibration curve and samples are calculated by using an Excel spreadsheet. The spreadsheet requires the entry of the absorbencies of the standards and samples, sample extract volumes, sample weights or volumes, percent solids and dilution factors.

12.6.2 Sample values are computed by comparing response with the standard curve.

12.7 Archiving of data.

12.7.1 Print a copy of spreadsheet and place in the data folder for that client.

12.8 Transfer of Data to LIMs (TOCS)

12.8.1 After the calibration curve has been completed, give the LIMs manager a copy of the Exel spreadsheet for the calibration curve including values for the slope and instrument intensities for blank and the lowest calibration standard.

12.8.2 Log into LIMS. Click “Win Results” or “Results” from LIMS toolbar. Select the appropriate samples by either typing in the sample ID’s or selecting the Login Record File.

12.8.3 Choose the result entry template “TOCSOL”, then click “OK”. A result entry spreadsheet will then be created with the following columns: TOCSO, TOCI_A, TOCI_1, TOC_1SW, %SOLIDS.

12.8.4 The data for samples should be entered into the columns as follows:

12.8.4.1 TOCI_1 = Area Counts for Sample

12.8.4.2 TOC_1SW = Sample weight in grams.

12.8.4.3 %SOLIDS = % Total Solids for Sample (Enter as a percentage, not a decimal).

12.8.4.4 TOCI_A = Area Counts for Sample (Fills in automatically).

12.8.4.5 TOCSO = Result for TOC in Solids (Fills in automatically).

12.8.5 Once the field TOCSO has been filled in by the computer, right click on that field and select “detailed edit” from the pull down menu. Confirm that the MDL and the date analyzed for the sample are correct. Proceed to the next sample.

12.8.6 Each method has tests for the required QC parameters.

12.8.7 Add QC parameters to the assigned samples by QC batching.

12.8.7.1 QC samples are added as individual tests to predetermined samples in LIMs. Access LIMs and go to ‘QC Batching’.3

12.8.7.2 Enter the required information into the database.

12.8.7.3 Once the data has been entered for all samples, go the QC section of the spreadsheet. If batching was performed correctly there should be some of these fields displayed in white. If not, right click on the dark gray fields in that same row so that all appropriate QC tests have been added.

12.8.7.3.1 For example, the data fields for the sample duplicate must be selected (white) before entering data into the spreadsheet fields.

13.0 Calculation of data.

13.1 Data solids are reported in "mg/kg" units.

13.2 Matrix spike recovery:

$$\%REC.= \frac{[\{\text{M.S. sample}\}-\{\text{sample}\}]*100}{\{\text{Spike Added}\}}$$

13.3 Relative Percent Difference:

$$\%RPD= \text{Abs.}\ \frac{[\{\text{Result1}\}-\{\text{Result2}\}]*200}{\{\text{Result1}\}+\{\text{Result2}\}}$$

13.4 %Recovery for IPC and QCS solutions:

$$\%REC. = \frac{\{Found\ value\}}{\{True\ value\}} * 100$$

13.5%Recovery for LCSS samples:

$$\%REC. = \frac{\{found\ value\}}{\{True\ Value\}} * 100$$

14.0 Data submission

14.1 The information that is required on the client's certificate is the NEA identification number, client identification, method code, sample results, detection limits, concentration units, and analysis dates.

14.2 The units used for reporting solid samples are mg/kg. Results are rounded to three significant figures.

14.3 For soil samples, if the sample analyses is off scale and the minimum sample weight of 1.0 mg was used, calculate the maximum concentration of TOC based on the µg of carbon of the highest calibration standard, average sample weight, and the percent total solids. Report the results as greater than the calculated maximum sample concentration.

15.0 Equipment maintenance.

15.1 Record the replacement of parts in the General Laboratory maintenance book.

15.2 Replace the drying tube if water droplets are observed inside the tube.

15.3 Replace the material in the scrubber tube when discolored.

15.4 Replace septa and tubing when worn.

15.5 If the baseline consistently rises with each day of use the IR detector must repaired by Horiba.

15.5.1 Remove the detector from the housing and wrap in bubble wrap. Place in a secure box with packing peanuts.

15.5.2 Type the PO# required for repair, the company name, company contact, type of service required, analyst name and phone number, and if necessary a return authorization number on company stationary and place in an envelope. Place the envelope in the box.

15.5.3 Two weeks are required for shipping and repair of the detector.

15.6 If the temperature for boat module oven fluctuates, either the oven or the thermocouple must be replaced.

16.0 QUALITY CONTROL

16.1 Initial Demonstration of Performance

16.1.1 Perform Method Detection Limit studies for solid matrices.

16.1.1.1 MDLs should be determined annually or when in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate they need to be redetermined.

16.2 Certification for analysts.

16.2.1 Analysts must read, understand, and use the latest version of the laboratory's SOPs that relate to their job responsibilities. The SOPs must be read during their initial training, annually, and when the SOPs are revised.

16.2.2 When possible, analysts should attend training courses related to their job responsibilities.

16.2.3 For each matrix processed with this method, the analyst must be capable to perform the following tasks:

16.2.3.1 Prepare and analyze four consecutive laboratory control samples within method quality control limits or within the limits supplied with the purchased material.

16.2.4 For each matrix processed with this method, the analyst must be capable of analyzing a blind sample successfully.

16.2.4.1 A blind sample must be analyzed during their initial training and annually thereafter.

16.3 Sample preparation quality control.

16.3.1 Laboratory reagent Blank/Preparation blank : Prepare and analyze at least one LRB with batch of 20 or fewer samples of the same matrix or batch.

16.4 Instrument and analysis quality control.

16.4.1 ICV/CCV:

16.4.1.1 Analyze ICV immediately after calibrating the instrument.

16.4.1.2 The source of the standards must be different than the source for the calibration standards.

16.4.1.3 Prepare at a concentration approximately equal to the midpoint of the calibration curve.

16.4.1.4 Analyze CCV every ten samples and at the beginning and the end of the analytical run.

16.4.1.5 Continuing Precision and Accuracy. To initiate a control chart, a representative sample of a well mixed sediment is analyzed 15 times to determine the analytical precison. A control chart displaying a control limit of three times the measured standard deviation for the 15 replicates is created.

For every sample batch (20 or less) take one sample and run in quadruplicate. Calculate the standard deviation and compare with the control chart limit.

If the sample being run in quadruplicate exceeds the three standard deviation limit, identify the error and rerun the samples in that batch along with the quadruplicte samples.

17.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QC MEASURES

17.1 Initial review of documentation

17.1.1 After the completion of the analysis run, the analyst reviews the logbook(s) and analytical data for completion and completes the required documentation.

17.1.2 The supervisor reviews the logbook(s) and data and records their initials and review dates on the appropriate documents.

17.1.3 Each QC measurement is reviewed and compared to the appropriate acceptance criteria.

17.1.4 The following section supplies the corrective action and or contingencies if the criteria for the QC measure are unacceptable.

17.2 Calibration curves**:**

17.2.1 Acceptance criteria: Correlation coefficient must be $\geq$0.997.

17.3 Linear dynamic range for samples:

17.3.1 Acceptance criteria: Determined sample concentrations that are greater than the highest calibration standard must be diluted and reanalyzed. Report the results from the diluted sample.

17.4 Laboratory reagent Blank/Preparation blank:

17.4.1 Acceptance criteria: The absolute value of the concentration must not exceed the PQL/PRDL of the analyte.

17.4.1.1 Not applicable if the sample concentration is > 10X blank level,

17.4.1.2 Or if positive result is reported for the blank but the analyte is not in the sample.

17.5 Laboratory fortified matrix/matrix spike accuracy.

17.5.1 Acceptance criteria: The spike recovery limits are 75 to 125%.

17.5.2 Not applicable if sample concentration is greater than 1/5 spike added.

17.6 Laboratory Duplicates/matrix spike and matrix spike duplicates precision

17.6.1 Acceptance criteria: A %RPD limit of $\pm$20% is used for analytes > 5X PQL or $\pm$PQL limit is used if the analyte concentration in the sample or duplicate is <5X PQL.

17.7 ICV/CCV and Initial Precision and Accuracy:

17.7.1 Acceptance criteria: A % recovery limit of 90-110% is used.

18.0 CORRECTIVE ACTION FOR OUT OF CONTROL DATA

18.1 Calibration curves:

18.1.1 Corrective action: If QC measure not within acceptance criteria, determine source of problem, correct problem and recalibrate instrument.

18.2 Laboratory reagent Blank/Preparation blank:

18.2.1 Corrective action: If QC measure not within acceptance criteria;

18.2.1.1 Reanalyze preparation blank and;

18.2.1.2 If still out, reanalyze all samples associated with the LRB.

18.3 Laboratory fortified blank/Laboratory control sample:

18.3.1 Corrective action: If QC measure not within acceptance criteria;

18.3.1.1 If LCS is high and sample results <PQL, no corrective action, ELSE,

18.3.1.2 Reanalyze LCS/LFB and;

18.3.1.3 If still out, re-extract and reanalyze all samples associated with the LCS.

18.4 Laboratory fortified matrix/matrix spike

18.4.1 Corrective action: Determine problem, re-analyze samples based upon analyst judgement.

18.5 Laboratory Duplicates

18.5.1 Corrective action: Determine problem, re-analyze samples based upon analyst judgement.

18.6 QCS/ICV/IPC/CCV:

18.6.1 Corrective action: If QC measures not within acceptance criteria stop the analysis, determine source of problem, correct problem and verify calibration and reanalyze all samples since last compliant QC measurement.

19.0 Contingencies for handling out of control or unacceptable data.

19.1 If the acceptance criteria for QC measures has been exceeded for requested analytes and the data is to be reported, the following procedures must be implemented:

19.1.1 The Quality assurance officer must be notified.

19.1.2 The data must be flagged with the appropriate qualifiers and case narrative.
19.1.3 The client must be notified about the data.

20.0 DEFINITIONS

20.1 Analytical Batch – The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. groundwater, sludge, ash, etc.)

20.2 Calibration – The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid and reagents or concentration of acids as used in the sample preparation.

20.3 Calibration Blank-A volume of reagent water acidified with the acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the instrument.

20.4 Calibration Standard (CAL) - A solution prepared from the dilution of stock standards solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

20.5 Calibration curve - If the correlation coefficient is < 0.997 or if the calculated recoveries for any of the calibration standards are not within 10% of the true value (except for the lowest standard), repeat analysis of the outlying standards until curve is within acceptance criteria.

20.6 Correlation Coefficient – The correlation coefficient for the calibration curve must be greater than or equal to 0.997 according to NYSDOH requirements.

20.7 Continuing Check blank (CCB) - Analyze the CCB solution after each ICV/CCV solution. If the absolute value of the CCB is $\geq$ the PQL, stop the analysis, correct problem, recalibrate the instrument and reanalyze all samples since the last compliant CCB.

20.8 Instrument Performance Check (IPC) Solution – Also known as CCV. A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

20.9 Laboratory Duplicates (LD1 and LD2) – Two aliquots of the same sample taken in the laboratory and analyzed with identical procedures. An analysis of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

20.10 Laboratory Fortified Blank (LFB) – Also known as a LCSW or LCSS. An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

20.11 Laboratory Fortified Sample Matrix (LFM) – An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

20.12 Laboratory Reagent Blank (LRB) – An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

20.13 Linear Dynamic Range (LDR) – The concentration range where the instrument response to an analyte is linear.

20.14 Matrix – The predominant material of which the sample to be analyzed is composed.

20.15 Matrix Spike – An aliquot of the sample is spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given matrix.

20.16 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

20.17 MSDS – Material safety data sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs. The thrust of the law is to have those who make, distribute, and use hazardous materials responsible for effective communication.

20.18 PQL – The Practical quantitation limit (PQL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

20.19 Quality Control Sample (QCS) – Also known as ICV**:** A solution of method analytes of known concentrations, which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.

20.20 Relative Percent Difference (RPD) – To compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

20.21 Replicate – Repeated operation occurring within an analytical procedure. Two or more analyses for the same constituent in an extract of a single sample constitute replicate extract analyses.

20.22 RCRA – Resource Conservation and Recovery Act, PL 94-580. Found at 40 CFR 240-271. EPA has jurisdiction. Enacted November 21, 1976, and amended since. RCRA's major emphasis is the control of hazardous waste disposal. It controls all soil-waste disposal and encourages recycling and alternative energy sources.

20.23 Reagent Water – Water in which an interferent is not observed at or above the minimum quantitation limit of the parameters of interest.

20.24 Rounding Rules – If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by:

20.24.1 If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number.

20.24.2 If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

20.25 Sample Delivery Group (SDG) – Unit within a single case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a case, received over a period of up to 14 calendar days (7 calendar days for 14-day data turnaround contracts). Data from all samples in an SDG are due concurrently.

20.26 Stock Standard solution - A concentrated solution containing one or more method analytes prepared in the laboratory or purchased from a reputable commercial source.

20.27 Water Sample – For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

21.0 POLLUTION PREVENTION/WASTE MANAGEMENT

21.1 Refer to NEA168.SOP for instructions for pollution prevention.

21.2 Refer to NEA089.SOP and NEA054.SOP for instructions for the disposal of waste generated during the procedures previously mentioned.

22.0 DETECTION LIMIT

22.1 The most recent MDL studies and PQLs are maintained by the Quality Assurance unit and are available for review.

23.0 REFERENCES

23.1 "Determination of Total Organic carbon in sediment," Lloyd Kahn, U.S.E.P.A. Region II, Edison NJ 1988.

23.2 Application Note: TOC-011 "Analysis of sludges and solids for carbon," Tekmar-Dohrmann, Cincinnati, OH 10/95.

23.3 NYS-OH ELAP manual item #271.

APPENDIX 16

DRAFT

STANDARD OPERATING PROCEDURE FOR
Classification of Soils for Engineering Purposes
Applicable matrix or matrices:
Standard Compound List and Reporting Limits:

Approvals and Signatures

Laboratory Director: _____ Date: _____
Michael Wheeler Ph.D.

QA Manager: _____ Date: _____
Kirstin L. McC[illegible]ken

Organic Prep Manager: _____ Date _____
Jon K. Zygmuntowicz

1.0 SCOPE AND APPLICATION

This method describes a system for classifying mineral and organo-mineral soils for engineering purposes based on laboratory determination of particle size characteristics, liquid limit and plasticity index and is used when precise classification is required.

2.0 SUMMARY OF METHOD

This classification system identifies three major soil divisions: coarse grained soils, fine grained soils and highly organic soils. These three divisions are further subdivided into a total of 15 basic soil groups.

Based on the results of visual observations and prescribed laboratory tests a soil is catalogued according to the basic soil groups and thereby classified. The various soil groups have been devised to correlate in a general way with the engineering behaviors of soils.

3.0 DEFINITIONS

NA

4.0 INTERFERENCES

See laboratory SOPs LM-SL-D422, LM-SL-D854 and LM-SL-D4318.

5.0 SAFETY

5.1 The toxicity or carcinogenity of each chemical used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be minimized as reasonably possible. A reference file of Material Safety Data Sheets (MSDS) for this test method is available to all personnel and must be read prior to performing this procedure. All laboratory personnel must be familiar with the laboratory environmental health and safety plan described in the STL Corporate Safety Manual (CSM).

6.0 EQUIPMENT AND SUPPLIES

See laboratory SOPs LM-SL-D422, LM-SL-D854 and LM-SL-D4318.

7.0 REAGENTS AND STANDARDS

See laboratory SOPs LM-SL-D422, LM-SL-D854 and LM-SL-D4318.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT & STORAGE

See laboratory SOPs LM-SL-D422, LM-SL-D854 and LM-SL-D4318.

9.0 QUALITY CONTROL

See laboratory SOPs LM-SL-D422, LM-SL-D854 and LM-SL-D4318.

10.0 CALIBRATION & STANDARDIZATION

See laboratory SOPs LM-SL-D422, LM-SL-D854 and LM-SL-D4318.

11.0 PROCEDURE

11.1 Perform ASTM Methods D422, D854 and D4318.

11.2 The soil is an inorganic clay if the position of the plasticity index versus liquid limit plot, Fig. 3, falls on or above the "A" line, the plasticity index is greater than 4, and the presence of organic matter does not influence the liquid limit.

11.3 Classify the soils as a lean clay, CL, if the liquid limit is less than 50. See area identified as CL on Fig 3.

11.4 Classify the soils as a fat clay, CH, if the liquid limit is greater than 50. See area identified as CL on Fig 3.

11.5 Classify the soils as a silty clay, CL-ML, if the position of the plasticity index versus the liquid limit plot falls on or above the "A" line and the plasticity index is in the range of 4 to 7. See area identified as CL-ML on Fig 3.

11.6 The soil is an inorganic silt if the position of the plasticity index versus liquid limit plot, fig. 3, falls below the "A" line or the plasticity index is less then 4, and presence of organic matter does not influence the liquid limit.

11.7 Classify the soil as silt, ML, if the liquid limit is less than 50. See area identified as ML on Fig. 3

11.8 Classify the soil as an elastic silt, MH, if the liquid limit is 50 or greater. See area identified as ML on Fig. 3

11.9 The soil is an organic silt or clay if organic matter is present in sufficient amounts to influence the liquid limit.

11.10 If the soil has a dark color and an organic odor when warm and moist, a second liquid limit test should be performed on a test specimen that has been dried at 110°C +/- 5°C, to a constant weight.

11.11 The soil is an organic silt or clay if the liquid limit after oven drying is less than 75% of the liquid limit of the original specimen determined before oven drying.

11.12 Classify the soil as organic silt or clay, OL, if the liquid limit (not oven dried) is less than 50%. Classify the soil as an organic silt, OL, if the plasticity index is less than 4, or the position of the plasticity index versus liquid limit plot falls below the "A" line. Classify the soil as an organic clay, OL, if the plasticity index is 4 or greater and the position of the plasticity index versus the liquid limit plot falls on or above the "A" line. See the area identified as OL (or CL-ML) on Fig. 3.

11.13 Classify the soil as an organic clay or organic silt, OH, if the liquid limit (not oven dried) is 50 or greater. Classify the soil as an organic silt, OH, if the position of the plasticity index versus the liquid limit plot falls on or above the "A" line. See area identified as OH on Fig. 3.

11.14 If less than 30% but 15% or more of the sample is retained on the No. 200 sieve the words "with sand" or "with gravel" (whichever is predominant) shall be added to the group name.

11.15 If 30% or more of the sample is retained on the No. 200 sieve, the words "sandy" or "gravelly" shall be added to the group name. Add the word "sandy" if 30% or more of the test specimen is retained on the No. 200 and the coarse grained portion is predominately sand, likewise for gravel.

11.16 When more than 50% of the test specimen is retained on the No. 200 sieve classify the soil as gravel if more than 50% of the coarse fraction is retained on the No. 4 sieve. Classify the soil as sand if 50% or more of the coarse fraction passes the No. 4 sieve.

11.17 If 12% or less of the test specimen passes the No. 200 sieve, plot the cumulative particle size distribution and compute the coefficient of uniformity, Cu and coefficient of curvature, Cc, as given in equation 1 and 2.

$$Cu = D_{60}/D_{10} \qquad (1)$$
$$Cc = (D_{30})^2/(D_{10} \times D_{60}) \qquad (2)$$

where: D_{10}, D_{30} and D_{60} = the particle size diameters corresponding to 10, 30 and 60%, respectively, passing on the cumulative particle size distribution curve.

11.18 If less than 5% of the test specimen passes the No. 200 sieve, classify the soils as well graded gravel, GW, or well graded sand, SW, if Cu is greater thank or equal to 4.0 for gravel or greater than 6.0 for sand and Cc is at least 1.0 but not more than 3.0.

11.19 If less than 5% of the test specimen passes the No. 200 sieve, classify the soil as poorly graded gravel, GP, or poorly graded sand, SP, if either the Cu or the Cc criteria for well graded soils are not satisfied.

11.20 If 12% of the test specimen passes the No. 200 sieve, the soil shall be considered a coarse-grained soil with fines. The fines are determined to be either clayey or silty based on the plasticity index versus the liquid limit plot.

11.21 Classify the soil as clayey gravel, CG, or clayey sand, SC, if the fines are clayey, that is, the position of the plasticity index versus liquid limit plot falls on or above the "A" line and the plasticity index is greater than 7.

11.22 Classify the soil as a silty gravel, GM, or silty sand, SM, if the fines are silty, that is, the position of the plasticity index versus liquid limit plot falls below the "A" line and the plasticity index is less than 4.

11.23 If the fines plot as a silty clay, CL-ML, classify the soil as a silty, clayey gravel, GC-GM, if it is a gravel or a silty, clayey sand, SC-MC, if it is sand.

11.24 If 5 to 12% of the test specimen passes the No. 200 sieve, give the soil a dual classification using two group symbols. The first group of symbols shall correspond to that for a gravel or sand having less than 5% fines (GW, GP, SW, SP) and the second symbol shall correspond to a gravel or sand having more than 12% fines (GC, GM, SC, SM).

11.25 The group name shall correspond t the first group symbol plus "with clay", or "with silt" to indicate the plasticity characteristics of the fines.

11.26 If the specimen is predominantly sand or gravel but contains 15% or more of the other coarse grained constituent, the words, "with gravel" or "with sand" shall be added to the group name.

11.27 If the field sample contains any cobbles or boulders or both the words "with cobbles" or "with boulders" shall be added to the group names.

12.0 CALCULATIONS

12.1 Compute the coefficient of uniformity, Cu and coefficient of curvature, Cc, as given in equation 1 and 2.

$$Cu = D_{60}/D_{10} \qquad (1)$$
$$Cc = (D_{30})^2/(D_{10} \times D_{60}) \qquad (2)$$

where: D_{10}, D_{30} and D_{60} = the particle size diameters corresponding to 10, 30 and 60%, respectively, passing on the cumulative particle size distribution curve.

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

See laboratory SOPs LM-SL-D422, LM-SL-D854 and LM-SL-D4318.

14.0 METHOD PERFORMANCE

14.1 An Initial Demonstration of Capability is required for each analyst before unsupervised performance of this method.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 The laboratory optimizes technology to minimize pollution and reduce the production of hazardous waste whenever possible.

15.2 The laboratory procedures for waste management comply with applicable federal, state and local regulations and are described in SOP LP-LB-001HAZWD.

16.0 REFERENCES

16.1 Annual Book of ASTM Standards, volume 04.08 Soil and Rock (I): D 420 - D4914, Section 4, Construction edition; American Society for Testing and Materials, Philadelphia, Pa., 1994.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

NA

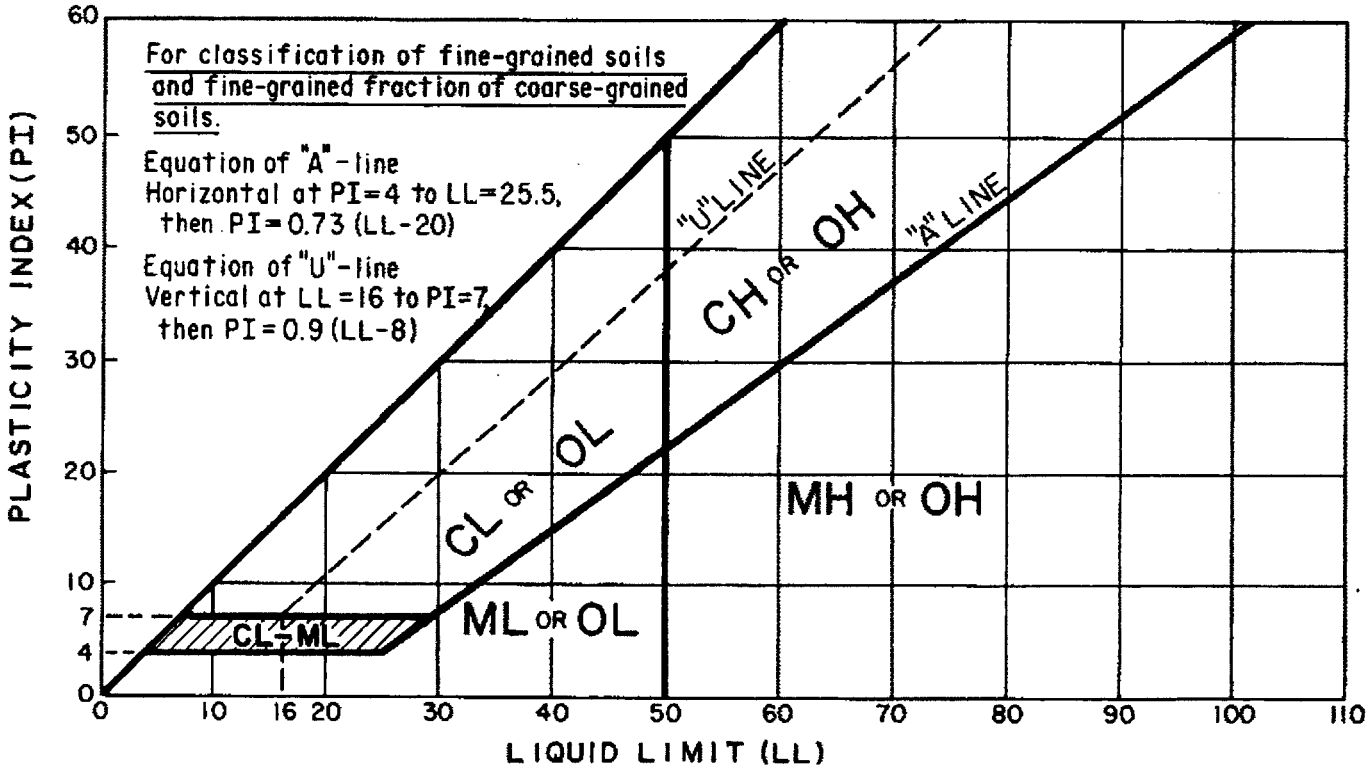
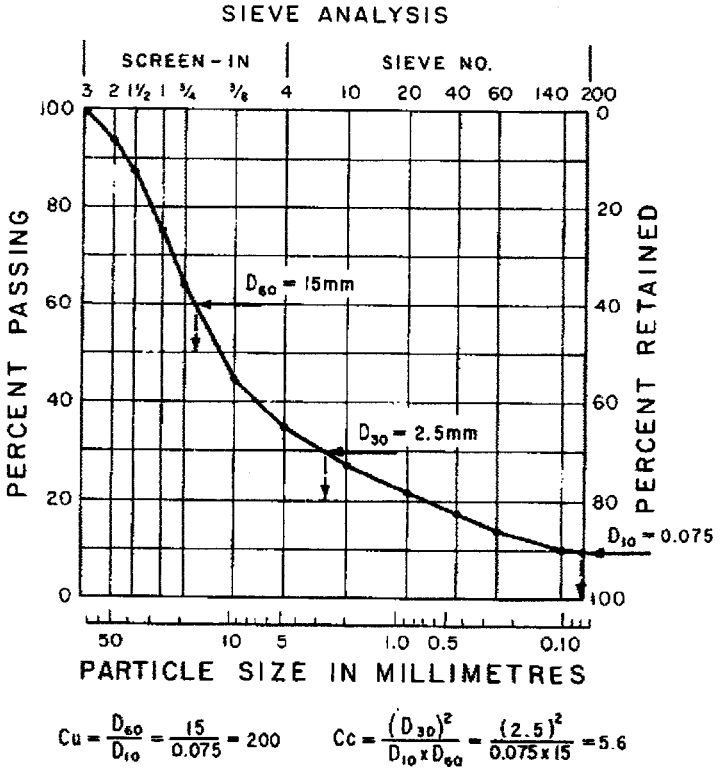


FIG. 3 Plasticity Chart



$$Cu = \frac{D_{60}}{D_{10}} = \frac{15}{0.075} = 200 \qquad Cc = \frac{(D_{30})^2}{D_{10} \times D_{60}} = \frac{(2.5)^2}{0.075 \times 15} = 5.6$$

FIG. 4 Cumulative Particle-Size Plot

GP, or *poorly graded sand,* SP, if either the Cu or the Cc criteria for well-graded soils are not satisfied.

12.4 If more than 12 % of the test specimen passes the No. 200 (75-μm) sieve, the soil shall be considered a coarse-grained soil with fines. The fines are determined to be either clayey or silty based on the plasticity index versus liquid limit plot on Fig. 3. (See 9.8.2.1 if insufficient material available for testing). (See Note 6)

APPENDIX 17

(The attached SOP includes Attachment A: *Ocean Surveys, Inc. Manual of Standard Operating Procedures.* This attachment contains SOPs for the operation and calibration of navigational and geophysical survey instrumentation. Not all of the SOPs included in this attachment apply to the Side Scan Sonar Survey SOP.)

STANDARD OPERATING PROCEDURE FOR SIDE SCAN SONAR SURVEYS

1. Side scan sonar activities will occur over a two to three week period on the upper Hudson River from Rogers Island to Federal Dam in Troy. Since this is a well-traveled navigational channel, the work will be coordinated with the Canal Corporation, as required by the Health and Safety Plan and the Community Health and Safety Plan. In addition, the sampling vessels will maintain contact with the Canal Corporation using marine band channel 13.

2. The side scan sonar survey will utilize GPS receivers (Trimble 7400 MSi) to acquire navigation data using shore-based reference stations with known coordinates and elevations. Differential correctors determined at these stations will be transmitted to the survey vessel where they will be used by the onboard receiver using Real Time Kinematic OTF software to determine the accurate position of the GPS antenna in the vertical and horizontal planes. These data will be logged on board at one-second intervals for the duration of the survey. Data quality parameters will also be logged and monitored by the onboard navigator with flags put on all data points which do not meet the quality limits set. The specified accuracy for this system is +/- 2 cm when satellite configuration is sufficient.

3. Before leaving dock, the side scan survey crew will check to make sure all navigation and instrument systems are working properly. Calibrate and set navigation instruments based on the instrument-specific standard operating procedures (Attachment A). Prepare survey equipment for start of daily survey operations including: deployment of side scan sonar tow fish into water, measurement of survey equipment offsets, daily speed of sound test, and other required pre-survey activities.

4. Navigate to coordinates of first transect. Transect coordinates and headings – the trackline -should be based, wherever possible, such that the vessel intersects as many Sediment Sampling and Analysis Program (SSAP) coring locations as possible during side scan sonar survey. SSAP sediment coring coordinates will be provided to the side scan sonar crew for import into the navigation computer. A Coastal Oceanographics "Hypack Max" will be used for trackline design, navigation, trackline control, and digital depth and RTK DGPS data logging.

5. Align survey vessel along longitudinal transect and confirm autopilot heading and operation. Start data acquisition and commence side scan sonar survey along transect. Conduct the side scan sonar survey using a high resolution side scan sonar system (Klein Model 595) with a dual frequency (100 and 500 kHz) tow fish. Export and log the side scan sonar imagery to the ISIS data acquisition platform. Enter all system annotations in the ISIS XTF notes field.

6. Use a digital depth sounder to collect water depth information along each transect. Log depth data to the Hypack Max system.

7. During the survey, perform periodic manual probing and visual characterization of sediments. Note coordinates and results of probing or characterization in the field log. Note coordinates of areas that may need additional confirmatory sampling and sediment grain size analysis to ground-truth the side scan sonar data in the field log.

8. Note relevant observations and changes in operational procedures to the field log. These may include: coordinates of observed obstructions or artifacts; areas where interferences or other conditions limit survey resolution or prevent bank-to-bank coverage; and coordinates

where adjustments to tow fish height, line spacing, or range scale are made.

9. At the end of each transect, confirm successful data acquisition and storage, navigation and equipment calibrations and settings. Log time and coordinates at end of each transect line surveyed.

10. Prepare equipment for navigation to next transect; navigate to next transect.

11. Repeat steps 4-10 for collecting data along a transect until bank-to-bank coverage has been achieved in each survey section. A line spacing of no more than 250 ft should be used and at least two transects – one on either side of the river – should intersect numerous SSAP sediment coring locations. Above and below dams, survey bank-to-bank along a lateral transect maintaining a safe operating distance (as determined by boat operator) from the dam and cautionary buoys

12. All raw survey data and information (e.g., field notes, instrumentation frequencies) must be documented electronically or in a field note book. At the end of each day, check daily computer data from the Hypack Max and ISIS systems for error flags. Output all notes to an ASCII file and store with the raw records. Back-up copies of the raw electronic data and make copies of all field log entries.

ATTACHMENT A

OCEAN SURVEYS, INC.
MANUAL OF
STANDARD OPERATING PROCEDURES

(Geophysical Survey Instruments)

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

1.0 INITIAL EQUIPMENT SETUP

This is a draft document. The most recent modification was on 07/31/02 by MLK. New versions will be distributed as they are created.

There are presently several documents that are associated with this that are not included at this time.

1 Caris offset drawing
2 Hypack offset drawing
3 System wiring document
4 System comm. Port settings and data formats

1.1 General Tasks Before Start of Survey

- Notify GE of vessel movement
- Obtain permits for movement through and between locks
- Obtain proper charts and update with all Notice to Mariners
- Verify availability of CG DGPS correctors and RTK stations
- Document equipment installation
    - Establish Boat 0,0,0
        - Vessel fore/aft centerline, aft edge of athwart ship I-Beam on A-Frame, point on aft deck slightly above waterline
    - Measure and record all offsets
        - Trimble 7400 MSi DGPS's
            - Navigation antenna X, Y, Z
            - Reference antenna X, Y, Z
        - Trimble 7400 RTK GPS
            - Antenna to waterline
            - X & Y to boat 0,0
        - Innerspace 448 X, Y, Z
        - TSS DMS 2i-05
            - X, Y, Z
            - Zero out mounting angles with appropriate vessel loading – see procedure in TSS section
        - Robertson Compass
            - X, Y

- Align to true heading of vessel centerline – see procedure in Compass section

- Sidescan Tow Point X, Y, - Z left at 0.0 m for proper Caris import of layback

- Subbottom Profiler Tow Point X, Y, - Z left at 0.0 m for proper Hypack import of layback

1.2 Equipment Setup

1.2.1 Trimble 7400 Receiver

- Initial Settings
  - RTCM Output = off
  - RTCM Input
    - Inputs ON
    - Port = 2
    - Format = USCG
    - ASCII Printout off
    - Beeper Off
    - Station = any
    - Age Limit 20 sec.
    - Integrity Monitor Off
  - Power Up Control
    - Do not default controls at power up
  - SV Enable/Disable
    - Disabled mode = none
  - Adjust local time
    - Time offset EDT-UTC = -4 hrs
    - Time Zone Identifier = EDT
  - Baud Rate Format
    - Port 1 = 9600-N-8-1
    - Port 2 = 9600-N-8-1
  - Remote Protocol
    - Data Collector Compatible
  - Reference Position
    - Lat = 35 50 40.91718
    - Lon = 075 39 19.57021
    - Height = -37.529

        - (Note, may be changed during survey by selecting **HERE** to get local position and current ellipsoid height for Lat/Lon – Fixed height)
      - Masks/Sync Time
        - Elevation Mask = 8
        - PDOP Mask = 5
        - SV Sync Time = 1.0
      - Positioning Modes
        - Weighted solution enabled
      - Lat/Lon Height Always
  - Power Controls
    - Charger and Power output disabled
  - NMEA 183 Output
    - Port 1 Enabled
      - GGA, VTG, ZDA
  - Cycle Printouts = Off
  - 1 pps output = disabled
  - Default controls – **DO NOT USE!!! RESETS TO FACTORY**
  - Modify
    - Units of Measure
      - Lat/Lon Degrees = Deg.Min.Sec.
      - Time = 24 Hr UTC
      - Position = WGS-84 LLH
    - Altitude Reference
      - Height above ellipsoid

1.2.2 MX-51 Beacon Receivers

- Initial Settings - DGPS1

  - **HUDSON FALLS, NY**
    Status: Operational
    RBn Antenna Location: 43° 16.21' N73° 32.31' W
    REFSTA Ant Location (A): 43° 16.2491' N73° 32.34705' W
    REFSTA Ant Location (B): 43° 16.2637' N73° 32.34534' W
    REFSTA RTCM SC-104 ID (A): 94
    REFSTA RTCM SC-104 ID (B): 95
    REFSTA FIRMWARE VERSION: RD00-1C19
    Broadcast Site ID: 844
    Transmission Frequency: 324 KHZ
    Transmission Rate: 200 BPS
    Signal Strength: 100uV/m at 135NM

- CTToolbox should be used to reload H11032R.CNF (config file) if necessary. The following settings are in H11032R.CNF
    - CONTROL/BASE STATION
        - Input using **HERE** at Hudson Falls
        - LAT 35 50 40.77420
        - LON 075 39 19.81768
        - HGT – 0035.870
        - ANT Height 000.000
    - CONTROL/SV ENABLE/DISABLE
        - ALL – ENABLE
    - CONTROL/GENERAL CONTROLS
        - ELEV. MASK: 08
        - PDOP MASK : 05
        - MEAS RATE 1 HZ
        - MOTION: KINEMATIC
    - CONTROL/POWER CHARGER
        - POWER OUTPUT MODE DISABLED
    - CONTROL 1PPS OUTPUT
        - 1 PPS OFF
        - ASCII TIME TAG PORT OFF
    - CONTROL SERIAL PORT OUTPUT
        - NMEA/ASCII OUTPUT
        - GGK
            - PORT 2
            - 1 HZ
        - ZDA
            - PORT 2
            - 1 HZ
        - All others off
    - STREAMED OUTPUT
        - ALL OFF
    - RT17/BINARY OUTPUT
        - ALL OFF
    - CMR/RTCM
        - BASE – MOVING
        - CMR PORT – OFF
        - NAME - cref
        - RTCM PORT – OFF
        - TYPE - 1
    - CONTROL/SERIAL PORT SETUP
        - PORT1 9600 8-NONE-1
        - PORT 2 9600 8-NONE-1 NONE

- PORT 3 9600 8-NONE-1
- PORT 4 9600 8-NONE-1 NONE
- CONTROL/INPUT SETUP
  - USE RTCM STATION – ANY
  - RTK/DGPS AUTO SWITCH RANGE – 20.0 KM

1.2.3 Compass

- Initial Calibration Procedure
  - Load vessel, as it will be for survey ops. Remove any large ferrous objects from the vicinity of the compass.
  - Position the vessel in open water
  - Apply power to the Robertson autopilot
  - Begin by turning the vessel to starboard.
  - Select **INSTALLATION/RFC COMP calibration**.
  - Calibration should complete after ~ 1 ¼ turns and should be verified by a display of **Calibration confirmed**.
- Determine and apply Compass Offset
  - Con the vessel on a straight line while observing the heading computed by the GPS system.
  - Adjust the offset by turning the autopilot knob to match the pilot compass heading to the gps heading. Note the applied offset. (This puts the pilot compass into "TRUE" heading.)

1.2.4 TSS DMS 2i-05

- Initial Settings
  - Set baud rate/format to 19200,N, 8,1
  - Heave bandwidth = SHORT
  - Output Rate = 50 hz.
  - GPS data input settings = NMEA Local 9600, 8, N, 1
    - Check GPS RAW and CALCULATED input
  - GYRO data input settings = NMEA Local 4800, 8, N, 1
    - Check Compass RAW & CALCULATED INPUTS
  - Data output format = TSS1 19200, 8, N, 1
  - Zero out mounting angles. Document mounting angles with screen grab.
    - Stabilize vessel with static loads approximating those that will be experienced during the survey.
    - Access TSS through communication program and set mount angles automatically by averaging data for 5 minutes
    - Accept values and screen grab settings

Restart TSS operation and exit from program

Mount Angle Setting Recorded
06/04/02

```
---------------------------------
DMS 2-05 Version 2.03 Terminal Mode
---------------------------------
Sensor Mounting

Orientation : Vertical
Roll  Mount Angle [  1.741  deg] :
Pitch Mount Angle [  1.711  deg] :
Yaw Mount Angle [  0.000  deg] :
```

- **Do Not Change These Settings!**

•

1.2.5 Innerspace 448

- Initial Settings
  - Verify the following initial settings
    - Gain = Approx. 10 o'clock setting
    - Range = 0-15 M
    - Mode = Meters
    - Chart Speed = 4
    - Range Multiplier = X1
    - Input default speed of sound of 1500 m/s
    - Set draft = 0.0
    - Tide = 0
    - Initial = 5
    - Gate = 2
    - Mode = Gated
    - Reply = 16
    - Alarm on during survey
    - Set variable power TX board to Low, to limit interference with SS and MB
    - Set internal TVG curve switch to open/open or +60 db. This was needed to receive quality data at the above mentioned low power setting with our combination of components
    - Set date & time – See back of paper carrier
    - Load paper per picture on back of paper door
      -

1.2.6 Klein 595

- Initial Recorder Setup

- Set system to factory defaults by pushing left button on the CPU board
    - This resets all values to factory default
    - It also resets all gain curves and other "adaptive controls prior to calibration
        - A calibration should be preformed, per the manuals description any time a component is changed, like a cable or fish
  - Set time/date in submenu
    - Add "*" to time and date to print it when an event is pressed. This can be used to log tuning changes and rub tests
  - Set system to the following values:
    - Auto CPU
        - Altitude = 0,0
        - Return = 0
        - Offset = 2
    - Auto TVG Port
        - Normal
        - Atten. = 9
        - Salt Water
    - Auto TVG Starboard
        - Normal
        - Atten = 9
        - Salt water
    - Printer = Off
    - Range = 25 Add "*" to field
    - Scale lines = 10 Add "*" to field
    - Source = Fish
    - Channel = 1 | 2
    - Speed = Manual –1.0 Set to avoid alarms
    - Altitude = Auto
    - Mapping Mode = Off
    - Altitude Alarm = Off
    - Auto Mark = Off
    - Event Count = Off
    - Event Mark = Off
    - Side Scan Expand = Off
    - Profiler Expand = Off
    - Nav Source = Nav3* - used for external Eventing option

- Follow the calibration found in the operations manual on 3-34 to tune for site conditions
- Document tune-up settings in SSS annotations
- Document tow configuration and Cable out in SSS annotations
    - Tow Point
        - See attached drawing for exact location
        - The tow point is a sheave mounted to a bowsprit. In operation the fish is lowered to1meter in the water as the vessel is moving at survey speed.
        - The cable is fair leaded back to the stern on the outside of the bowsprit mount. Cable out measurement is taken from the point of the sheave closest to the mount point
        - The layback was measured by observing the fish under survey conditions and measuring from the center of the xducers to the tow point.
        - Document any changes made to the recorder online in the Isis notes section
- Initial Fish Setup
    - Depression angle = 20 degree's
    - 500 KHz only
    - 100 KHz disabled in fish – SCR trigger is disconnected.
    - Attach depressor to fish

- Internal Jumpers
    - A/D board jumpers should be set to reflect proper software version (checked 050202)
    - Fish Tape I/O jumper should be set to either 15v for short cable or 24v for long cable (winch) (checked 05/2/02 set to 15v)
    - Verify which channel is tracking altitude on the Connector interface board

1.2.7 Bar Check

- Initial Setup and Calibration
    - Determine maximum depth of survey and depth units
        - Sheet A maximum depth is in the 10 meter range
        - Survey depth units are meters
    - Construct Bar Check per OSI standards
    - Type 1
        - .2 meter diameter lead disk with eye bolt
        - Imprint a "serial number" onto bar
            - "A"

        - "B"
    - Coated aircraft cable
    - Brass marker beads at appropriate intervals
        - Minimum of every 1 meter throughout the survey depths
        - This is to allow use of a "pocket rod" to read inter bead values
    - Also mark cable on both sides of bead with a "sharpie" to help identify bead slips
    - Measure bead locations with steel tape to the nearest 0.01 meter increment
    - Record bar s/n and all other information required on OSI Lead Line Calibration form
  - Recalibration
    - Recalibrate Bar Check every 6 months, or after any action that could possibly affect the condition of the Bar Check, such as snagging line on bottom.
    - Recalibrate at the completion of the survey
  - Maintenance
    - Periodically examine the eye bolts and cables

- Type II
    - Aluminum square-beam > width of boat with target at position of in hull xducer
    - Imprint a "serial number" onto bar
    - Coated aircraft cable
    - Brass marker beads at appropriate intervals
    - Minimum of every 1 meter throughout the survey depths
        - This is to allow use of a "pocket rod" to read inter bead values
    - Also mark cable on both sides of bead with a "sharpie" to help identify bead slips
    - Measure bead locations with steel tape to the nearest 0.01 meter increment
    - Record bar s/n and all other information required on OSI Lead Line Calibration form
  - Recalibration
    - Recalibrate Bar Check every 6 months, or after any action that could possibly affect the condition of the Bar Check, such as snagging line on bottom.
    - Recalibrate at the completion of the survey
  - Maintenance

- Periodically examine the eye bolts and cables

1.2.8 GE 1 Computer System

- Start Up
  - Verify DC Mains and Autopilot are off before powering up, or logging onto, system
  - Log on using default Logon
    - User Name osiuser
    - Password (blank)
- Verify time zone is set to (GMT) Greenwich Mean Time: Dublin, Edinburgh, Lisbon, London.
- DO NOT CHECK "Automatically adjust clock for daylight savings time.

- Start HyPack MAX with appropriate shortcut
  - Open new project named GE-1
    - Create folders in the project folder named DATA1
    - Set geodesy to UTM Zone 18 WGS 84
    - HYPACK HARDWARE SETUP
      - New File
      - NAV - NMEA183.DLL
        - Name = DGPS1
        - Update Frequency = 50ms
        - Type
          - Position
        - Options
          - Record raw data
          - Record quality data
        - Record
          - Always
        - Connect
          - Serial Port
            - COM3, 9600,8,none, 1,Flow Control = none
        - Offsets
          - Starboard = -.35
          - Forward = + .23
          - Height = +1.97
          - Latency = 0.860
        - Setup
          - Standard NMEA 0183 sentences to be used

            - GGA
        - HDOP Limit = 2.5
        - Minimum Satellites = 4
        - Use ZDA message for time tag = Disabled
        - Send alarm when non differential
- Depth – Innerspace 448 {Serial} - IN448.DLL
    - Name = 448
    - Update Frequency = 50
    - Type
        - Echo sounder
    - Options
        - Record raw data
        - Record quality data
        - Paper Annotation
    - Record
        - Always
    - Connect
        - Serial Port
            - COM6, 9600,8,none, 1
    - Offsets
        - Starboard = 0.0
        - Forward = 0.0
        - Height = +.8 NOTE!!! .8 meters used as "display offset". See Draft explanation
        - Latency = 0.000
    - Setup
        - Send annotation string with event mark
        - Multiply not needed
- Auto Pilot Compass – NMEA.DLL
    - Name = AP Compass
    - Update Frequency = 50
    - Type
        - Heading
    - Options
        - Record raw data
        - Record quality data
    - Record
        - Always
    - Connect
        - Serial Port
            - COM5, 4800,8,none, 1

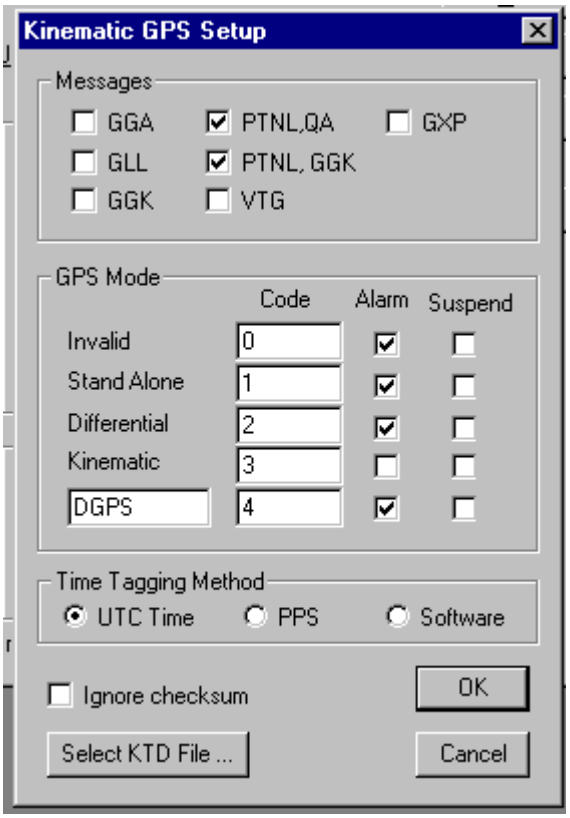
    - Offsets
        - All zero
    - Setup
        - Sentence to be used
- HDG
- Auto Pilot – NMEA.DLL
    - Name = AP XTE
    - Update Frequency = 500
    - Type
        - Output
    - Options
        - Record raw data
        - Record quality data
    - Record
        - Always
    - Connect
        - Serial Port
            - COM8, 4800,8,none, 1
    - Offsets
        - All zero
    - Setup
        - Sentence to be used
- GGA
    - Sentence to generate
    - APB
    - GLL output places = 4
    - XTE (Nautical Miles) checked
    - Output to hundredth decimal place = Enabled
    - XTE Factor = 0.0

- File Server – Delph Output – DELPH.DLL
    - Name = Isis Out
    - Update Frequency = 20000
    - Type
        - (nothing checked)
    - Options
        - Record raw data
        - Record quality data
        - Paper Annotation
    - Record
        - Always
    - Connect
        - Serial Port

        - COM7, 9600,8,none, 1
    - Offsets
        - All Zero

- TSS DMS2i-05 – TSS320.DLL
    - Name = DMS2i-05
    - Update Frequency = 50
    - Type
        - Heave Compensator
        - Other
    - Options
        - Record raw data
        - Record quality data
        - Paper Annotation
    - Setup
        - Motion reference Unit Only
    - Connect
        - COM 1 19200,8,N, 1
    - Record
        - Always
    - Offsets
        - Position
        - Starboard = -.44
        - Forward = +.47
        - Vertical = -.18
        - Yaw = 0
        - Pitch = 0
        - Roll =0
        - Latency =0

- Trimble 7400 RTK OTF - KINEMATIC1.DLL
    - Name – RTK
    - Type
        - Position
        - Echosounder
        - Sync. Clock
        - Tide Gauge
    - Record RAW
    - Record Quality
    - Setup



- SELECT KTD FILE
  - File 02ES007.KTD used for survey ops

- Connect
  - COM2 9600,8,N, 1, Flow Control = none
- Offsets
  - Position
  - Starboard = -1.50
  - Forward = +.25
  - Vertical = + 2.05
  - Yaw = 0
  - Pitch = 0
  - Roll =0
  - Latency =0
- Record
  - Always

- Create a second mobile named RTK. Transfer the RTK device to the second mobile

- URS-1 – VHW.DLL
  - Name = Speedlog
  - Update Frequency = 200
  - Type
    - Speed
    - Other
  - Options
    - Record raw data
    - Record quality data
  - Setup
    - none
  - Connect
    - COM 9 4800,8,N, 1, Flow Control = none
  - Record
    - Always
  - Offsets
    - None
- Settlement – DraftTable.dll
  - Name = Settlement
  - Update frequency = 100
  - Type
    - Draft
  - Setup
    - Create Draft table from Settlement and Squat test
    - Insert Draft table picture – set to 0.0 for squat test
  - Offsets
    - None
  - Connect
    - Ignored
  - Record
    - Always

1.2.9 GE-1 CARRIS OFFSETS to BOAT

DGPS1 (NMEA183.DLL)

STBD	+1.18
FWD	+0.02
Height	+1.97
Latency	+0.00

448 (INN448.DLL)

STBD	+1.53

FWD	-0.21
Height	+0.80
Latency	+0.00

Auto Pilot Compass (NEMA.DLL)

STBD	+0.00
FWD	+0.00
Height	+0.00
Latency	+0.00

Isis Output (DELPH.DLL)

STBD	+0.00
FWD	+0.00
Height	+0.00
Latency	+0.00

Auto Pilot (NEMA.DLL)

STBD	+0.00
FWD	+0.00
Height	+0.00
Latency	+0.00

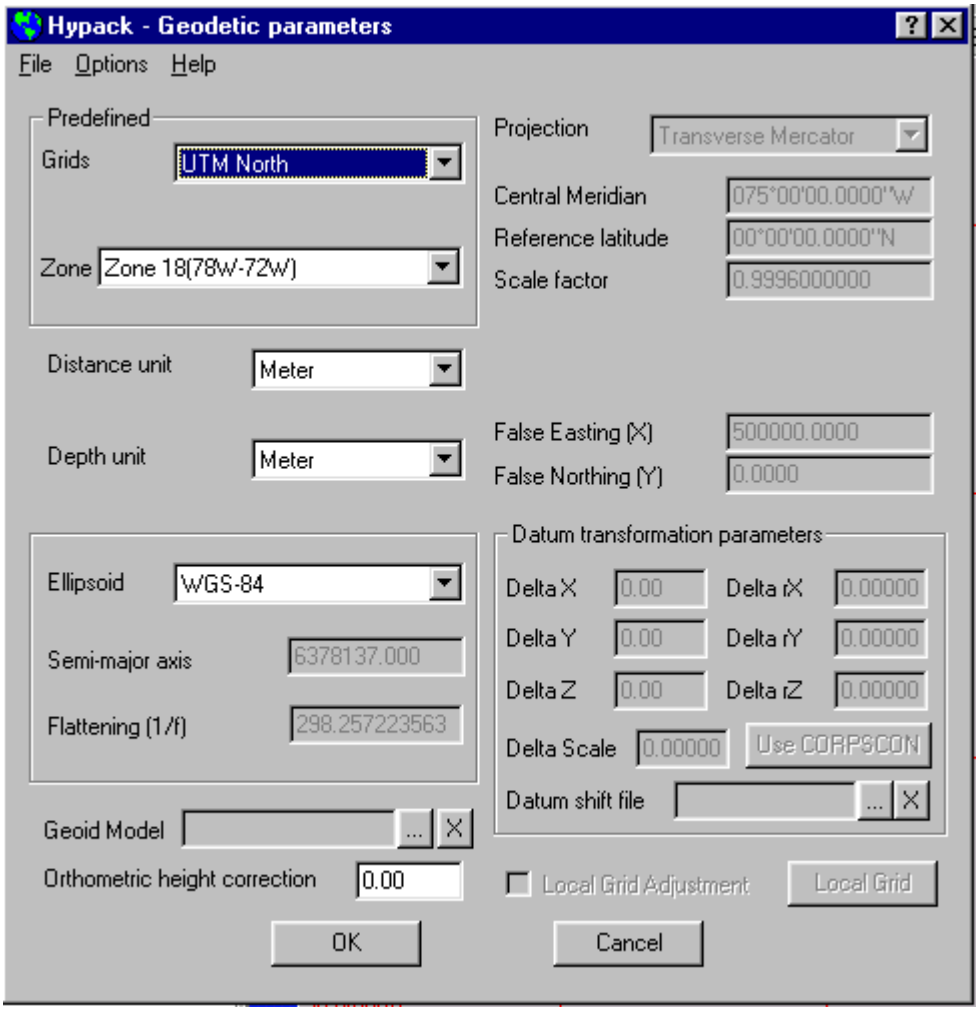
DMS 2i-05 (TSS 320.DLL)

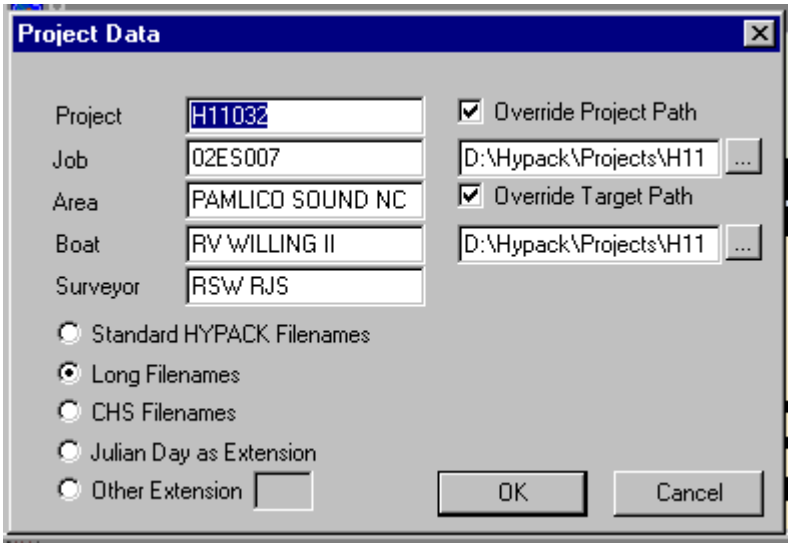
STBD	+1.09
FWD	+0.26
Height	-0.18
Latency	+0.00

RTK GPS_KINEMATIC.DLL

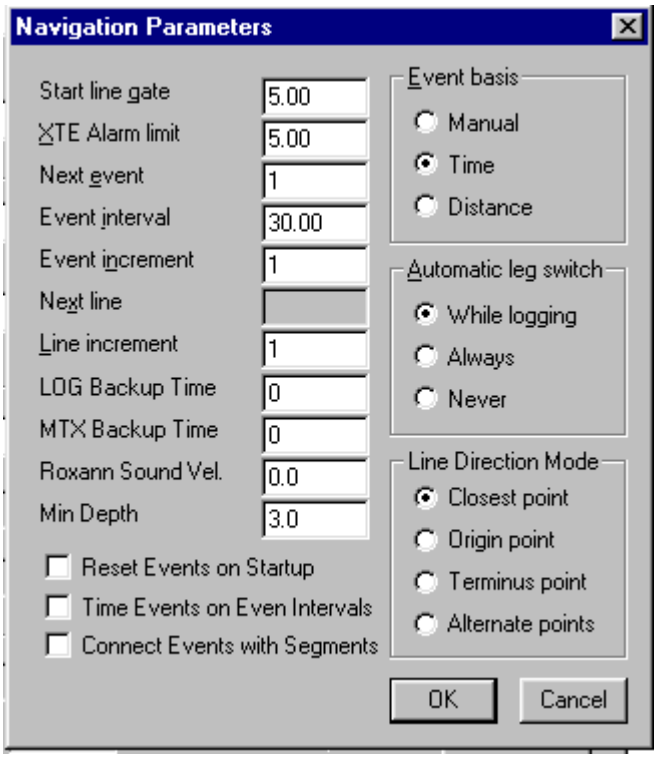
STBD	+0.03
FWD	+0.02
Height	+2.05
Latency	+0.00

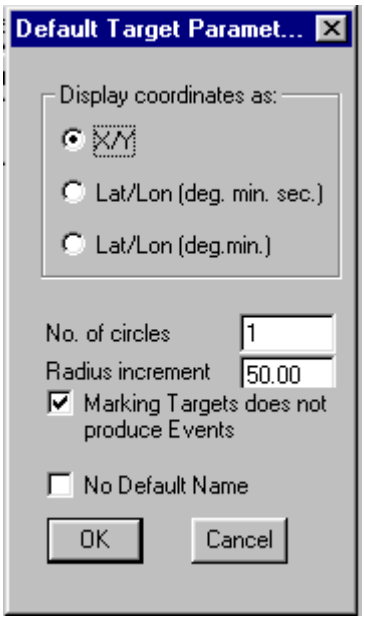
1.2.10 Other Hypack Max Settings


Hypack - Geodetic parameters
File Options Help
Predefined
Grids
UTM North
Zone
Zone 18(78W-72W)
Projection
Transverse Mercator
Central Meridian
075°00'00.0000"W
Reference latitude
00°00'00.0000"N
Scale factor
0.9996000000
Distance unit
Meter
Depth unit
Meter
False Easting (X)
500000.0000
False Northing (Y)
0.0000
Ellipsoid
WGS-84
Semi-major axis
6378137.000
Flattening (1/f)
298.257223563
Datum transformation parameters
Delta X
0.00
Delta rX
0.00000
Delta Y
0.00
Delta rY
0.00000
Delta Z
0.00
Delta rZ
0.00000
Delta Scale
0.00000
Use CORPSCON
Datum shift file
Geoid Model
Orthometric height correction
0.00
Local Grid Adjustment
Local Grid
OK
Cancel


Project Data
Project
H11032
Job
02ES007
Area
PAMLICO SOUND NC
Boat
RV WILLING II
Surveyor
RSW RJS
Override Project Path
D:\Hypack\Projects\H11
Override Target Path
D:\Hypack\Projects\H11
Standard HYPACK Filenames
Long Filenames
CHS Filenames
Julian Day as Extension
Other Extension
OK
Cancel

NOTE: XTE ALARM set to 100000 for Sea Trials





- **1.2.11 ISIS**

o Start Up

- Verify DC Mains and Autopilot are off before powering up, or logging onto, system. Note: if monitor does not come on (yellow power/signal indicator steady yellow on lower right corner of monitor) remove power from monitor for a few seconds, then restore and turn on monitor.

- Start Isis with Isis H11032 shortcut – **Only**
  - This calls up a specific configuration file

- File types and locations
  - H11032 ISIS Short Cut to Start Isis Desktop
  - H11032.LAY Window Layout E:\H11032 ISIS\H11032 Config\
  - H11032_140.CFG Isis configuration file D:\TEI\IsisSona\v5.91\
  - Survey. log Isis session log D:\root
    - Note: unable to redirect this file

- Initial Processor Settings
  - File Menu
    - Playback N/A
    - Record Setup
      - Sonar Setup
        - Pick standard analog
        - Select CHICO/CHICO PLUS Board
          - Channel 1 edit
            - Status = On
            - Name = Port
            - Type = Port SSS
            - Trigger = 1
          - Channel 2 edit
            - Status = On
            - Name = Stbd
            - Type = Starboard SSS
            - Trigger = 1
          - All other channels disabled
          - Sonar name to H11032 Klein 595 2 CH 500Khz
          - Frequency = 384.0,384.0
          - Horizontal Beam Angle = 0.2,0.2
          - Beam Width = 50.0, 50.0
          - Tilt angle = 20.0, 20.0
          - Name of server = ISISCHICO.EXE
          - Automatic control disabled
      - Serial Port 1 Heave, Pitch, Roll
        - Status = On

- Settings = 19200, 8, N, 1
- Template = TSS
- Convert Lat - Long = Disabled
- Filter Speed = Disabled
- Navigation Latency = 0.0

- Serial Port 2 Not used
- Serial Port 3 GPS for SSS
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = NMEA0183 NOCLOCK
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 4 GPS for Single Beam
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = NMEA0183
    - NMEA0183 SHIPPOS NOVTG
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 5 Compass
  - Status = On
  - Settings = 4800, 8, N, 1
  - Template = NMEA0183 NOCLOCK NORMC NOGLL NOVTG
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 6 May be used for Fish Altitude input
  - Better Tuning Has Made This Option Unused
    - Manual SSS Bottom Tracking Option
  - Status = Off
  - Settings = 9600 8, N, 1
  - Template = Manual
    - Modify Default = {/100}{-1.3}7
      - Change 1.3 to value needed to get correct altitude
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0

- Serial Port 7 Hypack feed for Line Control
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = (Leave Blank)
    - Allows events and start/stop info in from Hypack
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
- Serial Port 8 448 feed to Aux Sensor 1
  - Status = On
  - Settings = 9600, 8, N, 1
  - Template = Manual
    - Modify Default = {/100}1
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0
  - Serial Port 9 RTK INPUT
- Serial Port 10 Speed Log
  - Status = On
  - Settings = 4800, 8, N, 1
  - Template = {pattern=m}s
  - Convert Lat - Long = Disabled
  - Filter Speed = Disabled
  - Navigation Latency = 0.0

- File Format
  - Format = XTF
  - Media = Disable
  - Sample Size to Record = 16 bit
  - Samples per Channel = 1024
  - Processing Method = MAX
  - XTF File Header Notes
    - Vessel Name
    - Survey Area
    - Operator

- Configure
  - Playback Speed – as desired
    - Real Time Scrolling
      - Scroll without restoring covered data
        - This keeps system from locking up
    - Transducer Depth = 0.0
    - Ocean Tide

        - Apply Corrector = Disabled
        - Verify = 0.0
    - Sound Velocity = Average from first cast of the day
    - Multiple Pings = 1
    - Hypack DDE
        - Accept from Hypack = Disable All
        - Automatically Start Saving At Start of Line
            - Use File Name from Hypack = Enable
            - Generate File Names = Disable
            - Start Each File with = Enter Daily Directory Info
    - Cue Boxed = Disabled
    - Set Date and Time = Ignore – Will be automatically set during operation
    - Save Setup = Prompt User at Exit

- Color
    - Palette
        - SSS Colors = Grey Scale
        - Squelch = 0.0
        - Reverse Palette = Enabled
        - Strong Returns Red = Disabled
    - Grid Color
        - Voltage Grid
            - Line = Blue
            - Data = White
            - Dim = Both Enabled
        - Scale Lines Red

- View
    - Scale Lines
        - Apply Settings to = All the same
        - Scale line Unit = Distance
            - Spacing = 10
    - Depth Delay and Duration
        - Apply Settings to = All the same
        - Units = Off
    - Overlay
        - Show on Waterfall
            - Event Marks = Disabled
            - Event Text = Disabled
            - Bottom Track = Enable
        - Bookmarks

- Save Bookmarks = Enabled
- Display Bookmarks = Enabled

- Down Sample = Max
- Speed
  - Automatic = Enabled
  - Filter = Disabled
- Heading = Automatic
- Layback Correction
  - Apply Delta XY = Disabled
  - Apply Layback = Enable
    - Use Logged Layback = Disabled
    - Enter layback manually = Enabled
    - Compute layback from Cable Out = Disabled
    - Enter layback value in box provided (Currently 1.0M)
      - This field with be empty, enter value
        - Obtain value from chart
      - Click ACCEPT, current value changes to entry
      - NOTE: **DO NOT CLOSE WINDOW**
      - NOTE: CHECK AT START OF EACH LINE
      - NOTE: HAVE OPEN DURING CONTACT PICKING

- Tools
  - Target Setup
    - TargetPro.exe only
  - Target Setup
    - Height = 512
    - Width = 2048
    -
  - Target
    - File
      - **Set working Directory = Enter Daily Data Directory**
    - Tools
      - Configuration
      - Speed auto
      - Speed Corrected display = yes
      - Layback = manual
      - Horizontal beamwidth
        - Manual, 0.0
      - Local variation = 0.00
      - Latitude/longtitude
        - Deg Min Sec

        - Northing/Easting Display
            - Meters
        - Range Display Units
            - Meters
        - Speed display Units
            - Knots
        - Misc.
            - Automatic Audit Trail = yes
            - Object Detection on image load
                - None
    - Units = Meters
    - Constants = Use defaults
    - Set Contact Number = Start with 1 – Ensure number is consistent with contacts logged to date.
    - Speed Correct = Enabled

- Parameter Window – Current File Section
    - Switch Button
        - Record Data to File Name = Blank
        - Remaining storage = Enable D: and E:
        - File Grows larger than = Disable

Altitude - Absolute

Based on 595 Range Scale

Range	8% Minimum Altitude	20% Maximum Altitude
25	2.00	5.00

Maximum System Speed

Based on 595 Ping Rate

Range	Ping Rate / Second (Measured)	Maximum Speed (Knots)
25	27.00	17.50

Maximum Survey Speed

Based on 10% Buffer

Range	Maximum Speed (Knots)	90 %Maximum Speed (Knots)
25	17.50	15.75

- **1.2.12 Robertson Autopilot**

Introduction:
The factory technical representative for the parent company Simrad, is Rich Barnes (425-778-8821) who is located at Simrad, Inc., 19210 33rd Avenue West, Suite A, Lynwood, WA. 98036. The pilot was interfaced to NOAA1 to receive NMEA (modified) standard messages from Coastal Oceanographics HYPACK MAX Survey program. The vessel captain performs all operations related to the pilot.

Interface:
The pilot receives the following NMEA-0183 messages;
APB (modified by Coastal to send .#### nm of cross track error vs. .## nm, the NMEA standard)
VTG (standard)
GGA (standard)
Baud rate is 4800/N/8/1
NMEA input to the pilot is through TB 10 on the Junction Unit, Pins RX 1(+) and RX1 (-). There is no handshaking or error correction used. The Robertson RFC35R rate compass is used to provide vessel heading to all systems and outputs a NMEA message through TB10on the Junction Unit, Pins TX2(+) and TX2(-).

Operation:
The pilot starts in the **Helmsman** mode. The captain steers the vessel on to the trackline well ahead of the actual BOL and attempts to track down the line. When the vessel has stabilized online the pilot is put into the **Auto** mode. The pilot is "course steering" at this point. The captain observes the vessel motion and line tracking while adjusting the "course" using the left/right buttons on the control unit or remote control. When the vessel is steering the line and cross-track error has been reduced to a minimum (typically less than 1 meter), the captain changes to the **NAV** mode. The pilot will continue to steer in "course steering" mode for a period of time determined by an internal setting (currently at minimum – 100 sec). Then it will use the XTE value received from HYPACK MAX and attempt to adjust it's course to achieve zero XTE.

Some conditions prohibit the use of the **NAV** mode. One example is the use of a drogue chute to slow the vessel. Sea conditions that cause sudden large heading changes are another example. In these cases the pilot is left in the **Auto** mode and the left/right buttons on the control unit or remote control unit are used to con the vessel down the line.

Initial Setup:

Mechanical setup and alignment are performed at the time of installation and should require no further adjustment. There are many electronic settings that affect pilot operation. They fall in to several categories:

- Front Panel
    - Rudder – used to set the amount of rudder used by steering commands
    - Counter Rudder – used to set the opposing rudder used when crossing a course line
    - Weather – used to reduce pilot sensitivity in heavy seas
- Info Loop
- Weather Loop
- Debug Loop

Normally, only the Rudder setting is changed throughout the day. More rudder (higher #) causes closer tracking and quicker steering response. Too much rudder causes large heading swings. Too little rudder and the vessel will fail to closely follow the line.

2.0 PRE SURVEY OPERATIONS

2.1 Navigation System Check

Upon arrival in Hudson Falls a third order control disk will be located to facilitate the performance of a navigation confidence test. Two separate procedures will be performed. The first procedure is to determine the horizontal and vertical position of the project RTK GPS base station and certify it. The second procedure involves using the Trimble 7400Msi L!/L2 Kinematic OTF system to locate a check point in proximity of the survey vessel for future confidence checks.

The first procedure involves the following.

A RTK base will be set up with it's antenna positioned at a known height over a GE/QEA supplied point. The Trimble 7400Msi reference receiver is then configured to provide CMR correctors based on the following parameters.

Configuration Toolbox file D24_Base.cfg

1. Generate CMR correctors on Port 1
2. Kinematic base unit
3. A elevation mask of 13 degree's
4. A PDOP mask of 5
5. Reference position of 35 50 40.87561 Lat, 075 39 15.38597 Long, -37.75 Elev. (WGS-84 Ellipsoid height)
6. Antenna height set to 2.000 meters, Antenna mounted on a 2.00 meter rod
7. Antenna type set to L1/L2 compact resulting in a True Vertical Height of 2.062 meters

The project RTK base will be set up as a rover station, receiving corrections from the station set at various stations using the following parameters:

Configuration Toolbox file RTK_ROV.cfg

1. Receive CMR corrections on Port 1
2. Kinematic rover
3. A elevation mask of 13 degree's
4. A PDOP mask of 5
5. Output GGK on Port 2.

For reference, the RTCM-104 correctors will be relayed from the reference station to the project base station location with Pacific Crest Radio Modems Model RFM96W.

Finally, a Hypack Project will be setup to monitor the position in both WGS-84 Lat, Long and UTM Zone 18 NAD-83. The following parameters will be used.

1. Project = Base_Average
2. Kinematic DLL for GPS input configuration
3. System offsets were set to 0,0,0 for this test
4. Geodesy was set for the above listed UTM Grid.

Position observations will be recorded for a sixty minute period. These observations will then be averaged and assigned as the project RTK base stations horizontal (WGS-84 Lat Lon) and vertical elevation (WGS-84 Ellipsoid).

The project RTK base will then be set up as a reference station, sending corrections based upon the assigned position. The following parameters will be used:

Configuration Toolbox file BASE.cfg

1. Generate CMR correctors on Port 1
2. Kinematic base unit
3. A elevation mask of 8 degree's
4. A PDOP mask of 5
5. Reference position of Lat 35 50 37.98404 N , Long, 075 39 15.87987 , -23.826 Elev. (NAVD88)
6. Antenna height set to 000.00 and antenna type set to **UNKNOWN (0.0 offset)**

The data from each file will be processed through SB-MAX where it will be filtered to only GPS Mode 3 points with an HDOP of <=2.0. These values will then be averaged and also the min & max values will be observed.

2.2 Static Draft Measurement

- **Establishment of Vessel Reference Position**

Prior to survey operations, a Vessel Reference Position was set for use in post processing. Survey data will be collected by an Isis v5.91 system for processing under the Caris HIPS/SIPS software package. Single beam only data will be collected by a Coastal Oceanographics HyPack MAX v0.5b system for processing under the Caris HIPS/SIPS software package. During survey operations, no physical offsets will be entered into the Isis system. Therefore, all offsets and corrections should be handled by the Caris package. It should be noted that an average sound speed for the water column and Side Scan "Horizontal Layback" will be input into the Isis raw data package. This information will be discussed in the appropriate system sections.

With this in mind the following Reference Position was established based on the definition of a Vessel Coordinate System provided in the HIPS User's Guide.

> **Vessel Coordinate System**
> Vessel configuration is based upon an instantaneous, three-dimensional, vessel coordinate system. The
> Origin of the coordinate system is the reference position (RP). The axis is defined as follows:
> The Y-axis is oriented along the vessel's fore/aft axis, positive forward.
> The X-axis is oriented along the vessel's port/starboard axis, perpendicular to the Y-axis, positive
> to starboard.
> The Z-axis is perpendicular to the X-Y plane, and positive down (into the water).

The Y-axis is located approximately mid ship at the fore/aft centerline created perpendicular to the location of the A-Frame.
The X-axis is located at the approximate port/starboard center of the vessel.
The Z-axis was located at the rear deck level, slightly above the water line of the vessel during setup and sea trials

Once this point was established, measurements were made to determine the physical offsets of all survey equipment based on this coordinate system. These measurements were compiled and displayed in the AutoCAD 2000 file called R/V Willing.dwg. This drawing contains all sensor offsets.

During the establishment of system offsets a "Reference Mark" was set to aid in monitoring vessel Static Draft. The Reference Marks are located on the starboard single beam transducer mount vertical member, The distance from the Reference Mark to the Z-axis is 1.20 meters.

2.3 Monitoring Vessel Static Draft

To correctly process soundings, Caris needs to know the position of the Reference Point during survey operations. This point will move as equipment load, personnel, and fuel levels change. To

compensate for these changes the Static Draft is monitored daily. At the start of every survey day the motion sensor is monitored to determine vessel attitude and a measurement is made from the Reference Mark to the present waterline. If the vessel is experiencing a roll bias, due to fuel load, personnel are moved to steady the vessel at its standard attitude. This attitude was established during sea trials, by approximating vessel loads and "zeroing" the motion sensor.

- **Appling Static Draft**

The measurement is logged in the daily spreadsheet and is reduced to a static draft value that is subtracted from the distance to the zero vertical reference and the difference entered in Caris.

- **Static Draft Variation**

The Static Draft is monitored daily as mentioned above. The Static Draft of the vessel appears to have a maximum deviation of 0.01 meters. The data to date is summarized below:

Fuel Load	Static Draft (meters)
Full	0.080
.9	0.080
.8	0.080
7	0.079
.6	0.079
.5	0.079
4	0.079
.3	0.079
.25	0.079

2.4 KTD File Development for RTK GPS Water Level Data Collection and Raw Data Collection

We will be collecting RTK GPS water level elevations throughout the survey area and will be saving them as water elevations referenced to the NAVD 88 datum. This requires the preparation and use of a .KTD file. The KTD file models the difference between the ellipsoid height and the collection datum (NAVD 88) throughout the site.

3.0 HYDROGRAPHER OPERATIONS

3.1 Start of Day - System Start-up and Dock Side Checks

Upon arrival to the vessel on a planned survey day, perform the following functions or verify their occurrence. These items should be done every day before departure.

- Start generator and switch system power from shore to generator.
- If system was shut down the night before, turn on both UPS main power switches and wait for the units to power up. Trip the TEST switch once on both units to apply power to the outlets.

3.2 Start of Day – Electronics Systems Start-Up

- Verify DC Mains, 448, 595, and Autopilot are off before powering up, or logging onto, the computer systems.
- Verify that the monitors are all off via the switch on the monitor outlet strip.
- Power up the Triton Elics, NOAA 1 & NOAA 2 computers.
- Turn on the monitors via the switch on the outlet strip.
- Computer 1 & 2
  - Log on using default Logon
    - User Name osiuser
    - Password (blank)
- The Triton Elics machine is Windows 2000 and has no log on screen
- Wait for all three computer systems to fully boot
- Turn on DC Mains switch. This powers the DMS2i-05, 7400, T4000s, MX51s, CTD and radio modem
- Put the Autopilot in standby
  - Observe compass = 244 - 250 degrees
- Verify computer date/time on each system
  - Open the H11032 vessel log.xls and enter the crew arrival time, vessel departure time, and crew initials.

3.3 Start of Day - GPS Systems Check

- Activate REMCON
  - Select CLEAR to acknowledge power-up
  - Select POSITION
    - Verify Mode is RTK FIX
    - Verify position
      - Lat ~ 35 50 40.8
      - Lon ~ 75 39 19.6
- Minimize REMCON

3.4 Start of Day – Klein 595

- Check mount
- Check connector
- Check cable and lock ring

- Check Fish body screws
- Apply power to unit
- Press "any" button to start system
- Press enter once, and left arrow once to stop printer

3.5 Start of Day – Innerspace 448

- Verify paper supply in unit
- Set power to on to verify date and time – correct if necessary
- Set power back to standby
- Add Start of Day Annotation
    - Registry #
    - Julian Date
    - Calendar Date
    - Vessel
    - Transducer in use
    - Operators
    - Roll #

3.6 Start of Day – Logging

Open Survey Log
Log date and personnel on board
Log WX observations at start of day
Log activities at dock

3.7 Start of Day – HYPACK MAX

- Open Explorer
- Create a folders in the HYPACK/PROJECTS//DATA1/ folder with a naming scheme of ###MAX1 where ### is the Julian date of the survey day. (Daily survey directory) Create a separate folder for each survey day.
- Start Hypack MAX
    - Verify that correct Line File is Enabled
    - Verify that correct background chart is enabled
    - Verify Geodesy
- Start Survey
    - Open Dialog box under Options/Project Options
        - Set Project directory to the daily survey directory.
        - Set the Target directory to the daily survey directory.
        - Verify that the other information is correct and that Long Filenames are enabled.
    - Verify all alarms are off (except 448)

- Verify that all equipment is in normal locations (generator, etc.)
- Ensure vessel is in Reference position. Have vessel captain move the vessel as needed. In Survey, click on Targets, Select, and then Change File. Select the file NAVCHK.TGT from the project directory. Select the dockside nav-check point and right click on it to "select" target. Observe distance to target. If distance is excessive. (Value +/- 1.5 meters) determine what the problem is and correct it. Take a target (F5).
- Modify the target properties (F6) to name it *XXX AM NAV CHK* where XXX is the Julian Date. Add entries in Comments section: *Pitch X.X Roll X.X Hdg XXX.X* in which you record the observed pitch, roll, and heading as observed at the dock.
- Dockside Limits:
  - Pitch 0.0 +/- .2
  - Roll 0.0 +/- .5
  - Heading 246 +/-5 deg.
- Evaluate if values exceed the limits.
- Log the time in the "activity sheet" of the H11032 survey. Also, place an "x" in the roll, pitch, and heading columns on the same sheet to indicate they have been checked.

- **Dockside static draft:**
  - Observe the ROLL value from the MRU and move people to normal positions within the vessel, or as necessary to compensate for fuel load, to achieve a "zero" roll while measuring the static draft from "Reference Mark" to the water's surface. Record the measured value in survey log. Correct the measurement to true static draft value with formula provided. Also note the RTK tide displayed on the NOAA1 Hypack Max data display and enter it in the daily log sheet.
- **Dockside RTK water level check**
  - Observe the local water level reading and enter it in the RTK vs. Observed section of the daily log sheet. Compare the NAVD-88 value calculated by the log sheet with the value recorded from Hypack Max.

3.8 Start of Day – ISIS

- Open Windows Explorer
- Verify space unavailable on data drive E: > 10 GB. If less than 10 GB you need to clear out older (already archived) files to make space.
- Create a new directory on that drive in the H11032 ISIS folder based on the following format:
  - XXXISIS - With X = to Julian day
- Minimize Windows Explorer

- Start ISIS system from the H11032 ISIS shortcut. (This starts ISIS with the correct config file)
    - Set working directory for Isis under Configure>Hypack DDE> *Start each filename with* to daily directory
    - Set Target working directory under Tools>Target>File>Set Working Directory
- Verify next contact number is set in Tools>Target> Edit>Set Contact Number
- Set unit to Start Record to screen only- File>Start Recording>Display Only
- Set Layback—View>Layback>Enter value>Accept
- Set threshold in waterfall by right click—Threshold =1
- Set waterfall window values as shown below
- Open Sensor window- Windows>Status & Control>Sensors
- If you want to view 448 depth - Aux 1 displays depth
- Open Altitude window
- Click on symbol of Alt: in Telemetry window of Parameter Display

- **Annotations**
    - Annotations are kept in a WordPad document name JD###.TXT where ### is the Julian Date. This file is kept open on the Isis machine and annotations are copied and "pasted" into the **NOTE:** section of the .XTF.
    - SSS annotations must be recorded in the notes section of the Isis box at:
        - At start of line
        - When surface objects are noted
        - When SS tuning, range, cable out, or any other parameters are changed

4.0 CONFIDENCE CHECKS

Confidence Checks H11032-JD160-06092002-RV WILLING II/PORT

Confidence Checks H11032-JD160-06092002-RV WILLING II/STBD

Confidence Checks H11032-JD160-06092002-RV WILLING II/BOTH

Registry#/Julian Date/Calendar day/Towing Vessel/Channel

5.0 INTERFERENCE

H11032-JD160-06092002-RV WILLING II/Wake

H11032-JD160-06092002-RV WILLING II/Biologic

Registry#/Julian Date/Calendar day/Towing Vessel/Type of Interference

- **6.0 DURING TRANSIT TO SITE**

  - Ensure the shore power cable is stowed.
  - Remove all dock lines and depart.

7.0 ON-SITE – PRIOR TO SURVEYING

- Determine sound velocity and enter into machines
- Isis – **Configure/Sound Velocity**
- Hypack Max – **Options/Navigation/Roxann Sound Velocity**
- Innerspace 448 – Dial in as **Speed of Sound**
- Bar Check
- Depth confidence check
- Deploy SSS for appropriate tow
- Check SSS Range

7.1 Daily Average Speed of Sound

- Obtain speed of sound readings. Enter in 448, Isis, and in HYPACK MAX - Survey, under OPTIONS, Navigation Parameters as "Roxann Sound Vel. Verify value is representative of prior values.

- **7.2 BAR Check (Depth)**
  - Verify that the average speed of sound from the days first cast is entered into the 448
  - Lower the barcheck to the lowest 1.0 meter increment available referencing the 1 meter marks to the 448 draft mark on the transducer vertical pole.
  - Start the 448 paper and record the bar at one meter intervals to 1.0 meters.

- **7.3 Confidence Check (Depth)**

  - Check 448 to insure correct sound velocity entered, draft=0.0, tide=0. Mode Auto, gate 4, replies 8. Turn 448 from STBY to ON just prior to check to record date, time, speed of sound, and draft on paper record.
  - Record depth on paper record as Hydrographer lowers bar to seafloor. On the "MARK" given by the hydrographer as the bar is touching the seafloor, toggle the FIX MARK switch on the 448. The hydrographer will measure the distance from the seafloor to the water surface using the barcheck marks and

by measuring between marks. Take target.(F5) Name target XXX Depth Confidence Check. Return 448 to STBY mode.

- Annotate paper record with:
  - Depth Confidence Check
  - H11032
  - Julian Date XXX
  - Operator Initials
  - Bar Check = X.X m (meters)
  - Calculated 448 depth by adding displayed depth to daily static draft.

7.4 Confidence Check (Sidescan)

- While collecting data:
- ISIS operator will enter the appropriate annotation into the **NOTE:** section of the .XTF while online. The time is entered into the daily log and noted as a confidence check .
- At times other than during regular data collection
- A line can be run outside of regular data collection to demonstrate that the sidescan sonar system is able to detect targets out to the full extent of the selected range. The Hypack operator selects line 900 to record the data. The XTE value in *Survey/Options/Navigation Parameters* should be changed to 200000 to avoid unnecessary TEXT log entries. Start the line when ISIS is ready.

8.0 BEFORE ON LINE DATA COLLECTION

8.1 Computer 1 - Hypack Max

Start Survey

Verify correct line entered, and line azimuth is correct. Change if necessary.

8.2 Computer 2 - Hypack Max

Start Survey – start logging prior to BOL.

8.3 Innerspace 448

Turn 448 alarms on (if off) – verify digital depth is ok Start Paper

8.4 ISIS

Verify ISIS is ready.

8.5 Heave

Verify Heave is ready.

Create a target (F5) and change it's properties (F6) to DECK CTD = XXXX.X. (The value observed at the beginning of line)

9.0 START OF LINE

- Save / Clear any contacts in the Target window
- Verify SSS data quality and bottom track prior to start
- Verify coastal line start of Isis
    - Watch file size increment
    - Check destination directory for file

10.0 ONLINE

Observe digital depths, heave, and profile window to verify proper operation. In shallow areas assist the vessel helmsman by closely monitoring the depth of water. Immediately notify helmsman of hazardous condition. Watch water depth to QA/QC alt. of SSS. Watch vessel speed.

Observe Sidescan record in Isis. Mark targets & put target in Hypack so as to allow checking the target on the next pass.

Periodically observe Deck CTD value, DIM value, heave, vessel speed, and CTD time interval. Observe Navigation map for holes in Isis.

10.1 Gap Tracking - Sidescan

If a condition is observed that may create a gap in the Sidescan data the operator hits F5 on Computer 1 to create target. The operator then evaluates further. If a gap is declared the target will be called up for modification (F6). The default name in the target name field will be changed to XXX SS GAP; where XXX is the julian date. Further info will be entered into the notes field as follows:

Start & end time of gap, channel (port/stbd) Line designation
Example:
034 SS GAP
Notes: 16:37:00 to 16:37:45, Port Channel, Line 201_1549.034, type of interference
Ensure that Gap is entered in H11032 daily log.

10.2 Gap Tracking - Singlebeam

Hypack operator hits F5 and creates a target as SB gap is seen. Operator modifies target (F6) to change name to XXX SB GAP. (XXX is the Julian date) Ensure that Gap is entered in survey daily log file.

- **11.0 END OF LINE**

  - Save all contacts as follows, and report final contact number in log
    - Target>File>Save All>Yes if not saved already

12.0 END OF DAY

Review ASCII text file for alarms

12.1 End Of Day - ISIS

- Exit from Isis
- Close Target window if still active
- Log off machine or shut down based on required backup situation

12.2 Archiving Procedure

- Data from all sources is colleted in Computer 1archive for archiving and data transmittal preparation
- A separate directory is established for each survey day with a subdirectory structure where each type of data is stored
- The structure and file types are outlines below

DIRECTORY NAME		FILE NAMES	
XXX Data\Docs	All documents created	H11032 Survey Log.XLS	Summary of all activities
		Willing II_offsets_1_19.DWG	Vessel layout and system offsets
XXX Data\XXXisis	All Isis data files	*.XTF XXX.LOG *.CON, XXX-00-contact.TXT	All .XTF files from the day Daily Isis survey log Original Isis contact files

XXX Data\Max_Support	Hypack MAX support files	Varied file types	Setup and support files for Hypack MAX operation Hypack MAX operations and alarms summary .INI files used for MAX
XXX Data\XXXmax1	Hypack MAX data files and .log file	*.RAW *.TGT	All Hypack data lines .TGT is MAX target file

- A directory template is available with all subdirectories established with an XXX, copy this template to Computer 1 and replace XXX with Julian day.
- Removable Hard Drive
  - A copy of each days data are copied from Computer 1 to a removable hard drive at the end of each survey day.
  - The Drive is then taken to the project office where the data is archived.
- XTF Data
  - Move the survey log from D:\root to daily directory at the end of the survey day
- Hypack Data
  - Copy both the TGT and the TXT file for the day to the data archive.
- Document Files
  - Copy the Daily Survey Log to the Daily Directory Doc section
  - Copy the Master Log.XLS to the Daily Directory Doc section
  - Copy any other relevant documents or drawings to this section
- Misc Section
  - Place any other non-standard files into this directory.

- **12.3 <u>End of Day: System Shut Down and Dock Side Checks</u>**

Upon arrival at the dock, perform the following functions or verify their occurrence. These items should be done every day before departure from the vessel.

- Secure all dock lines and hook up the shore power cable upon arrival at the dock, log arrival time in vessel log.
-
- Read the vessel fuel gauge and enter the value in “Activities Section” of Daily Log
- Capacity is approximately 120 gallons

- Ensure vessel has all appropriate supplies for the next day. Fuel, disks, FEDEX supplies, food, paper supplies, and water.
- Switch the system over to shore power after verify unneeded systems are off.
- Turn off the DC Mains and Autopilot.
- Verify you have the Data package and any files that will be e-mailed with you.
- Ensure all lights and boat electronics are off. Check all windows. Ensure bilge pumps are on. Lock back door upon departure.

12.4 Misc. System Operations

12.4.1 Klein 595

- Lower fish into the water to test operation

- Deploy fish and note cable out for layback calculations.
- Verify SSS image quality on Isis

- End of Day
  - Power Off
  - Recover Fish
  - Inspect entire wet end of system for wear – damage

12.4.2 Innerspace 448

- On-site
  - Input average speed of sound from first SVP and verify entry into all other systems
    - 448 – Hypack – Isis
- Start of Line
  - Alarm on
    - Good bottom lock
  - Verify range, gain, mode, and gate settings for upcoming line conditions.
  - Verify proper sound velocity based on first cast
  - Unit in standby power unless performing confidence check or time check

- End of day
  - Turn unit off
  - Remove and archive sounding roll
  - Verify Sounding pole is raised
  - Verify paper supply on board

- Periodic Maintenance

- Clean print head

APPENDIX 18

STANDARD OPERATING PROCEDURES FOR CORE PROCESSING

1. Decontaminate all equipment prior to contact with core segments in a designated decontamination area. The decontamination steps are:
   (1) remove visible sediment from equipment using paper towels. Dispose of the towels in appropriate containers labeled as PCB waste;
   (2) wash thoroughly using laboratory grade detergent and a scrub brush in the laboratory sink (wash water can go down the sink drain);
   (2) rinse with distilled water;
   (3) rinse thoroughly with acetone under the hood in the laboratory, then allow to air dry;
   (4) rinse thoroughly with hexane under the hood in the laboratory, then allow to air dry; and
   (5) rinse with distilled water.

   Acetone and hexane rinsate will be collected and placed in appropriate disposal containers.

2. Transport the cores from the field staging area to the field processing facility at the end of each day for core sectioning and sample preparation. The cores must be kept on ice and maintained in a vertical position during transport and handling.

3. Upon the delivery of the cores to the processing laboratory, a hard copy of the corresponding field data will be presented to the processing lab coordinator. The field data sheet will be signed by both the sample collection/delivery personnel and the processing lab coordinator, and will serve as the chain of custody form from the field to the processing facility. Transcribe either electronically (diskette) or manually the field data for each core into the field processing database.

4. The processing laboratory coordinator will disperse the cores to each sample processing custodian for processing.

5. Before sectioning, the mass of the sediment contained within the core will be determined. Place the upright core on the scale and weigh to the nearest gram. Measure and record the depth of water in the core, and the total length of the core tube. Subtract the mass of the water and core tube from the total weight. The mass of the water and core tubing can be determined from the volume and the density of each.

6. Fasten the core tube in a clamping system (Figure 1) and place a container below the clamping system to collect water removed from the core and any spills that occur. Measure the total length of the core and record in the database.
   - If core stored in Aluminum tubing:
     – tap along the outside of the core tube with a spoon to estimate the sediment/water interface
     – drain the core by drilling a small hole about 1 in. above the estimated surface of the sediment and allow the water overlying the sediment core to drain, taking care not to disturb the surface of the sediment.
     – cut the core tube off approximately 1 in. above the estimated surface of the sediment

with a pipe cutter so the sediment/water interface can be seen
  - measure the total length of the recovered core and record in the database
  - mark the position of the top of the sediment on the outside of the core tube
- In Lexan® core tubes, the top of the sediment will be determined visually. Drain the core in the same manner used for the aluminum core tubes.

7. Based on the core length, mark the locations of where the core tube will be cut into segments (there are four different schemes according to which cores can be sectioned; Figure 2). The sample processing custodian will print labels for each jar necessary for each segment of the core.

8. The sample custodian will determine what analyses need to be performed on each core segment. The types of analyses selected for individual core segments depend on their position within the core, their physical characteristics or will be assigned on a random basis.
9. Verify the analyses for each core segment listed in the database (automatically assigned for Aroclor PCBs, TOC, moisture content, radionuclides, and archive samples). If necessary select additional analyses based on the field database tracking system (PCBs by USEPA Method 680, RCRA Metals & Dioxins, disposal characterization) or a combination of the tracking system and visual evaluation (Geotechnical characterization). Enter additional analyses in the database, print container labels and place on appropriate containers. Container specifications are provided in the QAPP. Update the field processing database, and generate hard copies of chain of custody forms.

10. Prepare a set of clean, 3-liter stainless steel bowls for all sectioned core segments. Mark bowls with core segment location (i.e., 0-2”). Place first bowl on balance to get a tare weight of the bowl. Create new entries in the field processing database by entering the top and bottom depth of each core segment.

11. Adjust the position of the core tube in the clamping system to provide adequate support and clearance for cutting the core into segments. For Lexan core tubes place a clean plastic cap on the top of the tube prior to each cut to minimize the loss of soft sediment during cutting.

12. Use a tubing cutter (aluminum core tube) or vibratory saw (Lexan® core tube) to cut the core tube at the bottom of the top core segment. Use a decontaminated blade to cut each segment (i.e., do not make two cuts with the same blade). Avoid disturbing the sediment. Use a clean stainless steel broad knife to separate the segment from the rest of the core after the core tube is cut, and place the segment into a stainless steel bowl (tare weight already established). Place the bowl with the core segment on the balance and obtain a weight.

13. Extrude the sediment from the core tube, and dispose of the tube in appropriate containers labeled for PCB waste. Give a physical description of each core segment to the sample custodian to record in the database. Characteristics include the general soil type based on the Unified Soil Classification System, approximate grain size, presence of observable biota, odor, and color. Classification of grain size will be a qualitative observation with the following types denoted: silt, fine sand, coarse sand, clay, organic matter, and gravel. The approximate proportion of each soil type within each sample will be estimated (i.e., primary, some, little, trace).

14. Identify any changes in sediment character within each segment. If changes in stratigraphy are observed within a core segment, then the nature and approximate length of the various layers will be verbally relayed to the sample custodian for inclusion in the database. Evidence of changes in stratigraphy include an abrupt change in grain size (e.g., from silt to wood chip layer) or change in soil color which may indicate oxidized or reduced sediments. If objects of cultural significance are observed during the core processing, note them in the database and set them aside for inspection by a qualified geomorphologist or archaeologist.

15. Homogenize the sediment in the 3 liter stainless steel bowls using a large stainless steel spoon. A 6 inch core segment will result in approximately 0.7 liters of sediment, a 24-inch segment will result in approximately 2.7 liters of sediment. Use the spoon to bring the sediment near the bottom of the bowl up to the top using a circular motion, similar to preparing food that requires mixing (e.g., cake batter). Repeat this procedure until all of the sediment near the bottom of the bowl has been brought to the surface at least twice. Continue mixing the contents of the bowl until an even texture and color is observed throughout the entire sample.

16. Fill the appropriately labeled containers with sample and package them in a cooler for shipment to the laboratories. The samples will be shipped out in batches of 20 environmental samples accompanied by appropriate QA/QC samples. Chill samples to 4°C with ice packed in Ziploc® bags or equivalent.

17. Process the next core segment as described in steps 13-17 until the whole core is sectioned and all sample jars are filled.

18. Prior to shipping the samples, confirm which project laboratory has capacity to receive samples the next day, and ship samples (with corresponding COC forms) accordingly *via* overnight delivery service or courier. All samples will be delivered to the analytical laboratories within 24 hours of processing, except for the samples for geotechnical characterization, which will be delivered to the laboratory on a less frequent basis.

19. Place all used stainless steel bowls and spoons at the decontamination station for proper decontamination prior to reuse.

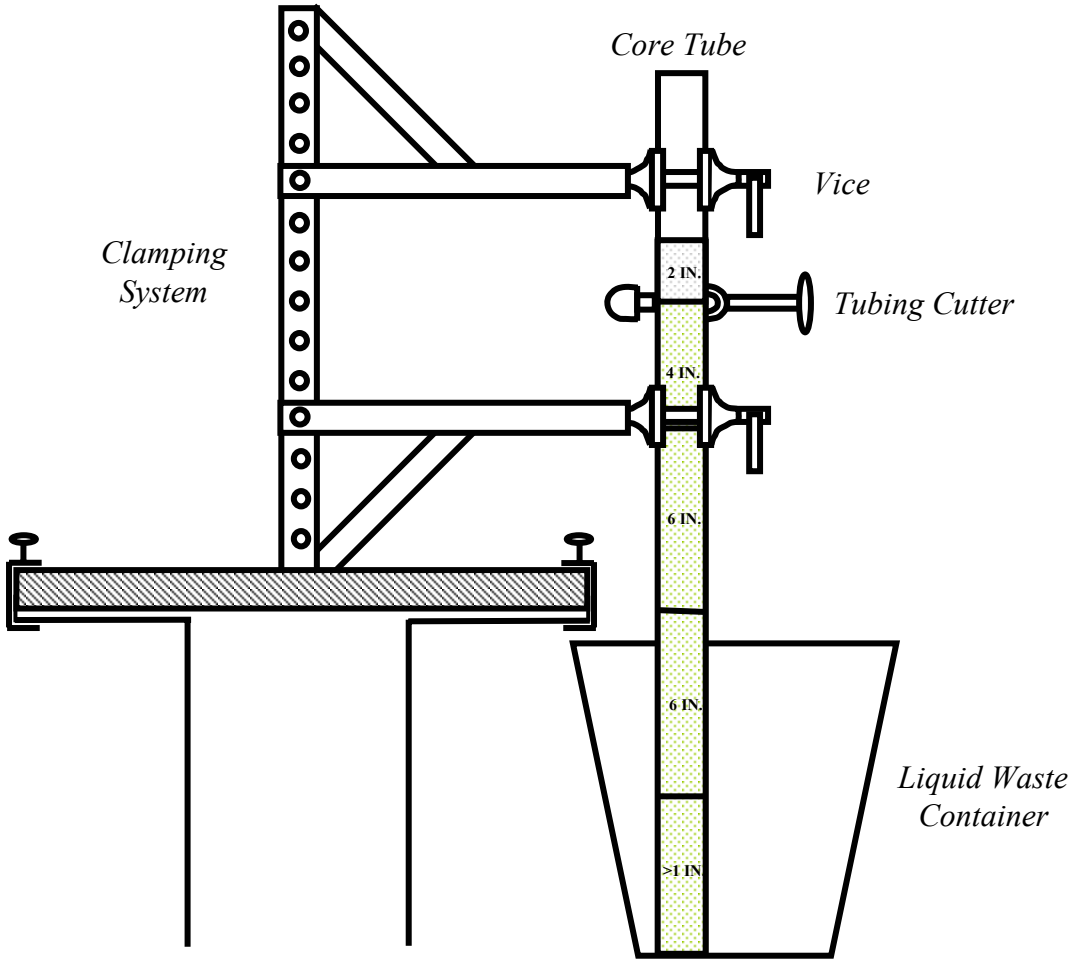


Figure 1. Core Clamping System Set-up.

SCALE : NONE

QEA Quantitative Environmental Analysis, LLC

GENrem 137 September 2002

IF: D:\GENrem\sop_Appendix_A_B.ppt

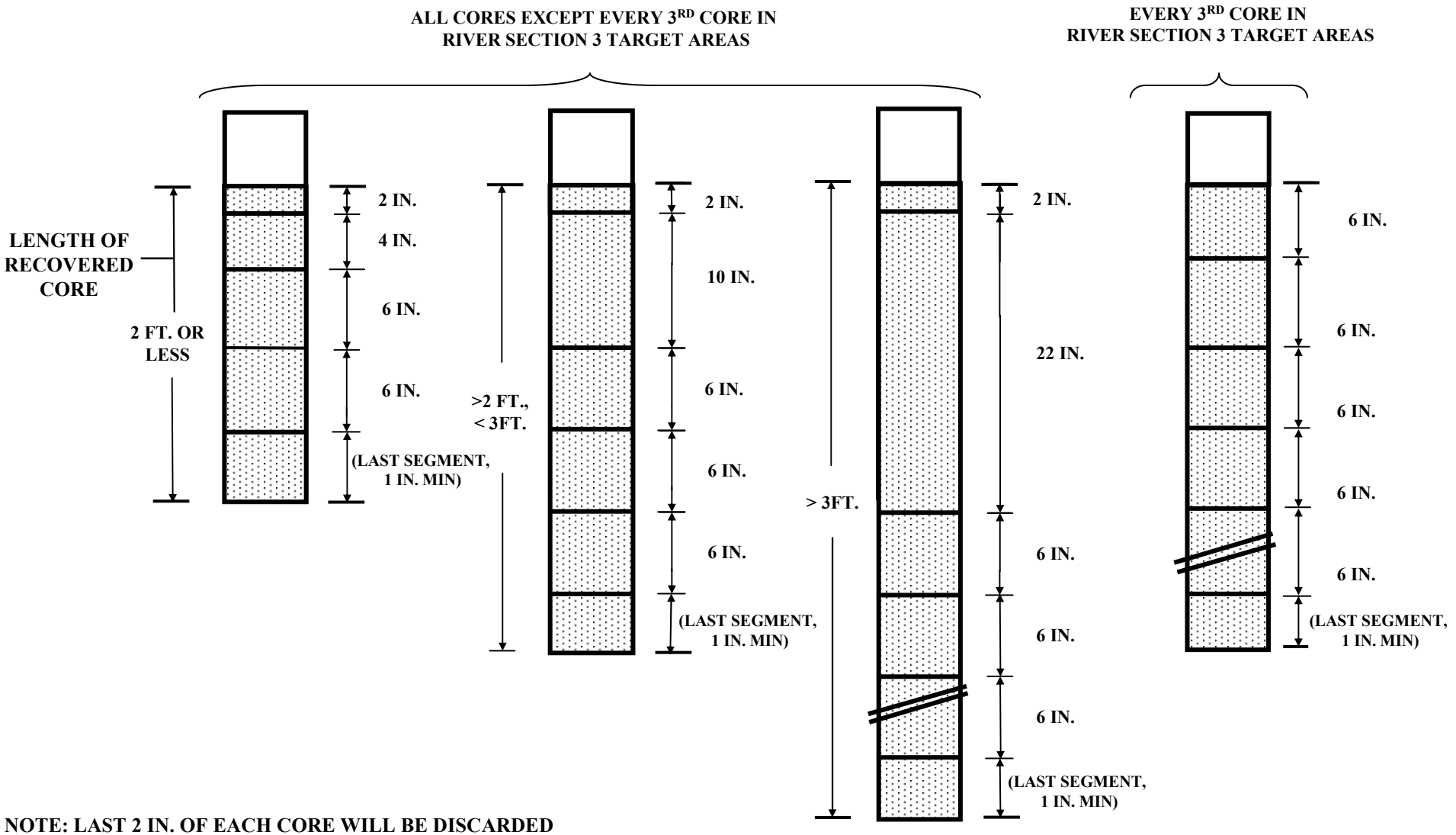


Figure 2. Core Segmentation Approach.

SCALE : NONE

QEA Quantitative Environmental Analysis, LLC

GENrem 137 September 2002

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APPENDIX 19
(Note: The SOP for ^{7}Berium is not included because the USEPA approved the removal of ^{7}Berium from the QAPP.)

APPENDIX 20

TELEDYNE BROWN ENGINEERING
ENVIRONMENTAL SERVICES

Procedure TBE-2008

Gamma Emitting Radioisotope Analysis

Rev. 0

Date of Original Issue: 03/29/02

Approved by:

_____Date_____
Keith O. Jeter, Operations Manager

_____Date_____
Martin R. Keller, Quality Assurance Manager

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APPENDICES

DETERMINATION OF GAMMA EMITTING RADIOISOTOPES

1.0 SCOPE & APPLICABILITY

1.1 This procedure presents the methods for determining gamma emitting radioisotopes by high purity germanium detectors with high resolution spectrometry in specific media: air particulate filters, charcoal filters, milk, water, vegetation, soil/sediments, biological media, etc.

1.2 No chemical separation and purification procedures are required for gamma ray analysis. This is a nondestructive analysis, and after completion of the assay, the aliquot can be used for other analyses. However, to identify a specific target gamma emitter, chemical separation can be employed to isolate the desired gamma emitter(s) when other gamma emitters are present in high concentrations (see Section 1.4).

1.3 For water samples, a procedure is included to pre-concentrate the samples by evaporation for greater sensitivity. Advantages gained include:

- Permits the analysis of more than one liter of water in comparison to the restriction of one liter maximum for the standard Marinelli geometry
- Filter geometry is significantly a more efficient geometry since the sample is concentrated directly in front of and close proximity to the detector

1.4 For in-plant samples, a radiochemical method that includes chemical separation and purification is presented for determining the Ce-141 and Ce-144 activities of in-plant samples that have high concentrations of other gamma emitters.

2.0 SUMMARY OF METHOD

2.1 GEOMETRIES. Each sample to be assayed is put into a standard geometry for gamma counting such as 1-liter wrap-around Marinelli containers, 300 mL or 150

mL bottles, charcoal cartridge or 2-inch filter paper source geometries. Calibration and counting efficiencies of the gamma counting system for these geometries must have been determined with standard (known) radionuclide activity traceable to the National Institute of Standards and Technology.

To improve the sensitivity for measurement of gamma emitting radionuclides in water matrices, the sample can be evaporated from any known volume of one liter or greater and the residue collected in a standard filter geometry.

2.2 COUNTING. Samples are counted on large (>55 cc volume) germanium detectors connected to dedicated data acquisitions and data computation systems. All resultant spectra are stored electrically.

2.3 CALCULATION. The analysis of each sample consists of calculating the specific activities of all detected radionuclides or the detection limits from a standard list of nuclides. If water samples were pre-concentrated by evaporation, the specific activities or detection limits are divided by the volume of water represented in the filter geometry.

2.4 IN-PLANT SAMPLES FOR CE-141/CE-144. The radiochemical isolation of cerium reduces the gamma counting background and improves the sensitivity of analysis by a factor of 100 or more compared to direct gamma spectral analysis. This method is an adaptation of the Los Alamos Collected Radiochemical Procedures La-1721, 3rd edition, September 1967.

2.4.1 Solid samples are leached in acid, then filtered. Aqueous samples need no special preparation. Stable cerium carrier is added to the sample, then cerium is purified by precipitating first as fluoride, then as hydroxide, and finally as oxalate. The cerium oxalate is collected by vacuum filtration, dried and weighed to determine chemical yield. The precipitate is mounted on a nylon planchet and is covered with Mylar film.

2.4.2 The sample planchet is analyzed on a high resolution germanium detector. Ce-141 is inferred by its emission at 145 keV (48.4% gamma abundance). Ce-144 is inferred by its emission at 134 keV (10.8% gamma abundance). Results are calculated using a counting efficiency curve derived by analyzing multiple nuclide standards prepared in the same counting geometry.

3.0 DEFINITIONS

3.1 MSDS – Material Safety Data Sheet

3.2 NIST – National Institute of Standards and Technology

3.3 TBE-ES – Teledyne Brown Engineering – Environmental Services

4.0 HEALTH & SAFETY WARNINGS

4.1 At a minimum, personnel performing this procedure are required to wear the following protective equipment: laboratory coats, safety glasses, and disposable gloves.

4.2 Appropriate precautions, as specified in the Laboratory Radiation Protection Program (RPP) Manual, will be adhered to when handling radioactive material.

5.0 CAUTIONS – N/A

6.0 INTERFERENCES – N/A

7.0 PERSONNEL QUALIFICATIONS

Analysts performing this procedure must be trained, qualified, and certified in accordance with the TBE-ES Quality Control Manual IWL-032-365, Sections 2.2 through 2.9 inclusive.

Analysts in training may perform this procedure only under the direct supervision and observation of a senior technician certified to perform this procedure.

8.0 EQUIPMENT & SUPPLIES

8.1 Gamma-Ray Spectrometer consisting of high resolution germanium detectors connected to Nuclear Data acquisition and data computation systems. For each detector, 2048 channels (1 KeV per channel) or 4096 channels (0.5 KeV per channel) are assigned for pulse height analysis).

8.2 Standard sample container geometries, as appropriate:

- 1-Liter wrap around Marinelli containers
- 300 mL or 150 mL bottles
- 2-inch filter paper for air particulates
- Charcoal cartridges
- Nylon planchets (see Section 8.6)

8.3 Evaporation supplies for filter geometry

- Beakers: 1, 2, or 4-liter graduated
- Hot plate
- 2-inch stainless steel planchet
- Kimwipes, or equivalent
- Marking pen, to write on beaker and planchets
- Fiber sample trays
- Heat lamps, Heat hood
- Parafilm
- Paper envelope to store prepared planchets

- HNO_3, concentrated, in a dropping bottle
- Distilled water in a wash bottle
- Laboratory aerosol, dispensable by drop

8.4 In-Plant Samples Ce-141/Ce-144: Preparation

8.4.1 Aqueous

- Centrifuge tubes, 50-mL disposable
- Pipets, 10-mL disposable and 1-mL Eppendorf or glass volumetric
- Rubber pipet bulb
- pH paper
- Hydrochloric acid (HCl) to adjust pH if needed
- Deionized water, in a wash bottle
- Cerium carrier solution, standardized

8.4.2 Resins and other solids

- Beakers, 150-mL
- Gravity filtration apparatus and glass fiber filters
- Balance, analytical
- Hood
- Spatula
- Heat lamps or drying oven
- Poly bottles
- Pipets, disposable (10-mL)
- Centrifuge tube, 50-mL plastic and centrifuge tube rack
- Hydrochloric acid (HCl), 6 M: for resins
- Nitric acid (HNO_3), 8 M: for non-resin solids

- Cerium carrier solution, standardized

8.5 In-Plant Samples Ce-141/Ce-144: Chemical Separation & Purification

- Glass rod
- Hot water bath: 250 or 400-mL beaker half full of water on a moderate hot plate
- Deionized water, in a wash bottle
- Hydrofluoric acid (HF), conc. **!! Extreme Hazard !! No Skin Contact !!**
- Boris Acid (H_3BO_3), saturated solution
- Nitric acid (HNO_3), concentrated
- Sulfuric acid (H_2SO_4), 2 M
- Ammonium oxalate, saturated

8.6 In-Plant Samples Ce-141/Ce-144: Mounting the Precipitate

- Filter paper, 2.8 cm No. 42 ashless disc
- Vacuum filtration apparatus
- Petri dishes, 4-way partitioned
- Hot air oven
- Dessicator
- Balance, analytical
- Spatula
- Gummed labels
- Nylon planchets, 2-inch with Mylar film and nylon ring
- Scissors or razor blade
- Deionized water
- Ethanol

9.0 PROCEDURE

9.1 Detection Capability

Gamma ray spectroscopy, using a germanium detector, provides a high resolution method of distinguishing many gamma emitting nuclides in a single sample.

Each of the most commonly observed nuclides listed in the ensuing Table 9.1 has at least one gamma ray with a unique energy. Consequently, each nuclide in the Table may be identified in the presence of any or all of the others. The Table 9.1 also lists the nominal detectable limits for three of the standard sample container geometries.

Table 9.1A Gamma Spectroscopy Detection Sensitivities[1] by High Resolution Germanium for Environmental Samples

Nuclide	Milk and Water[2] (pCi/L)	Animal, Fish, Soil Vegetation, etc. (pCi/g)	Filters (pCi/total filter)
Be-7	50	0.2	20
K-40	80	0.4	50
Mn-54	5	0.02	2
Co-58	5	0.02	2
Fe-59	10	0.04	3
Co-60	5	0.02	2
Zn-65	10	0.04	5
Zr-95-Nb-95	5	0.04	3
Ru-103	5	0.02	2
Ru-106	50	0.2	20
I-131	15	0.1	4
Cs-134	5	0.02	2
Cs-137	5	0.02	2
Ba-140/La-140	10	0.2	3
Ce-141	10	0.1	3
Ce-144	40	0.2	20
Ra-226	80	0.1	10
Th-228	10	0.02	10

[1]The detection limits are referenced to the count time and are based on two standard deviations of the background statistics.

[2]For water samples that have been pre-concentrated by evaporation onto a planchet, divide the values by the volume of water represented in the filter geometry.

Table 9.1B Ce-141/Ce-144 Minimum Detectable Activity (MDA)

Matrix	MDA[1]	Sigma Level[2]	Sample Volume	Chem Yield	Counting Interval (hour)	Counting Efficiency (cpm)	Backgd (cpm)
Ce-141[3]	$7x10^{-6}$ μCi/mL	4.66	10 mL	0.80	6		
	$4x10^{-5}$ μCi/g	4.66	2 g	0.80	6		
Ce-144[4]	$3x10^{-5}$ μCi/mL	4.66	10 mL	0.80	6		
	$2x10^{-4}$ μCi/g	4.66	2 g	0.80	6		

[1]Assumes there is no delay between collection and counting

[2]Sigma multiplier will be 4.66 unless otherwise specified by the client

[3] Half-life for Ce-141 is 32.5 days; therefore, delay in counting would significantly increase the MDA

[4] Half-life for Ce-144 is 284 days; therefore, delay in counting would increase the MDA

9.2 Sample Selection

9.2.1 Using the sample receipt form with the TBE-ES sample number, locate the sample (or sample group) in the sample receiving and storage room. Sign for the samples on the Receiving Room Log and return with them to the environmental laboratory.

9.2.2 Begin filling out the Radiochemical Preparation Logbook, entering the customer name, the sample numbers in order, the desired analyses, sample type, collection dates, the sample preparation date and the initials of the analyst.

After processing all samples within the sample group, begin filling out the Radiochemical Work Sheet – Gamma Spectroscopy. Using the laboratory logbook as a guide, fill in the customer name, collection date, sample type, analyst's initials, preparation date and aliquot used. Write the sample number of each sample in numerical order, and indicate the desired analysis (gamma spec).

9.2.3 Make an entry in the Gamma Spec laboratory logbook showing customer name, sample number, sample type, collection dates and desired analyses.

9.3 Sample Preparation

A laboratory sample for this SOP is defined as the material collected for analysis. A test source is prepared from laboratory sample material for purpose of determining its radioactive constituents. This is accomplished by putting the laboratory sample in a geometry suitable for the counting instrument, in this case a standard geometry that is user-friendly to the gamma spectrometer. The geometries used for the test source should be identical to the geometry of the calibration source, to the extent possible.

Important considerations in preparing test sources for gamma-ray spectrometry are geometry (shape), size, and homogeneity (uniformity) of source.

9.3.1 MILK AND WATER: Load environmental water and milk samples into 1-liter Marinelli containers.

9.3.2 WATER, larger volumes: For water volume exceeding the capacity of the 1-liter Marinelli, evaporate and mount the residue on a 2-inch stainless steel planchet, as follows:

9.3.2.1 Mark the sample number with a laboratory marking pen onto a clean, graduated 1, 2 or 4 liter beaker.

9.3.2.2 Shake the sample container to distribute any particulate matter evenly. Decant 1 liter or more of sample into the beaker and record the sample volume (and customer name and sample identification number) on the beaker with a marking pen.

9.3.2.3 Add approximately 1 mL concentrated HNO_3 to the sample from a dropping bottle. Place the beaker on a hot plate under the hood in the Gamma Preparation Room and set the hot plate for approximately 200°F temperature.

9.3.2.4 Evaporate the sample until the volume is reduced to 1-5 ml. Take care to reduce hot plate temperature as the sample volume

decreases in order to avoid loss by spattering from the beaker. Remove from hot plate.

9.3.2.5 Prepare a 2-inch stainless steel planchet for each water sample by first wiping it clean with a Kimwipe. Write sample number, customer name, and volume on the back of planchet with a marking pen.

9.3.2.6 Transfer the solution from each sample beaker to its correspondingly numbered planchet. Wash the beaker sparingly with deionized water using a wash bottle and collect the washings in the planchet.

9.3.2.7 Place the filled planchets in the fiber sample tray under heat lamps in the Light Hood. Add 1 drop of laboratory aerosol to each planchet. Evaporate to dryness. Remove and allow to cool.

9.3.2.8 Stretch parafilm over the planchet.

9.3.2.9 Insert the planchet into a new clean paper envelope on which the sample number, customer name, and volume have been inscribed.

9.3.3 AIR PARTICULATE FILTERS: Position two-inch diameter filter papers in front of the detector without change in geometry.

9.3.4 VEGETATION AND BIOLOGICAL MEDIA, e.g., food crops, fish, soils, etc.: Load into tared 300 or 150 mL plastic bottles or 1-liter Marinelli containers. Determine and record the net weight of the sample.

9.3.5 CHARCOAL CARTRIDGES: Position charcoal cartridges on the face only of the detector or on the face of the detector and up to four (depending on the number of charcoal cartridges in the weekly set) around

the cylindrical surface of the detector. If I-131 is observed, individually recount each cartridge, positioned on the face of the detector.

9.3.6 IN-PLANT SAMPLES FOR CE-141/CE-144: Refer to Appendix A for sample preparation and chemical separation and purification.

9.4 Calibration of Equipment For Gamma Ray Spectroscopy

The standard sample container geometries are the 1-liter Marinelli container, 300 mL and 150 mL polyethylene bottles, 2-inch diameter filter paper, a charcoal cartridge, and a 2" stainless steel planchet. Mixed gamma ray standards traceable to the National Institute of Science and Technology or best available are used to calibrate the various standard geometries.

Each standard is initially counted on each germanium detector and an efficiency versus energy curve is determined for each geometry for the energy range of approximately 50 KeV to 2 MeV.

On an on-going basis, once a week the check source standard is counted on each detector for energy, efficiency, calibration and resolution. A more detailed calibration procedure is described In PRO-042-44, "Calibration of Gamma Ray Spectrometers."

9.5 Sample Counting

9.5.1 Verify that the samples contain the same sample numbers as on the accompanying Radiochemical Work Sheet—Gamma Spec.

9.5.2 Write counting sequence numbers on the work sheet following the order that the sample numbers appear on the sheet. Begin with the number 1 if starting a new sample counting group; otherwise, use the number which follows the last sequence number assigned.

9.5.3 Write the counting start date and the number of the gamma-ray spectrometer used on the Radiochemical Work Sheet.

9.5.4 Measure an aliquot of sample in a standard geometry (one that has been calibrated). Record the amount on the work sheet.

9.5.5 Place the standard geometry with the sample aliquot on a shielded Ge(Li) detector and gamma count for a period of time that will meet the required sensitivity of measurement.

9.5.6 After the counting period the Nuclear Data system performs a peak search and identification. Print the gamma spectrum and/or store the spectrum on the appropriate computer-compatible device.

9.5.7 Calculate the radioactivity of the gamma emitters present in the sample.

9.5.8 For greater counting efficiency, reduce the size of the test source, as in Step 9.3.2. This will allow a greater amount of laboratory sample to be counted in a more favorable geometry.

9.6 Calculation of the Sample Activity or of the MDA

9.6.1 The Nuclear Data system performs a peak search and identification of all photopeak energies. The photopeak regions of the spectrum are integrated and the area under the baseline continuum is subtracted to determine the true photopeak area. Isotopes are identified by their appropriate photopeaks, and ratios to each other when more than one gamma photon is emitted by an isotope in the sample.

9.6.2 Radionuclide concentrations, A, (or detection limit based on the background if no peak is observed) are calculated by for a library of isotopes in pCi:

$$A = \frac{C}{2.22} \times BEV \quad \text{, where:}$$

C = net count rate, cpm, in the peak area above the baseline continuum

B = the gamma ray abundance of the radionuclide being measured (gammas/disintegration)

E = detector efficiency (counts/gamma) for the particular photopeak energy being considered

V = volume (or mass) of sample aliquot used (liters or gram)

2.22 = conversion factor from dpm/pCi

9.6.3 The calculation includes the efficiency of the detector for each gamma ray energy and for the sample geometry, the percent abundance for the gamma ray, the sample size, length of count, and references the results to the collection date.

9.6.4 The results are typed by a line printer and then transcribed onto a computer compatible format and manual data entry or directly by tape into the Interim Report system.

10.0 DATA AND RECORDS MANAGEMENT

10.1 All laboratory data and ancillary information shall be documented in bound laboratory logbooks or appropriate worksheets in permanent ink. Appropriate supervisory personnel shall review logbook entries and worksheets as required by the TBE-ES Quality Assurance Program.

10.2 Corrections to recorded data in logbooks or on worksheets shall be noted by drawing through the incorrect data with a single line and recording the date of the correction and the initials of the person making the correction. The correct data will be recorded in an unambiguous location in the immediate proximity of the incorrect data.

11.0 QUALITY CONTROL & QUALITY ASSURANCE

11.1 Sample duplicates shall be run to meet client requirements or, at a minimum, as required by the TBE-ES laboratory QC program.

11.2 Analysis blank and spikes shall be run to meet client requirements or, at a minimum, as required by the TBE-ES laboratory QC program.

11.3 A matrix spike consisting of a sample spiked with an appropriate standard (NIST traceable when possible) shall be run to meet client requirements.

11.4 If any batch control sample fails laboratory established quality control criteria (IWL-032-365, Section 9.1.2) or fails to meet specific client contract requirements, the samples comprising the controlled batch shall be reanalyzed.

11.5 Alpha and beta counters used in this analysis shall be controlled as set out in PRO-032-27.

11.6 The Laboratory Operations Manager or designee will interpret control charts. Five percent of the plotted values are expected to fall outside the $+2\sigma$ precision band on statistics alone. If a check source falls outside the $\pm 3\sigma$ precision band, another reading of the check source shall be made. If the second reading also falls outside the $\pm 3\sigma$ band, the counter is judged to be out of control & shall be taken out of service.

11.7 A counter control chart may show trends without being out of control by the above criteria. The Laboratory Operations Manager or a qualified designee shall interpret these trends and take corrective action. It is good practice to investigate trends which approach a 2 sigma control line. The instrument maintenance log shall be used to document the occurrence and interpretation of trends, and any corrective action taken.

11.8 When a counter is out of control, the Laboratory Operations Manager or the person he/she designates will examine the check source for defects. Re-

calibration of the counter may be necessary. New calibrations should be compared to previous calibrations to identify major changes in counter operations. Corrective action shall be documented in the maintenance log for that instrument.

11.9 When a counter is out of control for a given analysis, it may not be used for that analysis. A label must be placed on the instrument indicating its status.

12.0 REFERENCES

12.1 EPA-600/4-80-032, Prescribed *Procedures for Measurement of Radioactivity in Drinking Water,* U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1980. Procedures, except SM-19-7110B, are based on Method 901.1 "Gamma Emitting Radionuclides," augmented for non-aqueous matrices by TBE-ES technical personnel.

A1 In-Plant Sample Ce-141/Ce-144 Preparation and Chemical Separation and Purification

A1.1 Sample Preparation

This section describes how samples are aliquoted and prepared for chemical separations. Wear a laboratory coat, disposable gloves and safety glasses while carrying out the steps below.

A1.1.1 Aqueous Samples

A1.1.1.1 Write the Teledyne sample number or login number on a 50 ml disposable plastic centrifuge tube using a laboratory marking pen. Also write the analysis on the tube.

A1.1.1.2 Shake the sample container to mix, then withdraw 10 ml of sample using a disposable pipet and rubber bulb. Transfer the liquid to the labeled sample tube. Different aliquots may be used according to sample availability or desired detection limit. Write the measured aliquot in the laboratory data book.

A1.1.1.3 Test the sample for acidity by dipping a stirring rod into it, then touching to pH paper. If the sample is not acidic, add several drops HC1 from a dropping bottle, then stir and test again. Add deionized water from a wash bottle to bring the volume near 20 ml.

A1.1.1.4 Add 1.00 ml of standardized cerium carrier solution (nominally 10 mg Ce/ml) to the sample using an Eppendorf pipet or a glass volumetric pipet. Proceed to Section 9.4 for chemical separation procedures.

A1.1.2 Resin Samples

A1.1.2.1 Resin samples are leached in 6M HC1 without heating, then are filtered. The filtrate is diluted to 100 ml, then measured aliquots are taken for various analyses.

A1.1.2.2 Write the Teledyne sample number on a new 150 ml beaker. Obtain the tare weight of the beaker using the analytical balance. Record this figure in the laboratory notebook along with the client name, sample number and sample type.

A1.1.2.3 Working in a hood, use a laboratory spatula to scoop a representative aliquot of the sample from its container into the labeled beaker. The size of the aliquot will vary according to sample availability, overall sample activity and desired detection limit.

A1.1.2.4 Reweigh the sample beaker and record this gross weight in the laboratory notebook. Subtract the beaker tare weight and record the sample aliquot weight. Also note whether the sample is dry or wet.

NOTE: If the sample is wet and client wants results on a dry basis, place the sample beaker under heat lamps or in a drying oven and dry it before taking the final weight. In rare cases the client wants results on both a wet and dry basis. In these cases take a final weight on both a wet and a dry basis.

A1.1.2.5 Working in a hood, pour 6 M HC1 from a beaker into the sample beaker, covering the sample with about 75 ml of liquid. Allow the sample to leach for 2-5 hours without heating.

A1.1.2.6 Fold a glass fiber filter in quarters and place in a plastic funnel. Place the funnel in the mouth of a new poly bottle which has been marked at an appropriate volume level and which has been labeled

with the client name and sample number. Filter the sample into the bottle, washing the resin with 6 M HC1 and with water. Discard the filter and resin into a radioactive solid waste container.

A1.1.2.7 Add deionized water to the bottle, filling to the volume mark. Screw on the cap and shake to mix.

A1.1.2.8 Use a disposable pipet to draw a measured aliquot (usually 10 ml) from the sample bottle, transferring it to a 50 ml plastic "C" tube labeled with the sample number and the analysis. Record the measured aliquot and the dilution information in the laboratory notebook.

A1.1.2.9 Using a calibrated fixed or adjustable volume pipet, add 1.00 ml standardized cerium carrier (nominally 10 mg Ce/ml) to the sample. Proceed to Section 9.4 for chemical separation.

A1.1.3 Other Solid Samples

Solid samples other than resin are leached in 8M HNO_3 with heating, then are filtered. The filtrate is diluted to an appropriate volume, then measured aliquots are taken for various analyses.

A1.1.3.1 Write the Teledyne sample number on a new 150 ml beaker. Obtain the tare weight of the beaker using the analytical balance. Record this figure in the laboratory notebook along with the client name, sample number and sample type.

A1.1.3.2 Working in a hood, use a laboratory spatula to scoop a representative aliquot of the sample from its container into the labeled beaker. The size of the aliquot will vary according to sample availability, overall sample activity and desired detection limit.

A1.1.3.3 Reweigh the sample beaker and record this gross weight in the laboratory notebook. Subtract the beaker tare weight and record the sample aliquot weight. Also note whether the sample is dry or wet.

NOTE: If the sample is wet and client wants results on a dry basis, place the sample beaker under heat lamps or in a drying oven and dry it before taking the final weight. In rare cases the client wants results on both a wet and dry basis. In these cases take a final weight on both a wet and a dry basis.

A1.1.3.4 Working in a hood, pour 8 M HNO_3 from a beaker into the sample beaker, covering the sample with about 50 ml of liquid. Place the beaker on a moderate hot plate (setting near 2) and allow the sample to leach for 2 hours or longer, adding deionized water as necessary. Remove the sample beaker and allow to cool.

A1.1.3.5 Fold a glass fiber filter in quarters and place in a plastic funnel. Place the funnel in the mouth of a new 150 ml poly bottle which has been marked at an appropriate volume level and which has been labeled with the client name and sample number. Filter the sample into the bottle, washing the solids 8 M HNO_3 and with water. Discard the filter and resin into a radioactive solid waste container.

A1.1.3.6 Add deionized water to the bottle, filling to the volume mark. Screw on the cap and shake to mix.

A1.1.3.7 Use a disposable pipet to draw a measured aliquot (usually 10 ml) from the sample bottle, transferring it to a 50 ml plastic centrifuge tube labeled with the sample number and the analysis. Record the measured aliquot and the dilution information in the laboratory notebook.

A1.1.3.8 Using a calibrated pipet, add 1.00 ml standardized cerium carrier (nominally 10 mg Ce/ml) to the sample. Proceed to Section 9.4 for chemical separations.

A1.2 Chemical Separation and Purification

This section describes the isolation of cerium by precipitating the fluoride, then the hydroxide, then the oxalate. Wear a laboratory coat, safety glasses and disposable gloves while carrying out the following steps. **Exercise extreme caution when working with HF.**

A1.2.1 Precipitation of CeF3

A1.2.1.1 Add deionized water from a wash bottle to the sample tube to bring the liquid level to near 20 ml.

A1.2.1.2 Wearing a laboratory coat, disposable gloves and a face shield or safety glasses with side shields, and **exercising extreme caution**, add approximately 3 ml concentrated HF from its plastic squeeze container to the sample tube. Stir with a glass rod, but do not leave the rod in the sample tube. Using a deionized water wash bottle, rinse the rod while withdrawing it from the tube.

A1.2.1.3 Make a hot water bath by partly filling a 250 ml or 400 ml beaker with tap water and heating on a moderate hot plate (setting near 3). Place the sample tubes in the bath to precipitate CeF_3. Remove sample tubes from the beaker and place in a rack to cool.

A1.2.1.4 Equalize the liquid levels in the sample tubes and centrifuge for 10 minutes. Decant and discard the supernate into a radwaste beaker.

A1.2.1.5 Rinse the precipitate by adding approximately 5 ml deionized water to the sample tube from a wash bottle. Stir with a glass rod, then rinse the rod while withdrawing it from the tube. Equalize liquid

levels and centrifuge again for 10 minutes. Decant and discard the supernate into a radwaste beaker.

A1.2.1.6 Dissolve the CeF_3 precipitate by adding 1 ml saturated boric acid (H_3BO_3) solution, then 1 ml concentrated HNO_3. Stir (and heat in a water bath if necessary) until the precipitate dissolves.

A1.2.2 Precipitation of $Ce(OH)_3$

A1.2.2.1 Add deionized water from a wash bottle to the sample tube and bring the liquid level to near 20 ml. Stir and add concentrated NH_4OH from a dropping bottle until the solution is basic and particles of $Ce(OH)_3$ form. Do not heat.

A1.2.2.2 Centrifuge the sample for 10 minutes immediately after the preceding step. Discard the supernate into a radwaste beaker.

A1.2.2.3 Add 5 ml 2M H_2SO_4 to the sample tube and stir with a glass rod to break up the precipitate. Add 5 ml deionized water and heat in a water bath for a half hour or longer to dissolve the precipitate. Some particles may remain undissolved.

A1.2.3 Precipitation of $Ce_2(C_2O_4)_3$

A1.2.3.1 With the sample tube still in the water bath from the previous step, add approximately 20 ml saturated ammonium oxalate from a beaker. Stir, then continue heating in the water bath for 20 minutes or longer to precipitate cerium oxalate.

A1.2.3.2 Remove the sample tube and place it in a rack to cool. Proceed to section 6.0 to mount this final precipitate for gravimetric yielding and gamma counting.

A1.3 Mounting the Precipitate

A1.3.1 Prepare a 2.8 cm No. 42 ashless filter paper disc for each sample by mounting it on a vacuum filtration apparatus and rinsing with deionized water and ethanol.

A1.3.2 Place the prepared discs in 4-way partitioned petri dishes which have been marked with sequence numbers (one number per partition, beginning with 1). Write corresponding sequence numbers beside each sample number entry in the laboratory data book. The sequence number indicates the correspondence between a filter and the sample which will be mounted on it.

A1.3.3 Place petri dishes containing prepared filters in an approximately 100°C hot air oven for 10 minutes or longer to dry. Remove petri dishes and allow to cool in a desiccator.

A1.3.4 Weigh the filter discs on the analytical balance using a clean spatula to handle them. Record this tare weight beside the corresponding sequence number and sample number in the laboratory data book. Take care to replace each filter after weighing in the numbered petri dish partition from which it came.

A1.3.5 Using a laboratory spatula, take the tared filters in sequence number order and transfer to the vacuum mounting apparatus. Wet with deionized water. Using the laboratory data book to establish the correspondence between sequence number and sample number, filter each sample from its centrifuge tube onto its corresponding filter disc.

A1.3.6 Rinse precipitate on filter with deionized water and then with ethanol. Transfer each filter from vacuum mounting apparatus back to the numbered petri dish partition from which it came. Place petri dish in a 105-120°C hot air oven for 10 minutes or longer.

A1.3.7 Remove petri dish and allow to cool in desiccator. Weigh filters on the analytical balance within 5 minutes of removing from the desiccator. Write the weights beside the corresponding sequence numbers in the laboratory data book. Return each filter to its original partition in the petri dish.

A1.3.8 Write a gummed label for each sample designated Ce-141, Ce-144, or both. All labels must contain the sample number and customer. Fix each label to the back of a nylon planchet.

A1.3.9 Using the laboratory data book to establish the correspondence between sample number and sequence number, transfer each filter to its planchet and fix in place with a 2-inch piece of Mylar film and a nylon ring. Trim excess Mylar with scissors or a razor blade.

A1.3.10 Subtract filter tare weight from final weight for each sample. Write the difference (mount weight) in the laboratory data book. Divide the mount weight by the corresponding carrier yield figure (written on the cerium carrier flask) to obtain chemical yield. Enter the cerium yield percentage in the laboratory data book.

A1.3.11 Using the laboratory data book as a guide, begin filling out a Radiochemical Work Sheet for each sample. Enter sample number, company name, analysis (Ce-141, Ce-144, or both), collection date, aliquot used, sample type, chemical yield, and analyst's initials.

A1.3.12 Submit finished planchets and work sheets to the Counting Room for radioassay.

A1.3.13 Proceed to: Section 9.4.

APPENDIX 21

STL® STANDARD OPERATING PROCEDURE

TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE

AND SYNTHETIC PRECIPITATION LEACHING PROCEDURE

(SUPERSEDES: REVISION 0)

Prepared by: _____
Kurt Ill

Reviewed by: _____
Technology Standardization Committee

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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1. SCOPE AND APPLICATION

1.1. This SOP describes the application of the Toxicity Characteristic Leaching Procedure (TCLP), SW846 Method 1311. The Toxicity Characteristic (TC) of a waste material is established by determining the levels of 8 metals and 31 organic chemicals in the aqueous leachate of a waste. The TC is one of four criteria in 40 CFR Part 261 to determine whether a solid waste is classified as a hazardous waste. The other three are corrosivity, reactivity and ignitability. The TC Rule utilizes the TCLP method to generate the leachate under controlled conditions which were designed to simulate leaching through a landfill. EPA's "worst case" waste disposal model assumes mismanaged wastes will be exposed to leaching by the acidic fluids generated in municipal landfills. The EPA's model also assumes the acid/base characteristics of the waste will be dominated by the landfill fluids. The TCLP procedure directs the testing laboratory to use a more acidic leaching fluid if the sample is an alkaline waste, again in keeping with the model's assumption that the acid fluids will dominate leaching chemistry over time.

1.2. The specific list of TC analytes and regulatory limits may be found in Appendix A.

Note: The list in Appendix A does not include the December 1994 EPA rule for Universal Treatment Standards for Land Disposal Restrictions. Those requirements include 216 specific metallic and organic compounds and, in some cases, lower detection limit requirements (see 40 CFR 268.40). TCLP leachates are part of the new Universal Treatment Standards, but the conventional analytical methods will not necessarily meet the new regulatory limits. Consult with the client and with STL® Technical Specialists before establishing the instrumental methods for these regulations.

1.3. This SOP also describes the application of the Synthetic Precipitation Leaching Procedure (SPLP) which was designed to simulate the leaching that would occur if a waste was disposed in a landfill and exposed only to percolating rain water. The procedure is based on SW846 Method 1312. The list of analytes for SPLP may extend beyond the toxicity characteristic compounds shown in Appendix A. With the exception of the use of a modified extraction fluid, the SPLP and TCLP protocols are essentially equivalent. Where slight differences may exist between the SPLP and TCLP they are distinguished within this SOP.

1.4. The procedure is applicable to liquid, solid, and multiphase wastes.

1.5. The results obtained are highly dependent on the pH of the extracting solution, the length of time that the sample is exposed to the extracting solution, the temperature

during extraction, and the particle size/surface area of the sample. These parameters must be carefully controlled.

1.6. The reporting limits are based on the individual samples as well as the individual analysis techniques. However, the sample is determined to be hazardous if it contains any analyte at levels greater than or equal to the regulatory limits.

1.7. If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the procedure need not be run. If the total analysis results indicate that TCLP is not required, the decision to cease TCLP analysis should be remanded to the client.

1.8. If an analysis of any one of the liquid fractions of the procedure leachate indicates that a regulated compound is present at such a high concentration that, even after accounting for dilution from the other fractions of the leachate, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it may not be necessary to analyze the remaining fractions of the leachate. However, the remaining analyses should not be terminated without the approval of the client.

1.9. Volatile organic analysis of the leachate obtained using a bottle extraction, normally used for extractable organics and metals, can be used to demonstrate that a waste is hazardous, but only the ZHE option can be used to demonstrate that the concentration of volatile organic compounds is below regulatory limits.

2. SUMMARY OF METHOD

2.1. For liquid wastes that contain less than 0.5% dry solid material, the waste, after filtration through 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP leachate.

2.2. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solids and stored for later analysis. The particle size of the remaining solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. For TCLP, the extraction fluid employed for extraction of non-volatile analytes is a function of the alkalinity of the solid phase of the waste. For SPLP, the extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater the extraction fluid employed is a pH 4.2 solution. Two leachates may be generated: a) one for analysis of non-volatile constituents (semi-volatile organics, pesticides, herbicides and metals and/or b) one from a Zero Headspace Extractor (ZHE) for analysis of volatile organic constituents.

Following extraction, the liquid leachate is separated from the solid phase by filtration through a 0.6 to 0.8 μm fiber filter.

2.3. If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid leachate and these are prepared and analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3. DEFINITIONS

3.1. "Leachate" is used to refer to the TCLP solution generated from this procedure.

3.2. "Percent Wet Solids" is that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure.

4. INTERFERENCES

4.1. Oily wastes may present unusual filtration and drying problems. As recommended by EPA (see Figure 3), oily wastes will be assumed to be 100% liquid and analysis for total concentrations of contaminants will be performed. This applies specifically to samples containing viscous non-aqueous liquids that would be difficult to filter.

4.2. Wastes containing free organic liquids (i.e., those with separable non-aqueous liquid phases) will be assumed to be 100% liquid and totals analysis will be performed to determine if the oil exceeds TCLP limits.

4.3. Solvents, reagents, glassware and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks as described in the Section 9.0 and the individual determinative SOPs.

4.4. Glassware and equipment contamination may result in analyte degradation. Soap residue on glassware and equipment may contribute to this. All glassware and equipment should be rinsed very carefully to avoid this problem.

4.5. Phthalates may be eliminated by proper glassware cleanup and by avoiding plastics. Only glass, Teflon or Type 316 stainless steel tumblers may be used for leachates to be analyzed for organics. Plastic tumblers may be used for leachates to be analyzed for the metals.

4.6. Overexposure of the sample to the environment will result in the loss of volatile components.

4.7. Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL® associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include:

Methylene chloride

5.3.2. Chemicals known to be **flammable** are:

Methanol

5.3.3. The following materials are known to be **corrosive**:

Hydrochloric acid, nitric acid, sulfuric acid, acetic acid, sodium hydroxide

The following materials are known to be **oxidizing agents**:

Nitric Acid.

5.4. Gas pressurized equipment is employed in this procedure. Be sure all valves and gauges are operating properly and that none of the equipment, especially tubing, is over-pressurized. CAUTION: Do not open equipment that has been pressurized until it has returned to ambient pressure.

5.5. A rotary agitation apparatus is used in this procedure. Certain samples may break the glass jars used in the procedure. For these samples, extra caution, including plastic or polyethylene overwraps of the glass jar, may be necessary.

5.6. Secure tumbler and extraction apparatus before starting rotary agitation apparatus.

5.7. During sample rotation, pressure may build up inside the bottle. Periodic venting of the bottle will relieve pressure.

5.8. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.9. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL® associate. The situation must be reported **immediately** to a laboratory supervisor.

5.11. Due to the potential for ignition and/or flammability, do not attempt to dry non-aqueous liquid samples in an oven.

6. EQUIPMENT AND SUPPLIES

6.1. Extraction vessels

6.1.1. For volatile analytes - zero-headspace extraction (ZHE) vessel, gas-pressure actuated, Millipore YT3009OHW or equivalent (see Figure 2).

6.1.2. For metals - either borosilicate glass jars (1/2 - 1 gallons, with Teflon lid inserts) or 1 L HDPE (Nalgene or equivalent) bottles may be used.

6.1.3. For non-volatile organics - only borosilicate glass may be used.

6.2. Vacuum filtration apparatus, capable of 0 - 50 psi and stainless steel pressure filtration apparatus (142 mm diameter), capable of 0 - 50 psi.

6.3. Borosilicate glass fiber filters, 0.6 - 0.8 μm (Whatman GF/F 14.2 cm, 0.7 μm or equivalent). When analyzing for metals, wash the filters with 1 N nitric acid and de-ionized water prior to use. As an alternative, certified pre-washed filters may be used. Glass fiber filters are fragile and should be handled with care.

6.4. Rotary agitation apparatus, multiple-vessel, Associated Design and Manufacturing Company 3740-6 or equivalent (see Figure 1). The apparatus must be capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm.

6.5. ZHE Extract Collection Devices are used to collect the initial liquid phase and the final extract of the waste from the ZHE device, either of the following may be used:

6.5.1. Gas-tight syringes, 100 mL capacity, Hamilton 0158330 or equivalent, or

6.5.2. Tedlar bags

6.6. Top loading balance, capable of 0 - 4000 ± 0.01g (all measurements are to be within ± 0.1 grams).

6.7. pH meter and probe capable of reading to the nearest 0.01 unit, and with automatic temperature compensation.

6.8. pH probes.

6.9. Magnetic stirrer/hotplate and stirring bars.

6.10. VOA vials, 20 mL, with caps and septa.

6.11. Glass jars, 1/2 - 1 gallon, with Teflon lid-inserts.

6.12. Nalgene plastic bottles, 1 liter.

6.13. Miscellaneous laboratory glassware and equipment.

7. REAGENTS AND STANDARDS

7.1. Reagent water for non-volatile constituents must be produced by a Millipore DI system or equivalent. For volatile constituents, water must be passed through an activated carbon filter bed (Milli-Q or tap water passed through activated carbon). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Hydrochloric acid, 1 N: Carefully add 83 mL concentrated reagent grade HCl to 800 mL reagent water, cool and dilute to 1 liter with reagent water. Cap and shake to mix well.

7.3. Nitric acid, 1 N: Carefully add 64 mL concentrated reagent grade HNO_3 to 800 mL of reagent water, cool and dilute to 1 liter with reagent water. Cap and shake to mix well.

7.4. Sodium hydroxide, 1 N: Carefully add 40 g reagent grade NaOH pellets to 800 mL reagent water, stir until the pellets are completely dissolved, cool and dilute to 1 liter with reagent water.

CAUTION: Heat is generated during this process.

7.5. Acetic acid, glacial: concentrated, reagent grade liquid (HOAc).

7.6. pH calibration solutions: buffered to a pH of 4, 7, and 10. Commercially available. Fresh buffer solution must be used each day of analysis.

7.7. TCLP Leaching Fluids

7.7.1. General Comments

7.7.1.1. The pH of both solutions listed below should be monitored daily and the pH probes are to be calibrated prior to use.

7.7.1.2. The leaching fluids MUST be prepared correctly. If the desired pH range is not achieved and maintained, the TCLP may yield erroneous results due to improper leaching. If the pH is not within the specifications, the fluid must be discarded and fresh extraction fluid prepared.

7.7.1.3. Additional volumes of extraction fluids listed above may be prepared by multiplying the amounts of acetic acid and NaOH by the number of liters of extraction fluid required.

7.7.2. TCLP Fluid #1: Carefully add 5.7 mL glacial acetic acid and 64.3 mL of 1 N NaOH to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. When correctly prepared, the pH of this solution is 4.93 ± 0.05.

7.7.3. TCLP Fluid #2: Carefully add 5.7 mL glacial acetic acid to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with

reagent water, cap and shake to mix well. When correctly prepared, the pH of this solution is 2.88 ± 0.05.

7.8. Nitric acid, 50% solution: Slowly and carefully add 500 mL concentrated HNO_3 to 500 mL reagent water. Cap and shake to mix well.

7.9. Sulfuric acid / nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

7.10. SPLP Leaching fluids

7.10.1. SPLP solutions are unbuffered and exact pH may not be attained. The pH of TCLP and SPLP fluids should be checked prior to use. If not within specifications, the fluid should be discarded and fresh fluid prepared.

7.10.2. SPLP fluid #1: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 4.20 ± 0.05 This fluid is used for soils from a site that is east of the Mississippi River and for wastes and wastewaters.

7.10.3. SPLP fluid #2: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 5.00 ± 0.05. This fluid is used for soils from a site that is west of the Mississippi River.

7.10.4. SPLP fluid #3: This fluid is reagent water and is used for leaching of volatiles. Additionally, any cyanide-containing waste or soil is leached with fluid #3 because leaching of cyanide containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.11. Methanol and methylene chloride - used to aid in cleaning oil contaminated equipment.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples being analyzed for non-volatile organic compounds should be collected and stored in glass containers with Teflon lid liners. Chemical preservatives shall NOT be added UNTIL AFTER leachate generation.

8.2. Samples being analyzed for metals only can be collected in either glass or polyethylene containers.

8.3. When the waste is to be evaluated for volatile analytes, care should be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in

Teflon lined septum capped vials with minimal headspace and stored at 4 ± 2 ^{o}C). Samples should be opened only immediately prior to extraction.

8.4. Samples should be refrigerated to 4 ± 2 ^{o}C unless refrigeration results in irreversible physical changes to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

8.5. The minimum TCLP sample collection size is determined by the physical state or states of the waste and the analytes of concern. The amount of waste required varies with the percent solids. The lower the percent solids, the more waste will be required for preliminary and final testing. For aqueous samples containing between 0.5 and 10% solids, several kilograms of sample are required to complete the analyses. The general minimal requirements when the samples are 100% solids include: 1 - 32 oz jar for semi-volatile organic analysis and metals, and 1 - 4 oz jar for volatile organic analysis. Low density sample materials, such as rags or vegetation, will require larger volumes of sample. For liquid samples (less than 50% solids), minimum requirements are 2 - 32 oz jars for semi-volatile organic analysis and metals, and 2 - 8 oz jars for volatile organic analysis. If volatile organic analysis is the only requested parameter, 2 separate jars are required. If matrix spike or duplicate control samples are requested, additional sample volume is required. If sufficient sample volumes were not received, analyses cannot be started and the client should be notified as soon as possible.

8.6. TCLP leachates should be prepared for analysis and analyzed as soon as possible following extraction. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs. If precipitation occurs upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate shall not be acidified and the leachate shall be analyzed as soon as possible. All other leachates should be stored under refrigeration (4 ± 2 °C) until analyzed. ZHE leachates must be stored in VOA vials filled to eliminate all headspace.

8.7. Samples are subject to appropriate treatment within the following time periods:

Table 1 - Holding Times (days)

Parameter	Collection to Start of TCLP Leach	End of TCLP Tumble to Preparation	Start of TCLP Leach or Semi- volatile Prep Extraction to Analysis	Total Elapsed Time
Volatiles:	14	N/A	14	28
Semi-volatiles:	14	7	40	61
Mercury:	28	N/A	28	56
Other Metals:	180	N/A	180	360

NOTE: The initial holding time is measured from date of collection to date TCLP extraction started. (This should be the TCLP extraction date in QuanTims.) Semi-volatile method prep holding time is measured from the day tumbling is complete to the start of method extraction. Subsequent analysis holding times are measured from the date extraction (TCLP or method prep) starts**.** If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding holding times is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory limit. The Total Elapsed Time is to be used as guidance. If preps are initiated at the last possible moment of a holding time, the elapsed times may be exceeded.

9. QUALITY CONTROL

9.1. Quality Control Batch (QC Batch) - QA-003 defines a QC Batch as a set of up to 20 field samples of similar matrix that behave similarly and are processed using the same procedures, reagents and standards within the same time period. The same lot of reagents must be used within a batch. A minimum of one TCLP extraction blank (Method Blank), one Laboratory Control Sample (LCS), one Matrix Spike (MS), and one Matrix Spike Duplicate (MSD) will be prepared with each TCLP leachate batch.

9.2. Batching Samples - Groups of samples with visibly different bulk matrices (e.g., petroleum sludge and soil samples) must be batched separately for QC testing purposes.

9.3. TCLP Extraction Blanks - A minimum of one blank (using the same extraction fluid as used for the samples) must be prepared and analyzed for every batch of samples extracted in a particular vessel type. The blanks are generated in the same way as the samples (i.e., blanks will be tumbled and filtered with the samples). Extraction vessels will be uniquely numbered. Each time a new batch is set up the blank should be rotated sequentially to the next vessel to ensure all vessels are periodically checked. Consult the STL® QC Program and the individual analysis SOPs for blank acceptance criteria.

9.4. Laboratory Control Sample (LCS) - A LCS is required with each batch of 20 or fewer samples. The LCS shall be generated after a batch of TCLP leachates have been generated (i.e., at the time of the preparative digestion or extraction) by spiking an aliquot of the appropriate extraction fluid used for that batch. Consult the individual analysis SOPs for additional LCS guidance (i.e., spike amounts, spike levels, recovery criteria, etc.).

9.5. Matrix Spike (MS/MSD) - Matrix spikes are used to monitor the performance of the analytical methods on the matrix and to assess the presence of interferences. A MS/MSD pair are required with each batch of 20 or fewer samples.

9.5.1. Matrix spikes are to be added after filtration of the TCLP leachate. Spikes are not to be added prior to the TCLP leaching. <u>For metals, matrix spikes are to be added before preservation with nitric acid</u>.

9.5.2. The use of internal calibration or alternate methods may be needed when the recovery of the matrix spike is below the expected performance (see Section 9.6.2).

9.5.3. Consult the individual analysis SOPs for additional guidance on spike compounds and levels.

9.6. Corrective Actions

9.6.1. Consult the STL® QC Program and individual analysis SOPs for corrective action for blanks and LCS

9.6.2. Method of Standard Additions (MSA) shall be used for metals if all of the following conditions are met:

- Recovery of the analyte in matrix spike is not at least 50%,
- the concentration of the analyte does not exceed the regulatory level, and
- the concentration of the analyte measured in the sample is within 20% of the appropriate regulatory level.

If the matrix spike recovery is 5% or less due to dilution or matrix interference, contact the project manager and client for guidance. The client should also be contacted prior to initiation of any MSA steps. Refer to the individual analysis SOPs for details on how to perform MSA analysis.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to appropriate analysis SOPs.

11. PROCEDURE

11.1. GENERAL COMMENTS

11.1.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented on a Nonconformance Memo kept in the project file and described in the final report. The variation must be approved by a project manager, Technical Specialist and QA Manager. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2. PRELIMINARY SAMPLE EVALUATIONS (Refer to Flow Chart #1, Appendix D)

11.2.1. Preliminary TCLP evaluations (percent solids, particle size, selection of extraction fluid, and fluid/leachate compatibility) are required to be done using a minimum of a 100 gram aliquot of waste. This aliquot may also undergo the actual TCLP or SPLP extraction for Non-volatiles ONLY IF it has NOT been oven dried. If the solid portion is oven dried, a separate aliquot must be used for the actual leaching procedure.

11.2.2. Consult the holding times for the appropriate tests (Section 8.7) and prioritize extractions such that holding times are not exceeded.

11.2.3. Determine the total volume of TCLP leachate (solid phase leachate + liquid filtrate) that needs to be generated for analysis according to the following:

Table 2. Minimum Required Leachate Volume

Analysis	Required Volume (mL)
Volatiles	3 x 20
Semi-volatiles	400
Pesticides	200
Herbicides	200
Metals	300

11.2.3.1. SPLP - similar volumes are required for volatiles and metals. If semivolatiles, pesticides or herbicides are required, a full 1 L volume must be prepared for each test requested.

11.2.3.2. For TCLP and SPLP samples used for matrix spike and matrix spike duplicate analysis, three times the listed volumes are required.

11.2.4. **Sample Description** (enter data on Worksheet 1)

11.2.4.1. Record the number of phases observed in the sample. It is common that when more than one container of multi-phasic materials is received from the field, each container will show different amounts of each phase.

11.2.4.1.1. If the sample has multiple phases and is received in more than 1 bottle then the contents of each bottle should be combined in a single larger container prior to processing the sample further. If this is not

possible, then the alternate procedure described in the following section should be used.

11.2.4.1.2. Properly record the relative amounts of each phase by measuring the depth of the layers in each container after the contents have been allowed to settle. Determine the combined volume of each phase for all containers. Then mark the phase composition on a single container, mix thoroughly to obtain a representative subsample, and accurately measure the phase composition according to the following procedure. The two sets of values (combined volumes per phase and phase composition for one container) are used to determine the correct volume/mass adjustments on the final result. This procedure is not appropriate if testing will be done for volatile organic compounds.

11.2.4.2. Solid - record the visible presence of a solid material heavier than water. If the sample contains more than one solid phase (e.g., wood and sediment mixed with water), attach additional documentation to Worksheet 1, line A1.

11.2.4.3. Liquid - record the number of liquid phases observed in the sample according to apparent density. It may be impossible to distinguish apparent density if only one liquid phase is observed and there is no indication on the COC form. If this is the case, record it as aqueous material and let the subsequent analytical record show if the liquid is organic.

11.2.5. **Percent Solid Phase** (enter data on Worksheet No. 1)

11.2.5.1. Percent Solids and ZHE Extractions - The ZHE filtration apparatus cannot accurately determine percent solids less than 5%. If an extraction is to be performed solely for volatile organic compounds and the percent solids concentration is apparently greater than 5%, proceed to Section 11.4 (Procedure: ZHE Extraction Procedure, Volatile Constituents). Otherwise, continue with the steps in this section. The aliquot of sample used here cannot be used again for the ZHE extraction.

11.2.5.2. Determine Type of Filtration Apparatus Needed

11.2.5.2.1. If the waste will obviously yield no free liquid when subjected to pressure filtration (i.e., it is 100% solid), then proceed to Section 11.2.6 (Particle-size Reduction).

11.2.5.2.2. If the sample is mostly a non-viscous liquid (water or non-viscous organic liquid) of low solids content (<10%) or a highly granular, liquid containing waste vacuum filtration may be used.

11.2.5.2.3. If the sample is viscous (sludge or has high solids content), use pressure filtration.

11.2.5.3. Weight of filter - Measure and record this value before loading the filter into the filter holder (Worksheet 1, line B1).

11.2.5.4. Weight of subsample and filtrate for percent solids measurement

11.2.5.4.1. Assemble the filtration apparatus (use blunt forceps to handle the 0.6 to 0.8 μm filter membrane).

11.2.5.4.2. Homogenize the waste, transfer a minimum of a 100 g subsample to the weighing vessel. Measure and record the gross weight (Worksheet 1, line B2a).

11.2.5.4.3. Measure and record the tare weight of the filtration vessel (Worksheet 1, line B3b).

11.2.5.4.4. Transfer the sample to the filtration device attempting to spread the waste sample evenly over the surface of the filter. Measure and record the tare weight of the empty weighing vessel and any residual sample (Worksheet 1, line B2b).

11.2.5.4.5. Calculate and record the net weight of sample used for testing (Worksheet 1, line B2c).

11.2.5.5. Filtration for percent solids

11.2.5.5.1. Slowly apply gentle pressure or vacuum of 10 psi to the filtration apparatus. Allow the sample to filter until no SIGNIFICANT additional liquid has passed through the filter during a 2 minute period.

11.2.5.5.2. Repeat previous step by increasing the pressure in 10 psi increments until a maximum of 50 psi is reached. Stop the filtration when no additional filtrate is generated within a 2 minute period.

Note: Some samples will contain liquid material that does not filter (e.g., oil). Do not attempt to filter the sample again by exchanging filters. Viscous oils or any wastes which does not pass through the filter is classified as a solid.

11.2.5.5.3. Remove the filtrate collection vessel, weigh and record the gross weight (Worksheet 1, line B3a).

11.2.5.5.4. Calculate and record the net weight of filtrate (Worksheet 1, line B3c). This result will be used in the percent solids calculation.

11.2.5.5.5. Pour the filtrate into a graduated cylinder. Measure and record the volume of the aqueous phase (Worksheet 1, line B7). Measure and record the volume of any organic phase (Worksheet 1, line B8). If more than one organic phase is observed, enter "see below" and provide a description at the bottom of Worksheet 1. These results will be used in the final sample calculations (Worksheets 5 & 6).

11.2.5.5.6. Retain the filtrate for use in Section 11.2.8 (Determination of Filtrate/Extraction Fluid Compatibility), and for possible recombination with the filtrate obtained in Section 11.3.

11.2.5.6. Percent of Wet Solids

11.2.5.6.1. Calculate the total weight of wet solids using Equation 0 on Worksheet 1 and record the result on line B4.

11.2.5.6.2. Calculate the weight percent of wet solids using Equation 1 on Worksheet 1 and record the result on line B5.

11.2.5.6.3. If the percent wet solids result is $\geq 0.5\%$ and $< 5.0\%$, and it is noticed that a small amount of the aqueous filtrate is entrained in the wetting of the filter, proceed

to Section 11.2.5.7 to complete the percent solids measurement on a dry-weight basis.

Note: If obviously oily (non-aqueous) material is entrained on the filter, do not dry the filter; proceed to Section 11.2.6 (Particle-Size Reduction).

11.2.5.6.4. If the percent wet solids result is greater than 5.0%, proceed to Section 11.2.6 (Particle-Size Reduction) and mark "≥0.5%" on Worksheet 1, line B6c.

11.2.5.6.5. If the percent wet solids result is less than 0.5%, discard the solid phase. No leaching will be necessary; the filtrate is equivalent to the final leachate.

11.2.5.7. Weight percent of dry solids (skip this step for oily samples).

Note: These steps are required only if it is noticed that a small amount of the filtrate is entrained in wetting of the filter and the percent wet solids content is ≥ 0.5% and < 5.0 %.

11.2.5.7.1. Remove the filter with the wet solids from the filtration apparatus.

11.2.5.7.2. Dry the filter and solid phase at 100 ± 20 ° C.

11.2.5.7.3. Remove the filter from the oven and allow to cool in a desiccator.

11.2.5.7.4. Weigh and record the gross dry weight (Worksheet 1, line B6a).

11.2.5.7.5. Repeat the drying step. Weigh and record the second gross dry weight (Worksheet 1, line B6b). If the two weightings do not agree within 1%, perform additional drying and weighing until successive weighings agree within 1%.

11.2.5.7.6. Calculate the weight percent of dry solids using Equation 2 on Worksheet 1 and record the result on line B6c.

11.2.5.7.7. If the dry solids result is ≥ 0.5% and the sample will be extracted for non-volatile constituents, proceed to

Section 11.2.6 (Particle Size Reduction) using a fresh wet portion of waste.

11.2.5.7.8. If the percent solids result is less than 0.5%, discard the solid phase. No leaching will be necessary; the filtrate is the TCLP leachate. Proceed to Section 11.2.8 (Determination of Filtrate/Leachate Compatibility) to determine whether or not the material is a non-aqueous, immiscible liquid.

11.2.6. **Particle-size Reduction for Fluid Selection** (enter data on Worksheet 2)

11.2.6.1. The subsample used for fluid selection must consist of particles less than 1 mm in diameter (versus the less than 1 cm requirement for the material used for the actual extraction). The method requires a smaller particle size to partially compensate for the shorter duration of contact time with the leachate solution as compared to the full extraction. Inappropriate use of coarser materials could result in the selection of the wrong fluid type.

11.2.6.2. Surface area exclusion - size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. Enter "No" on Worksheet 2, line C1.

11.2.6.3. If the sample contains particles greater than 1 mm in diameter, crush, cut, or grind the solids to the required size. Enter "Yes" on Worksheet 2, line C1.

11.2.6.4. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick).

11.2.7. **Determination of Appropriate Extraction Fluid** (Worksheet 2)

11.2.7.1. If the solid content is greater than or equal to 0.5%, and if the sample is being analyzed for metals or nonvolatile organic compounds, the type of leaching solution must be determined.

11.2.7.2. Follow times, temperature, and particle size specified in this section as closely as possible. If reaction time between the acid solution and solid waste is too short or too long, the procedure may produce false pH readings.

11.2.7.3. For SPLP, refer to Section 7.10 for fluid selection. Matrix type must be specified by the client. Check special instructions or see

the project manager, then put a check mark by the fluid type selected (Worksheet 2, D).

11.2.7.4. The TCLP leaching fluid for all volatiles is Fluid #1.

11.2.7.5. For TCLP leach fluid determination for non-volatile analytes, continue with the following steps.

11.2.7.6. Calibrate the pH meter with fresh buffer solution in accordance with the pH SOP.

11.2.7.7. Weigh out a 5.0 ± 0.1 g subsample (less than 1 mm particle size) of the solid phase into a 250-mL beaker, and enter a "✓" on Worksheet 2, line C2. If 5.0 grams not used, enter the actual weight on line C2.

11.2.7.8. Add 96.5 ± 1.0 mL of reagent water, cover with a watchglass, and stir for 5 minutes on a stirrer, and enter a "✓" on Worksheet 2, line C3. If a different volume used, enter the actual volume on line C3.

11.2.7.9. Measure and record the sample pH (Worksheet 2, line C4).

Note: To avoid damaging the pH probe when organic liquid is present, use narrow range pH indicator paper.

11.2.7.10. If the pH is less than or equal to 5.0, use Fluid #1 and proceed to Section 11.2.8 (Fluid Compatibility).

11.2.7.11. If the fluid pH is greater than 5.0, add 3.5 mL 1 N HCl, cover with a watchglass. Slurry the sample briefly then heat at 50 ^{o}C for 10 minutes. Enter a "✓" on Worksheet 2, line C5 and C6).

Note: The heating cycle is a critical step. If the solid waste does not remain in contact with the acidic solution under specified time and temperature conditions, an erroneous pH may be measured.

11.2.7.12. Cool to room temperature.

11.2.7.13. Measure and record the pH immediately after the sample has reached room temperature (Worksheet 2, line C7).

11.2.7.13.1. If the pH is less than or equal to 5.0, use Fluid #1. Enter a "✓" on Worksheet 2, line D1.

11.2.7.13.2. If the pH is greater than 5.0, use Fluid #2. Enter a "✓" on Worksheet 2, line D2.

11.2.8. **Determination of Filtrate/Extraction Fluid Compatibility** (skip this step for SPLP extractions)

11.2.8.1. Place 5 mL of the appropriate leaching fluid (determined in the previous step) into a 20-25 mL vial.

Note: Use fluid type # 1 if simply testing the filtrate for a sample with less than 0.5% solids.

11.2.8.2. Add 5 mL of the initial filtrate, cap and shake.

11.2.8.3. If the phases are miscible, the initial filtrate and solid phase leachate will be physically recombined upon completion of the leachate generation. Enter a "✓" on Worksheet 2, line D3 for TCLP, or on line D1 for SPLP.

11.2.8.4. If the phases are NOT miscible, enter "No" on Worksheet 2, line D3. The initial filtrate and the solid phase leachate will be prepared and analyzed separately and the results mathematically combined (see Section 12.1.4).

11.2.9. For samples requiring analysis for semi-volatile organics, pesticides, herbicides or metals proceed to Section 11.3.

11.2.10. For samples requiring analysis for volatile organics (ZHE), proceed to Section 11.4.

11.3. **BOTTLE EXTRACTION PROCEDURE: NON-VOLATILE CONSTITUENTS: SEMI-VOLATILES, PESTICIDES, HERBICIDES, METALS** (Refer to Flow Chart #2, Appendix D)

11.3.1. All masses should be recorded to the nearest 0.1 g.

11.3.2. The aliquot used in the Preliminary Evaluation MAY be used for this procedure ONLY if it was not oven dried. If the sample is 100% solid or if the preliminary aliquot was not oven dried proceed directly to Section 11.3.7 (Particle Size Reduction). If the Preliminary Evaluation aliquot was oven dried then, using a fresh aliquot of sample, continue as described in Sections 11.3.3 through 11.3.6.

11.3.3. Examine the sample and determine the type of filtration to employ per Section 11.2.5.2.

11.3.4. Repeat the steps outlined in Sections 11.2.5.3 through 11.2.5.5.3.

11.3.5. Determine and record the volume (mass) of the initial filtrate. Cover with aluminum foil and retain for use as defined in Section 11.3.18.

11.3.6. Determine and record the "solid" phase mass by subtracting the mass of the liquid filtrate from the mass of the subsample.

11.3.7. Evaluate the solid portion of the waste for particle size. If it contains particles greater than 1 cm in size, prepare the solid portion of the waste for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size (i.e., capable of passing through a 9.5 mm, 0.375 inch, standard sieve). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. If particle size reduction was required, record this on Worksheet 3, line E1.

11.3.7.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding should be subcontracted out for particle size reduction. (Contact PA or PM.) Note that size reduction to fine powder is not appropriate, and could invalidate results. If necessary, consult client for guidance.

11.3.8. Determine the minimum total volume of solid phase leachate that needs to be generated. Refer to Section 11.2.3.

11.3.9. Divide the total volume of solid phase leachate required by 20 to determine the mass of solid phase required for leaching. Round this mass UP to the nearest 5g.

11.3.10. Weigh the required mass of solid phase into an appropriate bottle (plastic for metals only, glass for all others) and **slowly** add 20 times its mass of appropriate leaching fluid as determined under Section 11.2.7 (e.g., 20 g of sample would require 400 g of leaching fluid). Record the weight of the sample aliquoted for the extraction on Worksheet 3, line E2 and the amount of extraction fluid added on line F1.

11.3.11. Ensure any effervescence has stopped before capping the bottle tightly. Secure in a rotary agitator and rotate end-over-end at 28-32 rpm for 16-20

hours. The temperature of the room should be 23 ± 2°C. The room temperature and time should be checked at both the start and end of the extraction and recorded on Worksheet 3, lines G1 through G3.

NOTE: As agitation continues, pressure may build up within the bottle for some types of wastes. To relieve excessive pressure, the bottle may be removed and opened periodically in a properly vented hood to relieve any built-up pressure.

11.3.12. Remove the bottle and filter the sample using vacuum or pressure filtration by filtering through a new glass fiber filter as discussed in Sections 11.2.5.5.1 - 11.2.5.5.2. For final filtration of the TCLP leachate, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filters must be acid washed if metals are to be determined (see Section 6.3). The entire sample need not be filtered; however, sufficient volume should be generated to support the required analyses. Record the date and time the filtration is completed on Worksheet 3, Line G4.

11.3.13. If the waste contained no initial filtrate, this solution from 11.3.12 is defined as the TCLP leachate.

11.3.14. If the waste did yield an initial filtrate, consult the worksheet for initial filtrate/leachate compatibility. If they are compatible, they are to be combined in the correct proportions (see Section 12.1.4) and mixed well. This combined solution is defined as the TCLP leachate.

11.3.15. If the individual phases are NOT compatible, they are to be prepared and analyzed separately and the results combined mathematically. See Section 12.1.5.

11.3.16 Measure and record the pH of the TCLP leachate on Worksheet 3, Line 5. (Do not attempt to measure the pH of oily samples as the probe may be rendered inoperable.)

11.3.17. Prepare subsamples for metals for MS/MSD quality control testing using the appropriate TCLP spiking solution (do not spike for organics). Refer to the appropriate determinative SOPs for further guidance on the spike components, levels and action criteria.

11.3.18. Immediately preserve the leachate as follows:

Metals	pH < 2 w/50% HNO_3 for non-oils (do not acidify oils)
All others	Refrigerate to 4 ± 2 ^{o}C

Note: Refer to Section 8.6 if precipitation occurs upon preservation.

11.3.19. Label each sample with the appropriate information and submit to the appropriate analytical groups for prep and analysis with copies of the TCLP preparation worksheets.

11.4. **ZHE EXTRACTION PROCEDURE: VOLATILE CONSTITUENTS** (Refer to Flow Chart #3, Appendix D)

11.4.1. Use the ZHE device to obtain a TCLP leachate for analysis of volatile compounds only. Leachate resulting from the use of the ZHE shall NOT be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc...).

11.4.2. Due to some shortcomings of the method, losses of volatile compounds may occur. Extra care should be observed during the ZHE procedure to ensure that such losses are minimized. Charge the ZHE with sample only once and do not open the device until the final extract has been collected. Do not allow the waste, the initial liquid phase or the extract to be exposed to the atmosphere any longer than necessary.

11.4.3. If the TCLP extraction is for volatile components only, refer to Section 11.2.5.1 before proceeding.

11.4.4. All masses should be recorded to the nearest 0.1 g.

11.4.5. Assemble the ZHE apparatus. Test for leakage by closing all valves except the gas inlet/outlet valve and pressurizing to 50 psi. Allow to stand for 15 minutes and check the pressure on the built-in gauge to make sure it is not leaking. If the pressure is NOT 50 psi, consult your supervisor.

11.4.6. Adjust the ZHE piston in the ZHE body to the appropriate height (slightly moisten the O-rings with leaching fluid if necessary).

11.4.7. Consult the worksheet and examine the sample. If the sample appears to be different from the preliminary information found on the worksheet, consult your supervisor.

11.4.8. If the preliminary evaluations indicated the need for particle size reduction, homogenize the waste, weigh out a sufficient size subsample and prepare for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size as measured with a ruler (Do NOT sieve the sample). Size reduction is not required if the sample surface area is greater than or equal to

TABLE II. ICP and FLAA Soil Matrix Spike and Aqueous LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)	Soil MS Level ** (mg/Kg)
Aluminum	200	2000	200
Antimony	50	500	50
Arsenic	200	2000	200
Barium	200	2000	200
Beryllium	5	50	5
Cadmium	5	50	5
Calcium	5000	50000	5000
Chromium	20	200	20
Cobalt	50	500	50
Copper	25	250	25
Iron	100	1000	100
Lead	50	500	50
Lithium	100	1000	100
Magnesium	5000	50000	5000
Manganese	50	500	50
Molybdenum	100	1000	100
Nickel	50	500	50
Phosphorous	1000	10000	1000
Potassium	5000	50000	5000
Selenium	200	2000	200
Silver	5	50	5
Sodium	5000	50000	5000
Strontium	100	1000	100
Thallium	200	2000	200
Vanadium	50	500	50
Zinc	50	500	50
Boron	100	1000	100
Silica	1000	10000	1000
Tin	200	2000	200
Titanium	100	1000	100

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.3) to 100 mL of sample.

** Final soil spike concentration based on the addition of 1.0 mL working spike (7.3) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE III. GFAA Soil Matrix Spike and Aqueous LCS Spike Levels

3.1 cm^2 per gram If particle size reduction was required record this on Worksheet 4, Line H1.

Note: To minimize loss of volatiles, samples for volatiles that require particle size reduction should be kept in sample storage (at 4 ºC) until immediately before size reduction. Aggressive reduction which would generate heat should be avoided and exposure of the waste to the atmosphere should be avoided to the extent possible. Size reduction to a fine powder is not appropriate. Also see Section 11.3.11.

11.4.8.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding should be subcontracted out for particle size reduction (Contact PA or PM).

11.4.9. Place the ZHE apparatus on the balance and tare the balance.

11.4.10. Determine the appropriate size subsample to weigh using the percent solids information from Section 11.2.5 and record the weight used on Worksheet 4, Line H2.

11.4.10.1. For wastes that are 100% solids, a 25 g sample is used.

11.4.10.2. For wastes containing < 0.5% solids the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Filter enough of the sample to support all of the volatile analyses required.

11.4.10.3. For wastes containing ≥ 0.5% and < 5.0% solids, a 500 g subsample of waste is recommended.

11.4.10.4. If the sample has ≥ 5.0% solids, the appropriate sample size should be determined using the equation in Section 12.1.2.

Note: For wastes containing greater than 0.5% wet or dry solids (Section 11.2.5), the "solids" value from the ZHE filtration process may be used to determine the volume of fluid to load into the ZHE. This approach is recommended since the solids value from Section 11.2.5 may differ from the filtration solids due to sample variability or differences in the filtration apparatus.

11.4.11. Homogenize and transfer an appropriate size subsample of the waste into the ZHE and record the mass on Worksheet 4, Line I1.

11.4.12. Carefully place the glass fiber filter between the support screens and secure to the ZHE. Tighten all the fittings.

11.4.13. Place the ZHE in a vertical position; open both the gas AND liquid inlet/outlet valves. Attach a gas line to the gas inlet/outlet valve.

11.4.14. If the waste is 100% solid, slowly increase the pressure to a maximum of 50 psi to force out as much headspace as possible and proceed to Section 11.4.18.

11.4.15. If the waste is < 100% solids, carefully apply gentle pressure of 10 psi (or more, if necessary) to force all headspace slowly out of the ZHE. At the FIRST appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue gas pressure.

11.4.16. Assemble a syringe and place the plunger in all the way. Adjust the tension on the plunger to provide slight drag. Attach the pre-weighed syringe or Tedlar bag to the liquid inlet/outlet valve and open the valve. Record the tare weight of the collection device on Worksheet 4, Line 3b.

11.4.17. Carefully apply gas pressure of no more than 10 psi to force out the liquid phase. Allow the sample to filter until no SIGNIFICANT additional filtrate has passed in a 2 minute period.

Note: If the capacity of the syringe is reached, close the liquid inlet/outlet valve, discontinue gas pressure, remove the syringe and return to Section 11.4.15.

11.4.18. Repeat previous step increasing the pressure in 10 PSI increments until 50 psi is reached and no significant liquid has passed in a 2 minute period. Remove the collection device and record the total weight of the collection device with filtrate on Worksheet 4, Line 3a. Close the valve and discontinue gas pressure. Transfer the filtrate to VOA vials and label appropriately. Calculate the weight of filtrate collected and record on Worksheet 4, Line I3c.

Notes: If the original waste contained less than 0.5% solids (Section 11.2.5), this filtrate is defined as the TCLP leachate and you may proceed to Section 11.4.28. Otherwise, save the vials by storing at 4 C under minimal headspace conditions, for recombination as in Section 11.4.27.

The material remaining in the ZHE is defined to be the "solid" phase. Calculate the weight of the solid phase using Equation 4.

11.4.19. Based on the information from Sections 11.2.5 and 11.4.11 and using the formula in 12.1.3, determine the weight of fluid to load into the ZHE on the "solid" phase. The ZHE device has approximately a 500-mL capacity. Based on the need to add an amount of extraction fluid equal to 20 times the mass of the "solid" phase, the ZHE can therefore accommodate a maximum of 25 grams of "solid".

Note: The TCLP ZHE prep uses only TCLP fluid #1; the SPLP ZHE prep uses only SPLP fluid #1.

11.4.20. Load the fluid transfer reservoir with an excess of Fluid #1 and preflush the transfer line to eliminate air pockets. Be sure the required volume remains.

11.4.21. Attach the transfer line to the liquid inlet/outlet valve and open the valve. Carefully pump the required volume into the ZHE and close the valve. Disconnect the transfer line.

11.4.22. Check the ZHE to make sure all the valves are closed and manually rotate the ZHE (end-over-end) 2 or 3 times. Reposition the ZHE in the vertical position.

11.4.23. Pressurize the ZHE to 5-10 psi. Allow to stand for 10 minutes, and then recheck the pressure. If the ZHE appears to be leaking, follow the corrective action protocols recommended by the manufacturer and repeat the analysis.

11.4.24. Slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced during the introduction of the Fluid. Upon the first sign of liquid from the valve, close the valve.

11.4.25. Repressurize the ZHE to 5-10 psi and place in the rotary agitator. Rotate at 28-32 rpm for 16-20 hours. Room temperature should be 23 ± 2 °C. The room temperature and time should be checked at both the start and end of the extraction and recorded on Worksheet 4, lines J1, J3 and J4.

11.4.26. Confirm that the pressure of 5-10 psi was maintained throughout the leaching. If it was NOT maintained, return to Section 11.4.1 and repeat the leachate with a new aliquot of sample.

11.4.27. Attach a syringe or Tedlar bag and open the liquid inlet/outlet valve to collect the aqueous leachate and proceed as outlined in 11.4.19 - 11.4.20.

Record the volume/mass of the leachate and any oil phase on Worksheet 4, Lines J7 and J7a. Record the date and time the filtration is completed on Worksheet 4, Line J6.

Notes: If the waste contained an initial liquid phase, the liquid may be filtered directly into the same collection device holding the initial liquid phase of the waste.

A separate filtrate collection container must be used if combination would create multiple phases or there is not enough volume left within the filtrate collection container.

11.4.28. If the waste contained an initial filtrate (Section 11.4.18) that is miscible with the solid phase leachate (as determined in Section 11.2.8), the solid phase leachate and the initial filtrate are directly recombined in the correct proportions (see Section 12.1.4). If the individual phases are NOT compatible, they are to be collected, prepped and analyzed separately.

Note: Chill the filtrate and receiving vessels before recombining.

11.4.29. Following collection, store the TCLP leachate in 3 20-mL VOA vials with minimal headspace at 4 ± 2 °C and prepare for analysis as soon as possible using the appropriate organic extraction procedure (see Section 16.3).

11.4.30. If the individual phases are analyzed separately, combine the results mathematically by using the recombination calculation in Section 12.1.5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Calculation of Percent Wet Solids:

$$Percent\ \ Wet\ Solids = 100\left(\frac{Mass,"solid"\ phase}{Mass,initial\ subsample}\right)$$

12.1.2. Calculation of weight of waste to charge to ZHE:

$$Weight\ of\ \ waste\ to\ charge\ to\ ZHE = 100\left(\frac{25}{\%wet\ solids}\right)$$

12.1.3. Calculation of weight of extraction fluid to use:

$$Weight\ of\ Extraction\ fluid = \frac{20\,x\,\%\ wet\ solids\ x\ weight\ of\ waste\ to\ be\ extracted}{100}$$

12.1.4. Calculation of volume of initial filtrate phase to recombine with solid phase leachate:

$$\text{Volume of filtrate for recombination} = \left(\frac{Weight\ of\ solids\ leached}{Total\ weight\ of\ solids}\right)\left(\frac{Leachate\ recovered}{Fluid\ added}\right)\left(Volume\ of\ initial\ aqueous\ filtrate\right)$$

12.1.5. Mathematical recombination of analytical results:

$$Final\ Analyte\ Concentration = \frac{\left(V_1 \times C_1\right) + \left(V_2 \times C_2\right)}{V_1 + V_2}$$

V_1 = total volume of the initial filtrate phase (L).
C_1 = analyte concentration in initial filtrate phase (mg/L).
V_2 = volume of the theoretical solid phase leachate (L).
C_2 = analyte concentration in solid phase leachate (mg/L).,

12.2. REPORTING REQUIREMENTS

12.2.1. Follow these reporting conventions for multi-phase samples:

12.2.1.1. If both phases have positive results, use the values from each phase to calculate the recombined result. Use the reporting limit for each phase to calculate the recombined reporting limit.

12.2.1.2. If both phases are "ND," not detected, the recombined result is "ND," and the reporting limit is calculated from the reporting limit for each phase.

12.2.1.3. If one phase is "ND" and the other phase has a positive result, use the reporting limit for the "ND" phase and the positive value for the other phase to calculate the combined result. The combined reporting limit is based on the reporting limit for both phases. If the combined result is less than the combined reporting limit, then supply a footnote to indicate that "a positive result was detected below the calculated detection limit."

12.2.2. Units - regardless of the nature of the sample, all TCLP and SPLP results are reported in units of mg/L.

12.2.3. For limits and significant figures, consult the appropriate analytical methods (Section 16.3).

12.2.4. Anomalies - all anomalies observed during the leach procedure must be noted on the worksheet or an anomaly form. Some examples of such anomalies are:

12.2.4.1. Sample was monolithic - subsample was obtained by crushing, cutting, grinding, sawing, etc.

12.2.4.2. Insufficient sample - less than the required 100 g minimum was available.

12.2.4.3. Multiple phases - "X" phases were present.

12.2.4.4. Sample was oil - single phase.

12.2.4.5. Sample contained liquid which did not filter under test conditions.

12.3. REVIEW REQUIREMENTS

12.3.1. Review all applicable holding times. If a holding time was exceeded, confirm that a holding time violation form was properly documented and routed.

12.3.2. If Total analysis results are available, those results may be compared with the TCLP analysis results according to the following:

$$Total \geq 20 \times TCLP$$

NOTE: Assumes the sample is 100% Solids.

12.3.3. Total constituent analysis results can be used to demonstrate the TCLP protocol is unnecessary. In performing a TCLP analysis, there is a 20:1 dilution of the original sample with the leaching solution. Thus, if the "total constituent" result is less than 20 times the TC level, it is impossible for the leachate to "fail" and the TCLP does not need to be performed. For example, the TC level for lead is 5.0 mg/L (ppm). Therefore, if a sample of lead-contaminated soil contains less than 100 ppm total lead, a TCLP test need not be run for lead.

13. METHOD PERFORMANCE

13.1. Refer to individual analysis SOPs.

13.2. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure must be segregated and disposed according to the facility's hazardous wastes procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Method 1311, Toxicity Characteristic Leaching Procedure, Revision 0, July 1992, SW-846 Final Update I.

16.2. Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, November 1992, SW-846 Proposed Update II.

16.3. Related Documents

16.3.1. Toxicity Characteristic: Corrections to Final Rule. Method 1311, Federal Register, Vol. 55, No. 126, Friday, June 29, 1990.

16.3.2. Toxicity Characteristic: Final Rule. Method 1311, Federal Register, Vol. 55, No. 61, Thursday, March 29, 1990.

16.3.3. Technical Background Document and Response To Comments, Method 1311, Toxicity Characteristic Leaching Procedure, USEPA/OSW, April, 1989.

16.3.4. QA-003, STL® QC Program

16.3.5. CORP-IP-0003: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.6. CORP-MT-0001: Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis, Method 6010A and Method 200.7.

16.3.7. CORP-MT-0003: Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.3.8. CORP-MT-0005: Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1.

16.3.9. CORP-IP-0003: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.10. CORP-MS-0002: Determination of Volatile Organics by GC/MS based on Methods 8240B and 8260A.

16.3.11. CORP-MS-0001 : GC/MS Analysis Based on Method 8270B, SW846.

16.3.12. CORP-GC-0001: Gas Chromatographic Analysis Based on Methods 8000A, 8010B, 8020A, 8080A and 8150B, SW846.

16.3.13. CORP-OP-0001: Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW846 3500 Series, 3600 Series, 8150 and 600 Series Methods.

17. MISCELLANEOUS

17.1. Modifications/Interpretations from Reference Methods

17.1.1. Section 8: Preliminary Evaluations. Section 7.1 of the source method states that the sample aliquot used for the preliminary evaluation "...may not actually undergo TCLP extraction." Section 7.1.5 of the source method indicates that the portion used for the preliminary evaluation may be used for either the ZHE or non-volatile extraction if the sample was 100% solid. Section 7.1.5 further indicates that if the sample was subjected to filtration (i.e., < 100% solid) that this aliquot may be used for the non-volatile extraction procedure only as long as sufficient sample is available (minimum 100 g). Samples which have been subjected to the oven drying step may not be used for TCLP extraction because solid phase degradation may result upon heating.

17.1.2. Section 11.2.5.6.3: Percent Solids Determination. Section 7.1.2 of the source method indicates that "if the percent wet solids is ≥ 0.5% and it is noticed that a small amount of the filtrate is entrained in wetting of the filter"

that the filter should be oven dried to determine percent dry solids ". Drying of oil or organic matrices can both be hazardous and inappropriate. Additionally, it may be impossible to achieve a constant weight when performing this step. Due to safety concerns, if obviously oily or heavy organic matrices are entrained on the filter, the filter is not oven dried.

17.1.3. Section 11.2.8: Preliminary Determination of Filtrate/Extraction Fluid Compatibility. Section 7.2.13 of the source method provides no guidance as to how to make this determination. As a result, the procedure herein was developed and incorporated into the Preliminary Determinations section.

17.1.4. Section 9.2: TCLP Extraction Blanks. Section 8.1 of the source method states that a minimum of one blank for every 20 extractions "...that have been conducted in an extraction vessel." STL® has interpreted this to mean one blank per twenty samples leached per TYPE of leaching vessel (i.e., Bottle or ZHE) per leach fluid used.

17.1.5. Section 11.2.7.9: Determination of Appropriate Extraction Fluid. Method 1311 does not address the appropriate approach to take if the pH equals 5.0. This SOP requires that Fluid #1 must be used if the pH is less than or equal to 5.0.

17.1.6. Section 9.4: QA/QC - Matrix Spikes. Section 8.2 of the source method states "A matrix spike shall be performed for each waste type..." and "A minimum of one matrix spike must be analyzed for each analytical batch." Further, Section 8.2.3 of the source method also states "The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist." The standard STL® QAPP is designed to address the performance monitoring of analytical methodology through the LCS program. A minimum of one MS and MSD will be prepared for each TCLP leachate batch. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS/MSD results have immediate bearing only on the specific sample spiked and not all samples in the batch.

17.1.7. Section 8.2.2 of the source method states that "In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level." The method also states "If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration but may not be less than five times the method detection limit". For several analytes, spiking at the regulatory level is inappropriate to the range of analysis afforded by the determinative

methods. Due to the wide range in these levels, STL® spikes at the levels specified in the determinative SOPs.

17.2. Modifications from Previous SOP

None

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete TCLP preparation raw data package:

- Completed worksheets (Appendix C).
- Non-conformance summary (if applicable).
- Anomaly documentation (if applicable).

APPENDIX A

TABLES

Table 3 - Toxicity Characteristic Analytes and Regulatory Levels (Final Rule)

Contaminant	mg/L
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresols	200.0
m-Cresols	200.0
p-Cresols	200.0
Total Cresols (used if isomers not resolved)	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
2,4-Dinitrotoluene	0.13
1,1-Dichloroethylene	0.7
Endrin	0.02
Heptachlor (& epoxide)	0.008
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

APPENDIX B

FIGURES

Figure 1 & 2 - Rotary Agitation Apparatus and Zero Headspace Extraction Vessel (ZHE)

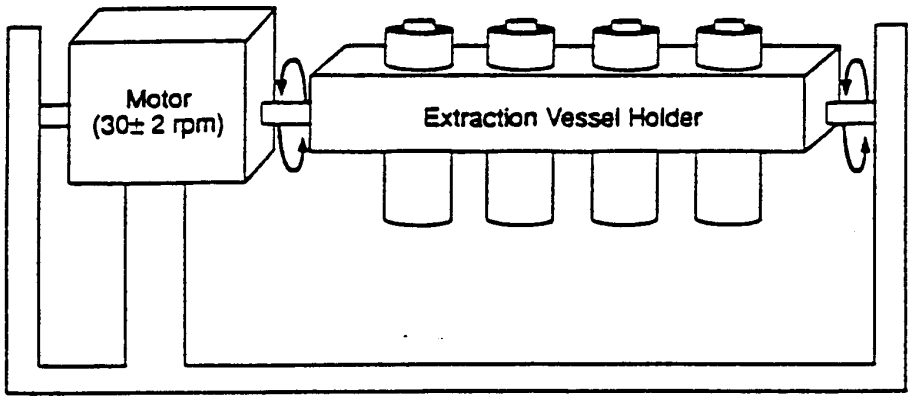

Figure 1. Rotary Agitation Apparatus

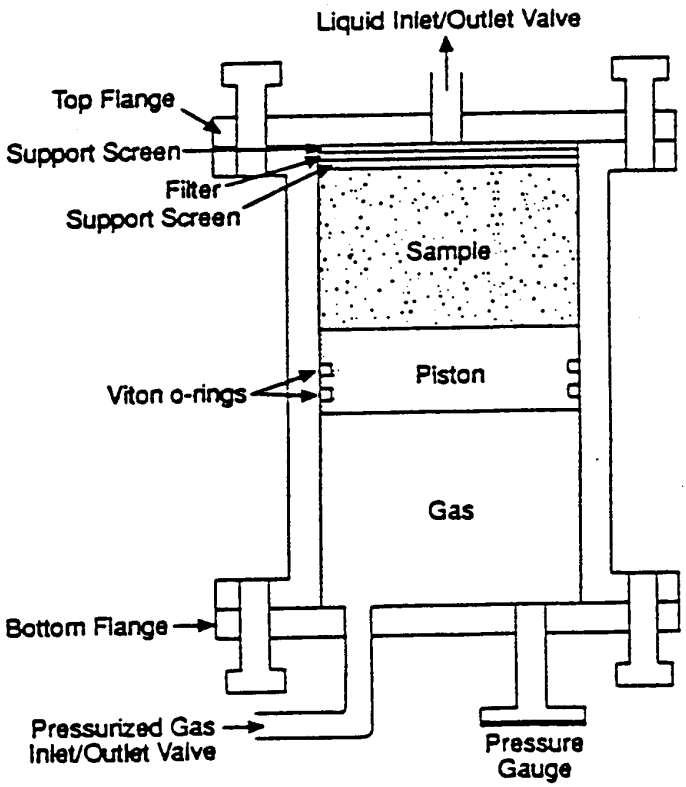

Figure 3 - US Environmental Protection Agency Memorandum #35, Page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
SOLID WASTE AND EMERGENCY RESPONSE

MEMORANDUM # 35

DATE: June 12, 1992

SUBJECT: Notes on RCRA Methods and QA Activities

From: Gail Hansen, Chief
Methods Section (OS-331)

This memo addresses the following topics:

- o 1992 Symposium on Waste Testing and Quality Assurance
- o SW-846 Update
  - Final Rule for January 23, 1989 Proposed Rule
  - Notice, Proposed Rulemaking for the Second Update to the Third Edition
- o Chlorofluorocarbon 113 (CFC-113) Solvent Replacement Update
- o Environmental Monitoring Methods Index (EMMI)
- o Sampling Work Group Formation
- o MICE Update
- o Oily Waste Analysis
- o Electronic SW-846 Availability.

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Figure 3 - US Environmental Protection Agency Memorandum #35, Page 10

Oily Waste Analysis

One of the most frequently asked questions on the MICE Service concerns the application of the TCLP, Method 1311, to oily wastes. Many callers request technical guidance on the extraction of oily wastes due to the difficulty in the filtration on these types of waste. In many cases, an oily waste does not filter completely due to premature clogging of the glass fiber filter. This can result in the retention of standing liquid on the glass fiber filter. Material that do not pass through the glass fiber filter at the conclusion of the filtration step is defined by the method as the solid phase of the waste. The solid phase is then subjected to the leaching procedure of the TCLP. For oily wastes, clogging of the glass fiber filter can result in an overestimation of the amount of solid material available for leaching.

To solve this problem, the Agency recommends a conservative approach, one that probably will overestimate the amount of leaching. Rather than performing the TCLP extraction on the unfiltered portion of the oily waste, assume the waste is 100% liquid (e.g., will pass through the glass fiber filter) and perform a totals analysis on the oily waste to determine if the oil exceeds the appropriate regulatory level.

Filterable waste oil generated during the TCLP must be analyzed for a variety of organic and inorganic analytes. The OSW recognizes the difficulty in achieving acceptable performance for the analysis of waste oil using methods currently provided in SW-846. As a result, the Agency will provide several new methods for the preparation and analysis of oil samples to the Organic Methods Workgroup in July. In addition, a microwave assisted digestion procedure should improve the analysis of metals and will be proposed as part of the Second Update of the Third Edition of SW-846. Brief descriptions of these techniques are provided below, for additional information on the organic procedures contact Barry Lesnik at (202) 260-7459. For additional information on microwave digestion contact Ollie Fordham (202) 260-4778.

The use of purge-and-trap (Method 5030) for volatiles in oil generally results in severe contamination of analytical instrumentation. Traps, transfer lines and chromatography columns may become contaminated with oil. This leads to elevated baselines, hydrocarbon background in subsequent analyses, and cross-contamination. Headspace (Method 3810) is currently allowed only as a screening procedure in SW-846. The Agency is evaluating the use of headspace in conjunction with isotope dilution mass spectrometry for the quantitative analysis of volatiles in oil. Headspace reduces interference problems encountered with purge-and-trap. However, headspace quantitation can be questionable because the distribution of analytes is not

APPENDIX C

WORKSHEETS

TCLP/SPLP Worksheet 1 - Sample Description

Lot Number						
Laboratory Sample No.						
A. Sample Description						
Number of phases						
1. Solid						
2. Liquid						
a. lighter than water						
b. water						
c. heavier than water						
B. Percent Solid Phase						
1. weight of filter (g)						
2. weight of subsample						
a. gross weight (g)						
b. tare weight (g)						
c. net weight (g)						
3. weight of filtrate						
a. gross weight (g)						
b. tare weight (g)						
c. net weight (g)						
4. total weight wet solids[0]						
5. weight percent wet solids[1] (%)						
6. weight percent dry solids (%)						
a. gross dry weight (g)						
b. final gross dry weight (g)						
c. percent dry solids[2] (%)						
7. volume of initial aqueous filtrate (mL)						
8. volume of initial organic filtrate (mL)						

[0] $\text{Total Weight of wet solids} = \left(B2c - B3c\right)$

[1] $\text{Weight percent wet solids} = 100\left(\frac{\text{Total weight wet solids, } B4}{\text{Weight of subsample, } B2c}\right)$

[2] $\text{Weight percent dry solids} = 100\left(\frac{\left(\text{Gross dry weight, } B6b\right) - \left(\text{weight of filter, } B1\right)}{\text{Weight of subsample, } B2c}\right)$

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 2 - Selection of Extraction Fluid

TCLP

Lot Number.					
Laboratory Sample No.					
C. Extraction Fluid Determination—does not apply to determination of volatile organic components.					
1. particle size reduction? yes/no (<1 mm)					
2. sample weight, ✓ if 5.0 ± 0.1 g					
3. volume of water, ✓ if 96.5 ± 1.0 mL					
4. initial pH (after 5 min. mixing time)					
5. if pH >5.0, ✓ if 3.5 mL 1N HCL					
6. ✓ if heated and held at 50^0C for ten minutes					
7. secondary pH (at room temperature)					
D. Selection of Extraction Fluid					
1. ✓ if pH from § C (4) or § C (7) is <5.0, use extraction fluid No. 1.					
2. ✓ if pH from § C (7) IS >5.0, use extraction fluid No. 2					
3. ✓ if filtrate and fluid are miscible					

SPLP

Laboratory Sample No.					
Field Sample No.					
D. Selection of Extraction Fluid (✓ one)					
Fluid 1: Soils—East of the Mississippi River; Wastes; or Wastewaters.					
Fluid 2: Soils—West of Mississippi River					
Fluid 3: If VOCs or Cyanide containing wastes.					
1. ✓ if filtrate and fluid are miscible					

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 3 - Extraction for Metals, Semi-Volatile Organic Components and Pesticides/Herbicides

Lot Number					
Laboratory Sample No.					
E. Determination of Samples Size for Leach Testing—the method requires a minimum 100 gram sample size for extraction					
1. particle size reduction? yes/no (<9.5 mm)					
2. weight of wet solids after filtration (g)					
F. Determination of Amount of Extraction Fluid—the selection of the correct extraction fluid is found in Section D., Worksheet No. 2					
1. Fluid weight = 20 x solids weight (g)					
G. Record of Extraction Test—the extraction period is specified as 18 ± 2					
1. room temperature initial (^oC) final (^oC)					
2. vessel number					
3. extraction start time					
4. extraction stop time					
5. date and time filtration complete					
6. pH of leachate					
7. volume of leachate (for multiphase samples only) (mL)					
8. volume of initial aqueous filtrate for recombination[3] (mL)					
9. combined initial aqueous + leachate (mL)					

$$^{3}Volume\ of\ filtrate\ used\ for\ recombination = \left(\frac{Weight\ of\ solids\ leached, E2}{Total\ weight\ of\ solids, B4}\right)\left(\frac{Leachate\ recovered, G7}{Fluid\ added, F1}\right)\left(Volume\ of\ initial\ aqueous\ filtrate, B7\right)$$

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 4 - Zero Headspace Extraction (ZHE)

Lot Number					
Laboratory Sample No.					
H. Determination of Sample Size for Leach Testing—maximum 25 grams					
1. particle size reduction? yes/no (<9.5 mm)					
2. weight of wet solid (g)					
I. Determination of Amount of Extraction Fluid No. 1					
1. weight of material added to ZHE (g)					
2. volume of filtrate in syringe (mL)					
3. weight of filtrate in syringe					
a. gross weight (g)					
b. tare weight (g)					
c. net weight (g)					
4. wet solids in ZHE[4] (g)					
5. weight of fluid to add[5] (g)					
J. Record of ZHE Extraction Text—the extraction period is as 18 ± 2 hours.					
1. room temperature initial (°C) final (^{o}C)					
2. ZHE vessel number					
3. extraction start date & time					
4. extraction stop date & time					
5. ✓ if still under positive pressure					
6. filtration completed date & time					
7. volume of filtrate recovered after leaching (mL)					
a. volume of oil recovered after leaching (mL)					
8. volume of initial aqueous filtrate for recombination[6] (mL)					
9. combined initial aqueous + leachate (mL)					

[4] Solids remaining in ZHE $= \left(Material\ added, I1\right) - \left(Weight\ of\ filtrate\ in\ syringe, I3\right)$

[5] Weight of fluid to add $= 20\left(Wet\ solids\ in\ ZHE, I4\right)$

[6] Volume of filtrate used for recombination $= \left(\frac{Weight\ of\ solids\ leached, I4}{Total\ weight\ of\ solids, B4}\right)\left(\frac{Leachate\ recovered, J7}{Fluid\ added, I5}\right)\left(Volume\ initial\ aqueous\ filtrate, B7\right)$

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 5 - Organic Results

TCLP/SPLP ZHE Worksheet No. 5
Organic Results

Sample Number: _____

Organics Preparation		Volume	Units
Combined initial Aqueous/Leachate from § J9	V_A		mL
Oil phase Volume for Calculations[7]	V_O		mL

Analyte		Oil Phase			Combined Initial Aqueous/Leachate			Final Results	
Compound	Std. Reporting Limit (mg/L)	Dilution Factor	Result C_O	Reporting Limit	Dilution Factor	Results C_A	Reporting Limit	Result C_{Final}	Reporting Limit

$$C_{Final} = \frac{\left(C_A \times V_A\right) + \left(C_O \times V_O\right)}{V_A + V_O}$$

[7] Volume of oil phase for calculation $= \left(\frac{Wet\ solids\ leached, I4}{Total\ solid, B4}\right)\left(\frac{Leachate\ recovered, J7}{Fluid\ added, I5}\right)\left(Initial\ volume\ of\ oil, B8\right) + \left(Oil\ recovered\ from\ leaching, J7a\right)$

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 6 - Metals Results

Metals Results

Sample Number : _____

Metals Preparation		Volume	Units
Combined Initial Aqueous/Leachate from §G8	VA		mL
Oil phase volume for calculations[8]	VO		mL

Analyte		Oil Phase			Combined Initial Aqueous/Leachate			Final Results	
Element	Std. Reporting Limit (mg/L)	Dilution Factor	Result C_O	Reporting Limit	Dilution Factor	Results C_A	Reporting Limit	Result C_{Final}	Reporting Limit
Arsenic	0.5								
Barium	10								
Cadmium	0.1								
Chromium	0.5								
Lead	0.5								
Mercury	0.0002								
Selenium	0.25								
Silver	0.5								

$$C_{Final} = \frac{(C_A \times V_A) + (C_O \times V_O)}{V_A + V_O}$$

$$^{8}\text{Volume of oil phase for calculation} = \left(\frac{\text{Wet solids leached, E2}}{\text{Total solid, B4}}\right)\left(\frac{\text{Leachate recovered, G7}}{\text{Fluid added, F1}}\right)\left(\text{Initial volume of oil, B8}\right) + \left(\text{Oil recovered from leaching, G7a}\right)$$

Notes: If sample contains no solids, volume of oil phase (V_0) is the volume of the initial organic filtrate

In cases where analytes are detected in only one phase, a footnote indicating a result reported below the reporting limit should be included.

Comments: _____

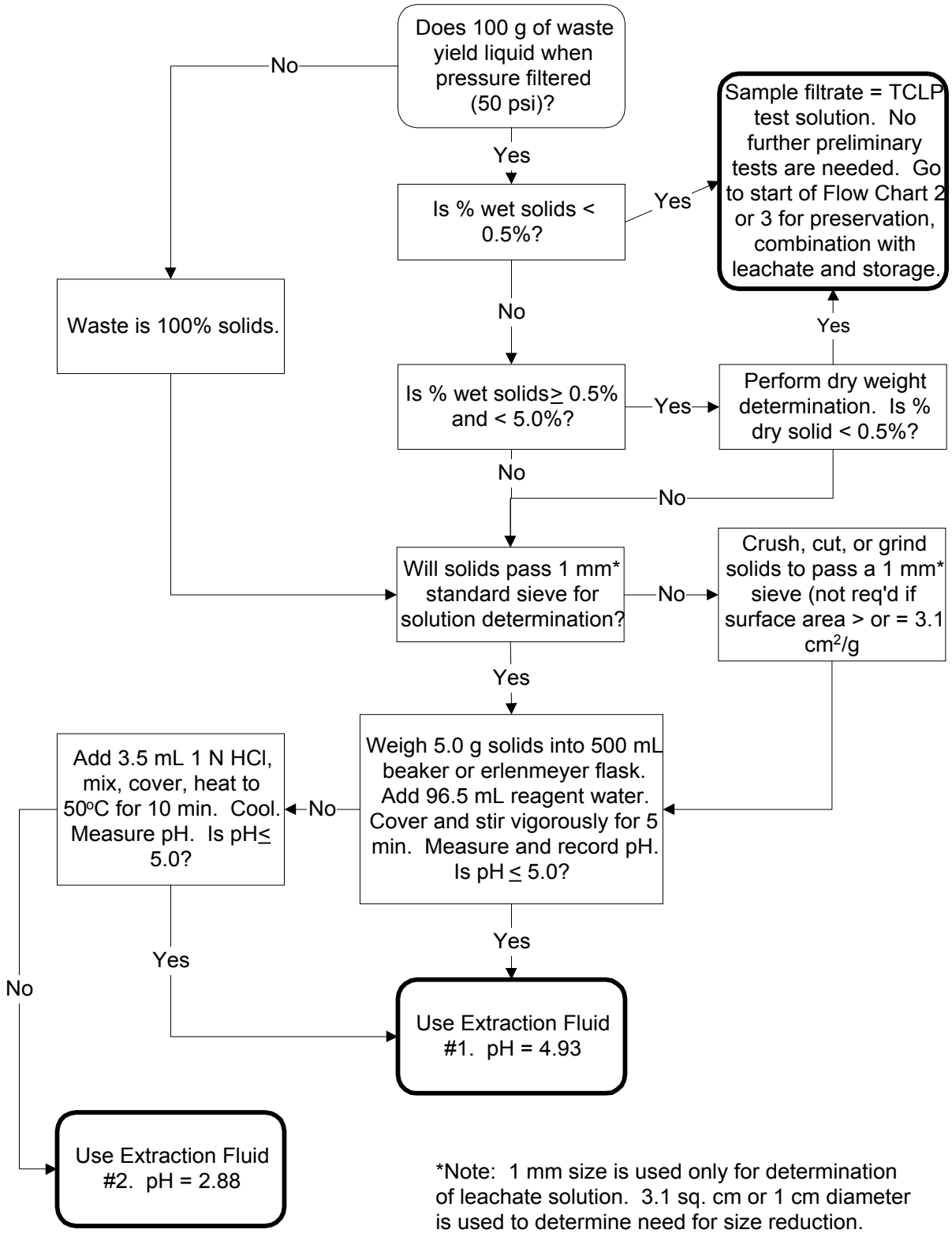
_____

Analyst: _____ Date: _____

APPENDIX D

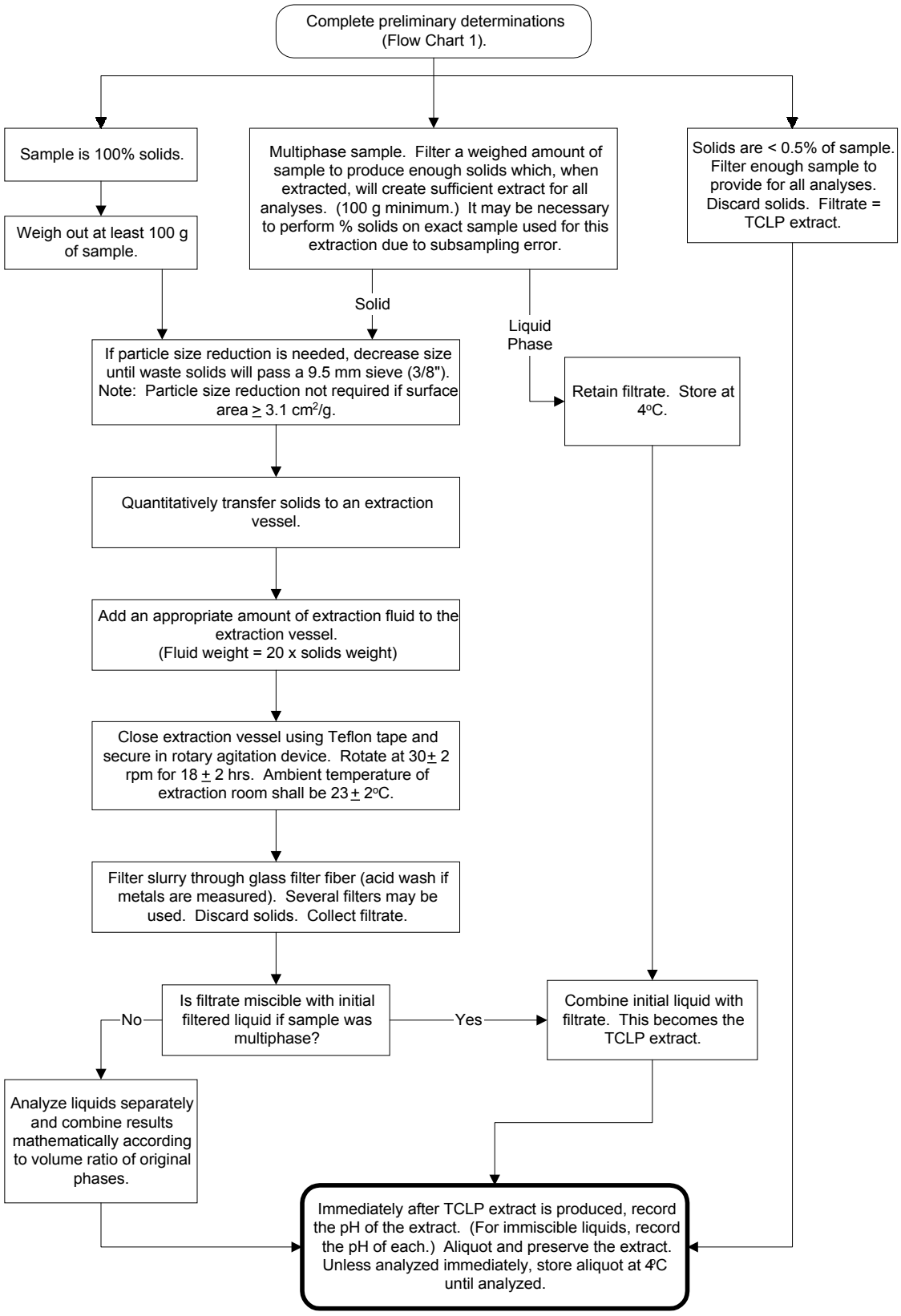
FLOW CHARTS

Flow Chart 1. Preliminary Sample Evaluation (Section 11.2)

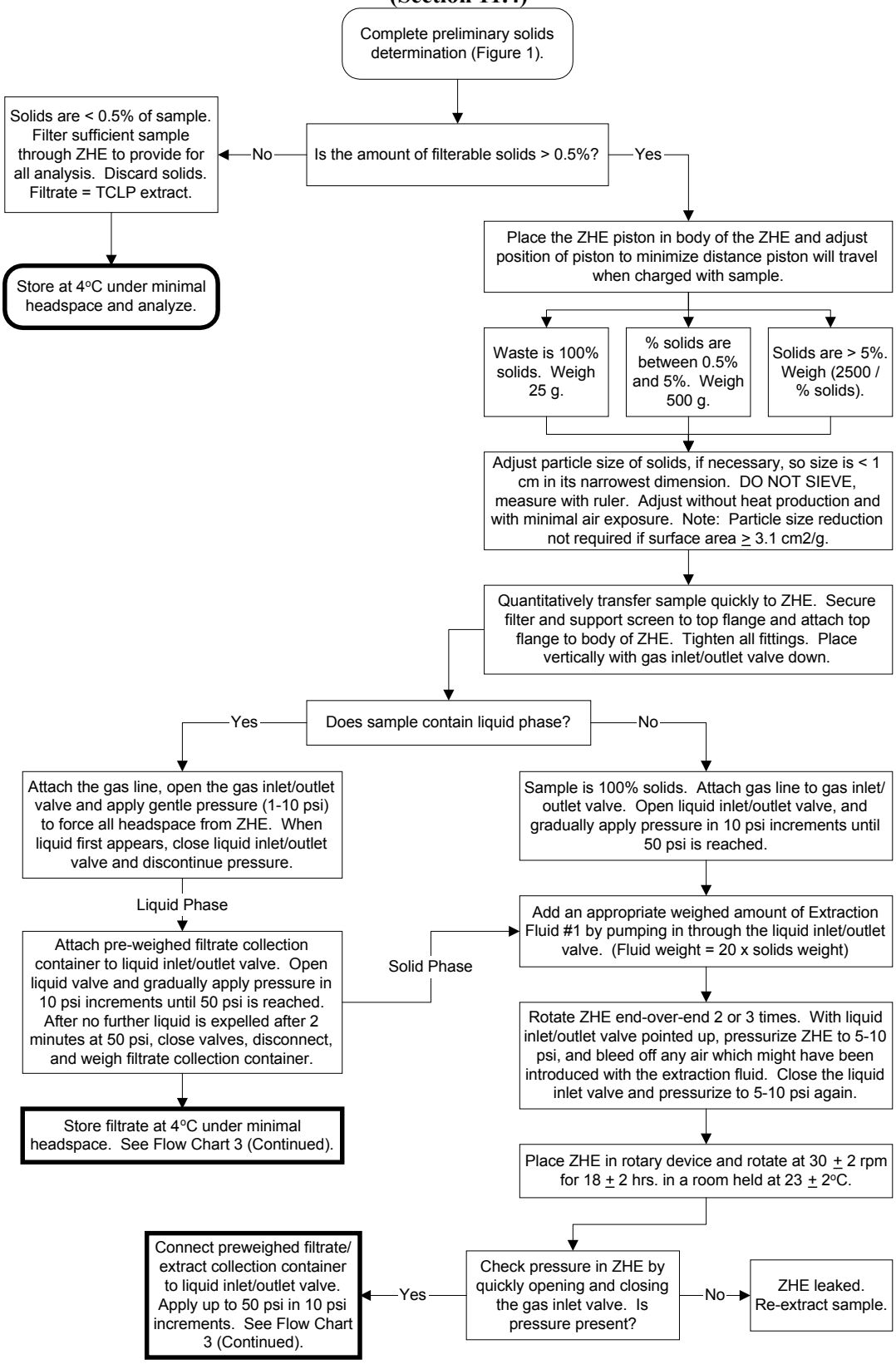


*Note: 1 mm size is used only for determination of leachate solution. 3.1 sq. cm or 1 cm diameter is used to determine need for size reduction.

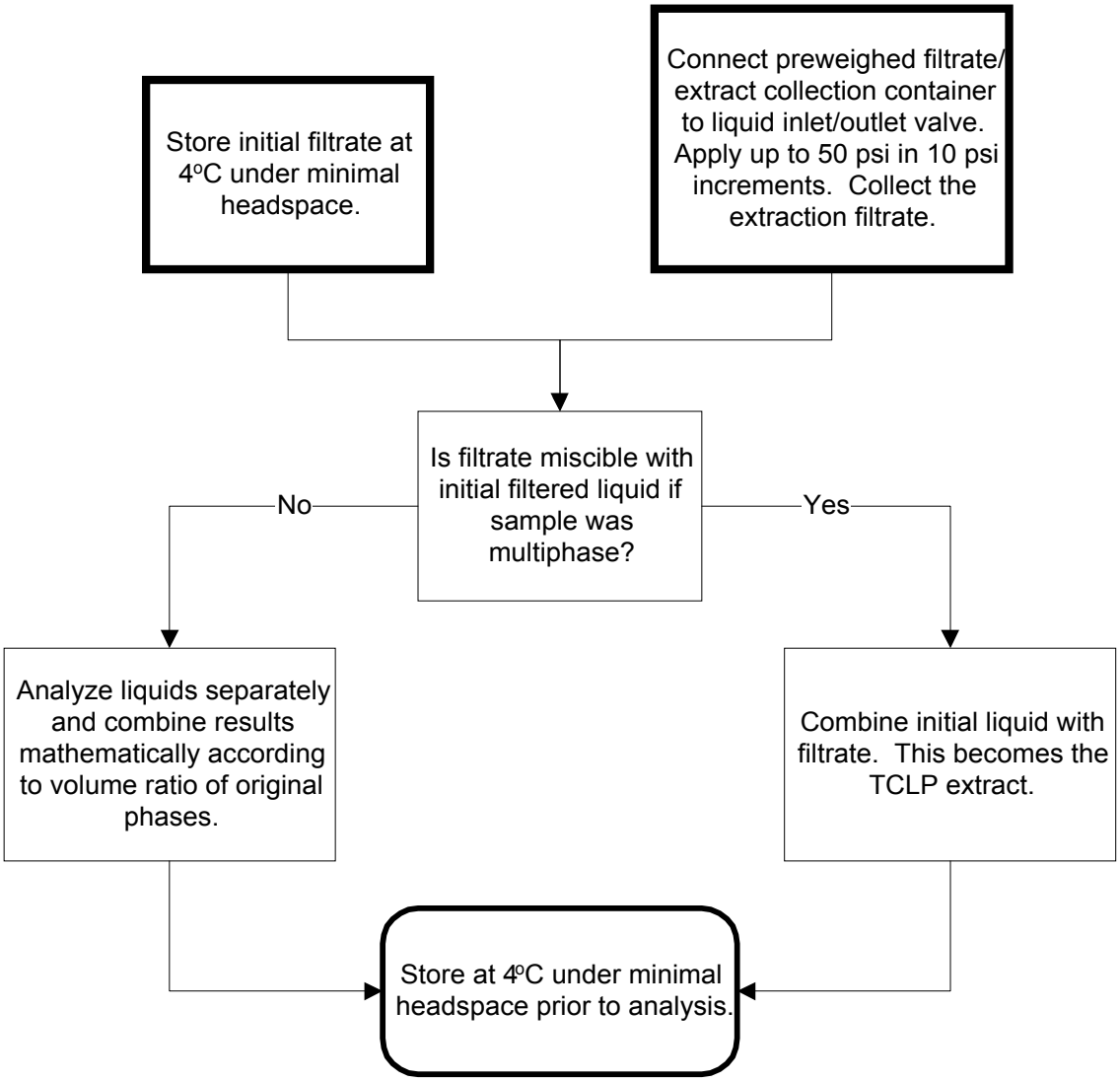
Flow Chart 2. Bottle Extraction, Non-Volatile Constituents (Section 11.3)



Flow Chart 3. ZHE Extraction, Volatile Constituents (Section 11.4)



Flow Chart 3. ZHE Extraction
(Continued)



TCLP (Method 1311)

STL Pittsburgh
450 William Pitt Way
Pittsburgh, PA 15238
412-820-8380

Analyst	Room Temp.	Date	Checked By	Date	pH Instrument	Probe	Balance
Lot #	Client Codes		Solution # 1 – Log book #			Solution # 2 – Log book #	

Fluid Determination

Sample ID	Wgt/Vol		Init. pH	Final pH	Tumbler RPM	Extract fluid #1 or #2
1.						
2.						
3.						
4.						
5.						
6.						
7.						
8.						
9.						
10.						
11.						
12.						
13.						
14.						
15.						

TCLP Extraction

Sample ID	Wgt (g) Wet/Dry	Fluid Vol.	Vessel glass/plastic	Start time of filtration	Final pH after Tumbling	Conc. HNO_3 to Acidity (for Metals)
1.						
2.						
3.						
4.						
5.						
6.						
7.						
8.						
9.						
10.						
11.						
12.						
13.						
14.						
15.						

Extract(s) (Record line number from above)	Extract(s) Received: Date	Time	Analyst	Location	Extract(s) Relinquished: Date	Time	Analyst	Location

Comments

* = Sample determined to have free liquid, % solid determination was performed.

<5 = Extraction fluid # 1 5.7mL Glacial acetic acid dil 500mL + 64.3mL HaOH dil to 1L (pH 4.93 ± 0.05)

>5 = Extraction fluid #2 5.7mL Glacial acetic acid dil to 1L (pH 2.88 ± 0.05)

Date/Time On		Date/Time Off		Agitation Apparatus RPM's 30±2 checked by	
	pH calibration	(4.0)		(7.0)	(10.0)
Date					
Date					
Filter Lot #					

STL - Pittsburgh **(ZHE) LEACHATE LOGBOOK** **Logbook ID: OP90**

Lab Smp ID #	Client ID	Weight (gm)	Vessel	Extraction Fluid No. / Volume	pH	On Date	On Time	On Initials	Off Date	Off Time	Off Initials
1.											
2.											
3.											
4.											
5.											
6.											
7.											
8.											
9.											
10.											
11.											
12.											
13.											
14.											
15.											
16.											
17.											
18.											
19.											
20.											

Extract(s) Received

Extract(s) (record line # from above)	Date	Time	Analyst	Location

Extract(s) Relinquished

Date	Time	Analyst	Location

= Sample determined to have free-liquid, % solid determination was performed
<5 = Extraction fluid No. 1 5.7ml Glacial Acetic Acid dil 500mL + 64.3 mL of 1 N NaOH dil to 1 L (pH 4.93 + 0.05)

Room Temp: Thermometer PPMs: (4.0) (7.0) (10.0) (30+-2)

Date:	pH Calibration			
Date:				

Reviewed by: Date: Comments:

STL - Pittsburgh **(SPLP) LEACHATE LOGBOOK** **Logbook ID: 0P91**

Analyst | Date | Reviewed by | Date | pH Instrument | Probe | Balance

Lot Number(s) | Solution #1 - Logbook Number | Solution #2 - Logbook Number

Work Order #	Comments	Init pH	Extract Fluid #1, #2 or #3	Weight (gm) Wet / Dry	Fluid Volume	Vessel Glass / Plastic	Final ph after tumbling	Conc HNO3 to Acidify(for Metals)
1.								
2.								
3.								
4.								
5.								
6.								
7.								
8.								
9.								
10.								
11.								
12.								
13.								
14.								
15.								
16.								
17.								
18.								
19.								
20.								
21.								
22.								

Extract(s)	Extract(s) Received				Extract(s) Relinquished			
(record line # from above)	Date	Time	Analyst	Location	Date	Time	Analyst	Location

* = Sample determined to have free liquid, % solid determination was performed

Extraction Fluid 1 = Samples that are EAST of the Mississippi River. Prepared by adding an aliquot of a 60/40 % by weight mixture of H2SO4 and HNO3 to reagent water (pH 4.20 +- 0.05)

Extraction Fluid 2 = Samples that are WEST of the Mississippi River. Prepared by adding an aliquot of a 60/40 % by weight mixture of H2SO4 and HNO3 to reagent water (pH 5.00 +- 0.05)

Extraction Fluid 3 = This is a reagent water and is used to determine cyanide leachability

Date/Time on		Date/Time off		Agitation Apparatus RPM: 30 +- 2
	(4.0)		(7.0)	(10.0)
Date				
Date				

APPENDIX 22

Controlled Copy
Copy No:_____
Implementation Date: 04/19/02

SOP No. C-MS-0002
Revision No. 3.0
Revision Date: 04/19/02
Page: 1 of 62

STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHOD 8260B, 624 AND 524.2

(SUPERSEDES: REVISION 1)

Prepared by: Keith Dudeck

Approved by: Keith Dudeck
Technology Specialist

Approved by:
Quality Assurance Manager

Approved by:
Environmental Health and Safety Coordinator

Approved by:
Laboratory Manager

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LIST OF TABLES

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Volatile Organic Compounds in waters, wastewater, soils, sludges and other solid matrices. Standard analytes are listed in Tables 5 and 6.

1.2. This SOP is applicable to method 8260B. Appendices A and B present modifications to the procedures in the main SOP that are necessary for analysis of drinking water by method 524.2 and wastewater by method 624.

1.3. This method can be used to quantify most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4. The method is based upon a purge and trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 200 µg/L for 5 mL standard level waters, 1 to 40 µg/L for low level waters, 5 to 200 µg/kg for low-level soils, and 250 to 25,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1, 3 and A-1.

1.5. Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates, and laboratory control spike samples.

2. SUMMARY OF METHOD

2.1. Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2. Aqueous samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If especially low detection limits are required, soil samples may be preserved with sodium bisulfate or frozen and purged directly.

2.3. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40^{o}C (40^{o}C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components which are detected with a mass spectrometer.

2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3. DEFINITIONS

3.1. Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will normally start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

3.1.1. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is received, an LCS/LCSD will be used in the place of an MS/MSD. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

3.2. Method Blank

A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

3.3. Laboratory Control Sample (LCS)

Laboratory Control Samples are well characterized, laboratory generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

3.4. Surrogates

Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, LCS, and MS/MSD is spiked with surrogate

standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

3.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike. Matrix spikes and duplicates are used to evaluate accuracy and precision in the actual sample matrix.

3.6. Calibration Check Compound (CCC)

CCCs are a representative group of compounds which are used to evaluate initial calibrations and continuing calibrations. Relative standard deviation (%RSD) for the initial calibration and % drift or % deviation (%D) for the continuing calibration response factors are calculated and compared to the specified method criteria.

3.7. System Performance Check Compounds (SPCC)

SPCCs are compounds which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the inital continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3. Matrix interferences may be caused by non-target contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. The Chemical Hygiene Plan (CHP) gives details about the specific health and safety practices which are to be followed in the laboratory area. Personnel must receive training in the CHP, including the written Hazard Communication plan, prior to working in the laboratory. Consult the CHP, the STL Health and Safety Policies and Procedures Manual, and available Material Safety Data Sheets (MSDS) prior to using the chemicals in the method.

5.3. Consult the STL Health and Safety Policies and Procedures Manual for information on Personal Protective Equipment. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan) and a laboratory coat must be worn in the lab. Appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Disposable gloves shall not be reused.

5.4. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined, therefore each chemical compound should be treated as a potential health hazard. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.4.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Acrylonitrile, benzene, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, 1,4-dichlorobenzene, and vinyl chloride.

5.4.2. Chemicals known to be flammable are: Methanol.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in the STL Health and Safety Manual. These employees must have training on the hazardous waste disposal practices initially upon assignment of these tasks, followed by an annual refresher training.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes: 10 µL and larger, 0.006 inch ID needle.

6.2 Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

6.2. Balance: Top-loading balance capable of weighing 0.1 g

6.3. Glassware:

6.3.1. Vials: 40 mL with screw caps and Teflon liners.

6.3.2. Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

6.4. Spatula: Stainless steel.

6.5. Disposable pipets: Pasteur.

6.6. pH paper: Wide range.

6.7. Gases:

6.7.1. Helium: Ultra high purity, gr. 99.999%.

6.7.2. Nitrogen: Ultra high purity, from cylinders of gas generators, may be used as an alternative to helium for purge gas.

6.7.3. Compressed air: Used for instrument pneumatics.

6.7.4. Liquid nitrogen: Used for cryogenic cooling if necessary.

6.8. Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

6.8.1. Sample Purger: The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.

6.8.2. Trap: A variety of traps may be used, depending on the target analytes required. For most purposes the Vocarb 3000 trap is suitable. Other traps, such as Vocarb 4000, or Tenax / Silica gel / Charcoal may be used if the Quality Control criteria are met.

6.9.3 Desorber: The desorber should be capable of rapidly heating the trap to at least 180°C. Many such devices are commercially available.

6.9.4 Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low level soil analysis.

6.10 Gas Chromatograph/Mass Spectrometer System:

6.10.1 Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming.

6.10.2 Gas Chromatographic Columns: Capillary columns are used. Some typical columns are listed below:

6.10.2.1 Column 1: 20m x 0.18 ID DB-624 with 1 μm film thickness.

6.10.2.2 Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 AMU every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng or 25 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

6.10.3 Data System: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra

against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

6.10.4 Cryogenic Cooling: Some columns require the use of liquid nitrogen to achieve the subambient temperature required for the proper separation of the gases.

7 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Methanol: Purge and Trap Grade, High Purity

7.1.2 Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See section 9.4) Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight. Other methods of preparing reagent water are acceptable.

7.2 Standards

7.2.1 Calibration Standard

7.2.1.1 Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10° to -20°C.

7.2.1.2 Working standards: A working solution containing the compounds of interest is prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

7.2.1.3 Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.2.1.4 If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

7.2.2 Internal Standards: Internal standards are added to all samples, standards, and blank analyses. Refer to Table 7 for internal standard components.

7.2.3 Surrogate Standards: Refer to Table 8 for surrogate standard components and spiking levels.

7.2.4 Laboratory Control Sample Spiking Solutions: Refer to Table 9 for LCS components and spiking levels.

7.2.5 Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Table 9.

7.2.6 Tuning Standard: A standard is made up that will deliver up to 50 ng on column upon injection. A recommended concentration of 25 ng/μL of 4-Bromofluorobenzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.

8 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Holding times for all volatile analysis are 14 days from sample collection.

8.2 Water samples are normally preserved at pH $\leq$ 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

8.3 Solid samples are field preserved with sodium bisulfate solution or in water and frozen for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4 There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 μg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore samplers or to use field preservation.

8.5 Sample collection for medium level analysis using EnCore samplers.

8.5.1 Ship one 5 g (or 25 g) EnCore sampler per field sample position.

8.5.2 An additional bottle must be shipped for percent moisture determination.

8.5.3 When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). The 5 mL of methanol will contain the surrogate and the matrix spike

solution if one is required. Obtain the weight of the soil added to the vial and note on the label.

8.5.4 Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol.

8.5.5 Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.6 Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4 $\pm$ 2 °C until analysis.

8.6 Sample collection for medium level analysis using field methanol preservation

8.6.1 Prepare a 2 oz sample container by adding 25 mL purge and trap grade methanol. (If a 5 g sample is to be used, add 5 mL methanol to a VOA vial. The vial will contain surrogate and matrix spike solution, if necessary).

8.6.2 Seal the bottle and attach a label.

8.6.3 Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4 Ship with appropriate sampling instructions.

8.6.5 Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6 At client request, the methanol addition and weighing may also be performed in the field.

8.6.7 When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.7 Low level procedure

8.7.1 If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation or freezing the EnCore may be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

8.7.2 A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3 The soil sample is taken using a 5g EnCore sampling device and returned to the lab. It is recommended that two EnCore samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4 Prepare VOA vials by adding approximately 1 g of sodium bisulfate to 5 mL of reagent water or 5 mL of water.

8.7.5 Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6 Weigh the vial to the nearest 0.1g and note the weight on the label.

8.7.7 Extrude the soil sample from the EnCore sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note. Sodium bisulfate preserved samples may be stored in the refrigerator, while water preserved vials must be frozen.

8.7.8 **Note:** Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at $<10^{o}C$ until analysis.

8.7.9 Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

8.8 Unpreserved soils

8.8.1 At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A. It is no longer included and is likely to generate results that are biased low, possibly by more than an order of magnitude.

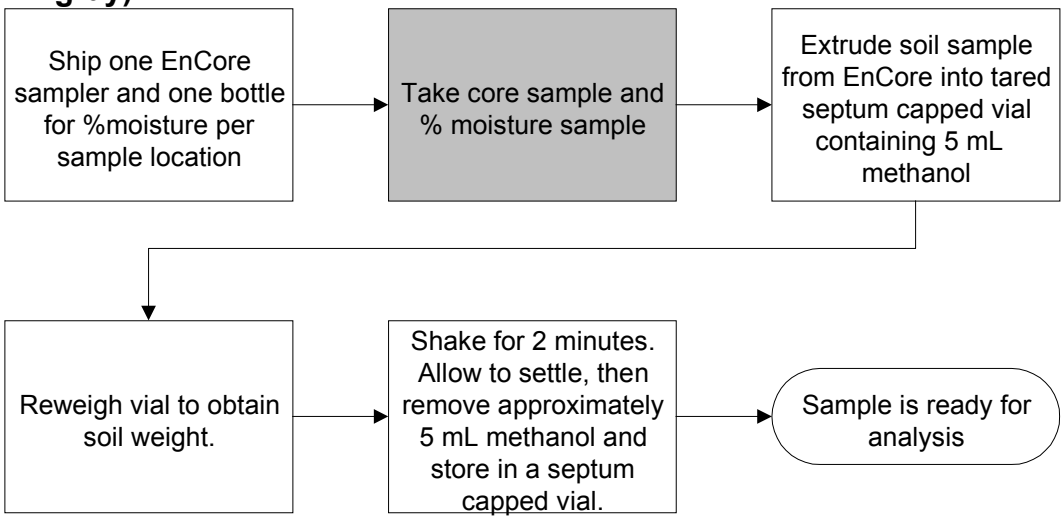
8.9 Aqueous samples are stored in glass containers with Teflon lined septa at $4^{o}C$ +/- $2^{o}C$, with minimum headspace.

8.10 Medium level solid extracts are aliquoted into 2 mL glass vials with Teflon lined caps and stored at $4^{o}C$ +/- $2^{o}C$. The extracts are stored with minimum headspace.

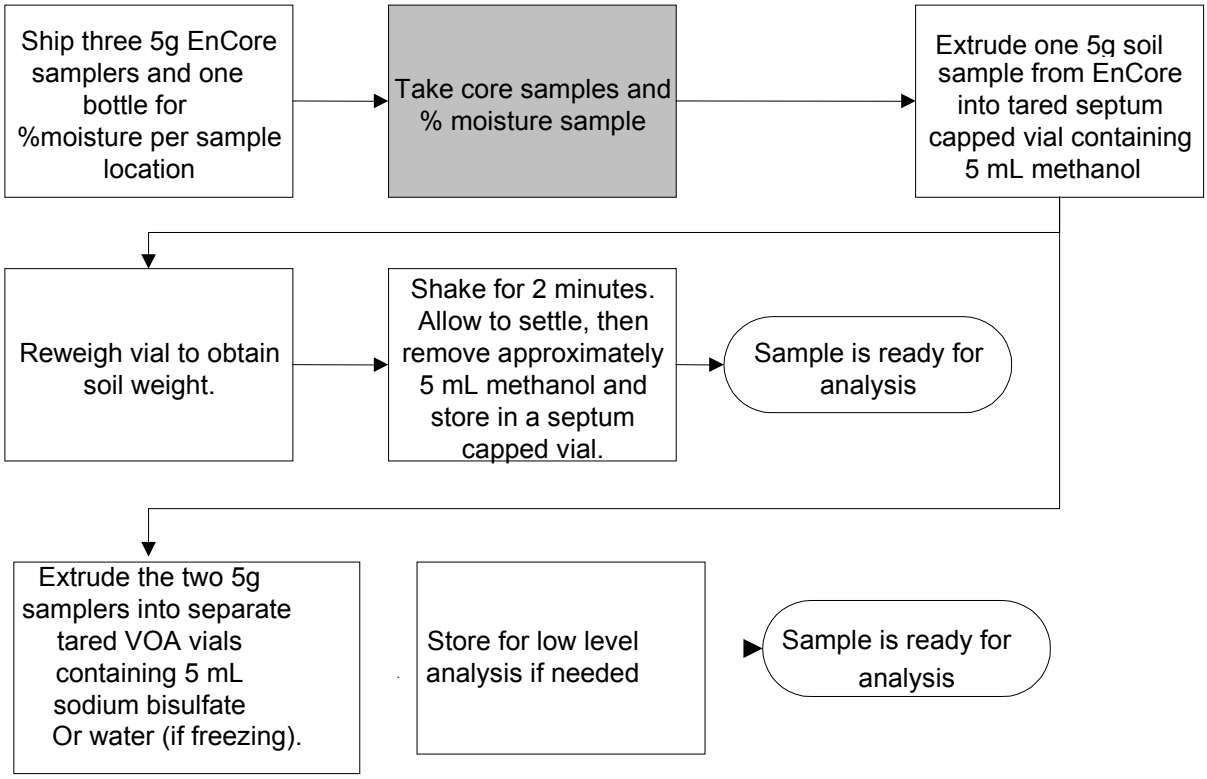
8.11 The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore sampler (before the sample is added to methanol, sodium bisulfate or frozen) is 48 hours.

8.12 A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

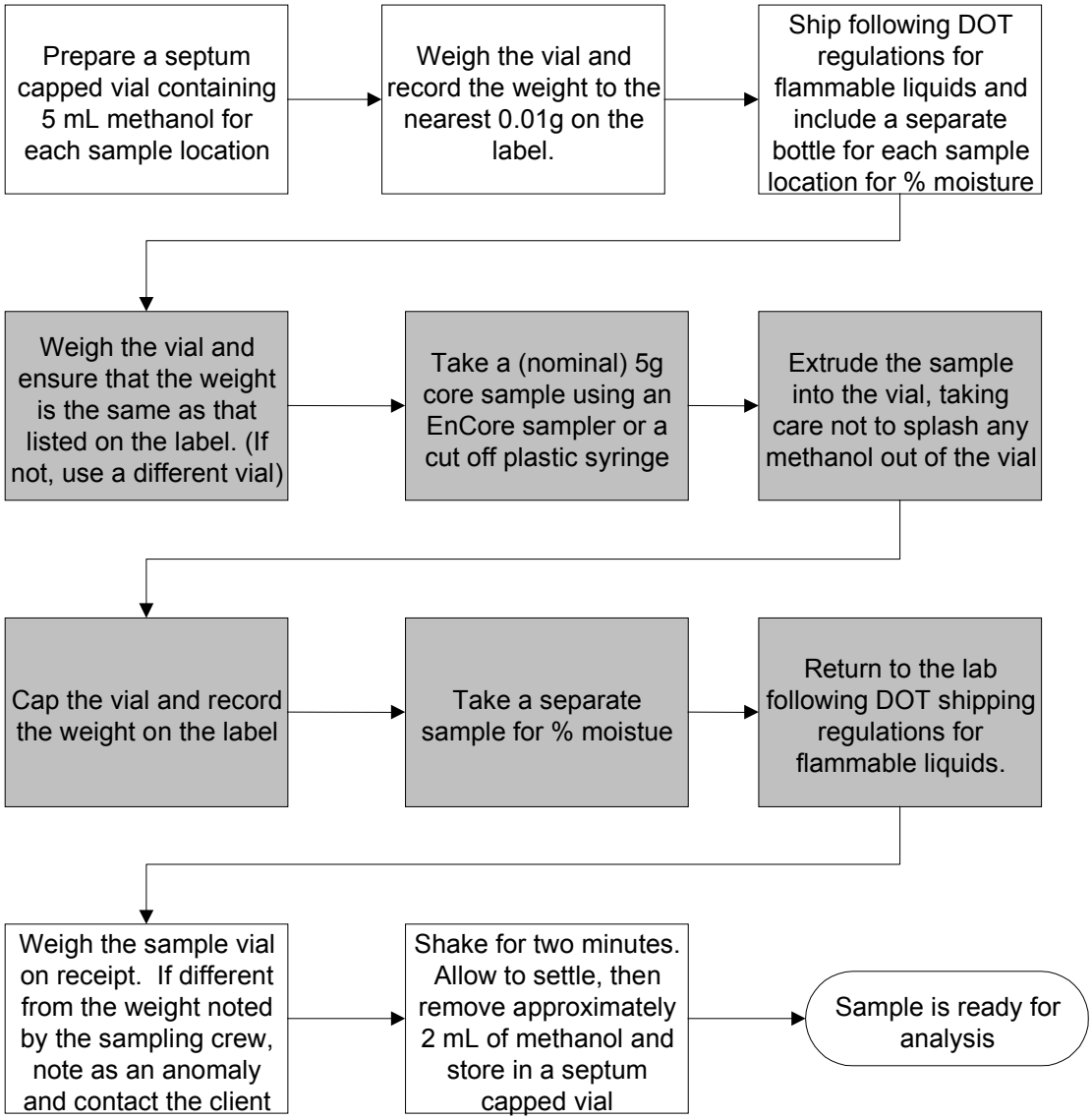
EnCore procedure when low level is not required (field steps in gray)



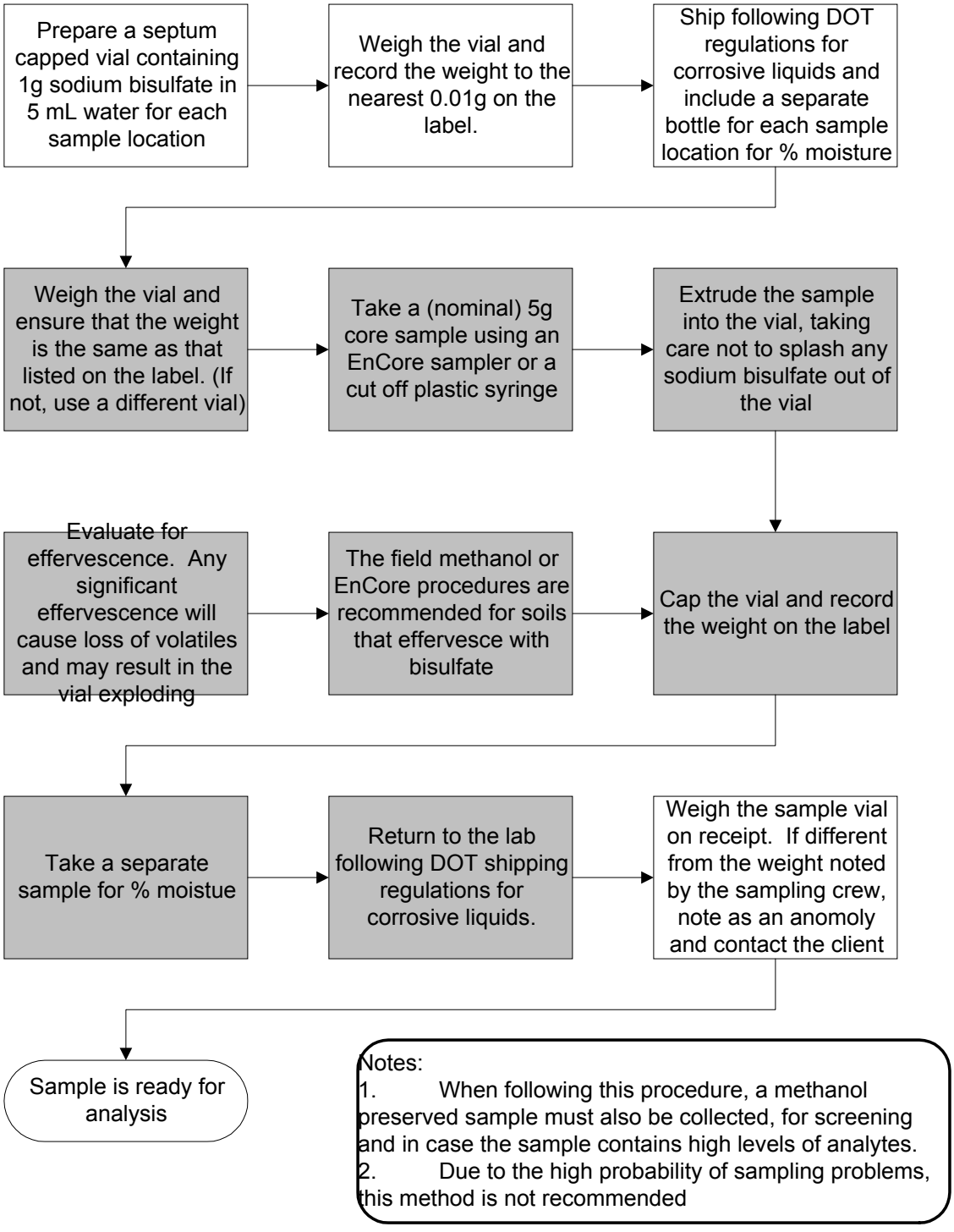
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



9 QUALITY CONTROL

9.1 See Document QA-003 "STL Quality Control Program" for additional detail.

9.2 Initial Demonstration of Capability

9.2.1 Section 13 and method detection limit (MDL) studies must be acceptable before analysis of samples may begin. MDLs should be analyzed for low and medium soils and aqueous samples.

9.2.2 For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of a standard at the reporting limit and a single point calibration.

9.3 In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, matrix spikes and LCS. Precision limits for matrix spikes / matrix spike duplicates are 0 to mean relative percent difference + 3 standard deviations.

9.2.3 All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.4 Refer to the QC Program document (QA-003) for further details of control limits.

9.4 Surrogates

Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Table 8. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

- Samples that have major matrix interference, which is obvious from the chromatogram, will not be rerun for confirmation of matrix interference.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.4.1 If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

9.4.2 Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.5 Method Blanks

For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. *If the first method blank does not meet criteria, a second blank may be put on. The method blank must meet criteria before proceeding.* For low-level volatiles, the method blank consists of reagent water. For medium-level volatiles, the method blank consists of 100 ul of methanol. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is more than five times the reporting limit. Such action must be taken in consultation with the client.

- Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

9.5.1 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.5.2 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

9.5.3 Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.6 Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS is analyzed after the calibration standard. The LCS contains a representative subset of the analytes of interest (See Table 9), and must contain the same analytes as the matrix spike. If any control analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS.)

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.6.1 Refer to the STL QC Program document (QA-003) for further details of the corrective action.

9.6.2 If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client. *Unless otherwise agreed only the control analytes (table 9) are used to evaluate analytical performance control.*

9.7 Matrix Spikes

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 9. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any control component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.8 Nonconformance and Corrective Action

Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

9.9 Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10 STL QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10 CALIBRATION AND STANDARDIZATION

10.4 Summary

10.4.1 Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluoro-benzene (BFB) to establish that a given GC/MS system meets the standard mass

spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system. The use of separate calibrations is required for water and low soil matrices.

10.5 Recommended Instrument Conditions

10.5.1 General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	to give at least 5 scans/peak, but not to exceed 2 second/scan
Injector Temperature:	200–250°C
Source Temperature:	According to manufacturer's specifications
Transfer Line	Temperature: 250–300°C
Purge Flow:	40 mL/minute
Carrier Gas	Flow: 15 mL/minute
Make-up Gas Flow:	25–30 mL/minute

10.5.2 Gas chromatograph suggested temperature program

10.5.2.1 BFB Analysis

Isothermal:	170°C

10.5.2.2 Sample Analysis

Initial Temperature:	35°C
Initial Hold Time:	4 minutes
Temperature Program:	15°C/minute
Final Temperature:	200°C
Final Hold Time:	0.1 minutes

10.6 Instrument Tuning

10.6.1 Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 10 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

10.6.2 Acceptable procedures for BFB tuning are as follows:

10.3.2.a The peak apex, or the scan immediately before the apex, or the scan immediately after the apex, or the average of these three scans may be used. The average of the apex and the scan before or after the apex may also be used.

10.3.2.b Background subtraction is optional. If background subtraction is used, a single scan must be subtracted. This single scan must be prior to and within 20 scans of the start of BFB elution but must not be part of the BFB peak.

10.3.2.c If the instrument has a built in macro that checks the BFB, use of this macro with no manual manipulation is also acceptable. (Assuming, of course that the correct ion ratios are being checked.)

10.3.2.d NOTE: If the background scan selected includes significant ions at 95 or 174 0r 176 for BFB, then the scan is almost certainly part of the BFB peak and is not acceptable.

10.7 Initial Calibration

10.7.1 A series of five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. *Typical calibration levels for a 5 mL purge are: 5, 20, 50, 100, and 200 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Typical calibration levels for a 25 mL purge are 1, 5, 10, 20, and 40 µg/L.* Again, some analytes are prepared at higher levels. Tables 2 and 4 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. However, the same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

10.7.2 It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for same tests. For example, the Appendix IX list requires the Primary standard (Table 5) and the Appendix IX standard (Table 6). If acceptable analytical performance can be obtained the primary and appendix IX standards may be analyzed together.

10.7.3 Internal standard calibration is used. The internal standards are listed in Table 7. Area requirements are +/- 50 – 200% of continuing calibrationTarget compounds should reference the nearest internal standard. Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See equation 1, Section 12, for calculation of response factor.

10.7.4 The % RSD of the calibration check compounds (CCC) must be less than 30%. Refer to Table 12 for the CCCs.

10.7.4.1 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.7.5 The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 11 for the SPCC compounds and required minimum response factors.

10.7.6 If the average of all the %RSDs in the calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

10.7.6.1 If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient (coefficient of determination for non-linear curves) must be $\geq$ 0.990.

10.7.6.2 If the average of all the %RSDs in the calibration is > 15% then calibration on a curve must be used for all analytes with %RSD > 15%. The analyst should consider instrument maintenance to improve the linearity of response. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient, r (coefficient of determination, r^2 for non-linear curves) must be $\geq$ 0.990. If a client requests a non-standard target compound that is a poor performer (alcohols for example), the laboratory may not be able to assure linear performance. In this case, a best fit curve would be provided and an assessment of the quality of the data would be provided in the narrative. If in the judgement of the laboratory, data of usable quality cannot be generated, this will be reported to the client immediately.

10.7.7 Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.7.8 If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.7.9 A separate five point calibration must be prepared for analysis of low level soils. Low level soils analysis requires the use of a closed vial autosampler such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1 g sodium bisulfate, if using sodium bisulfate preservation or 5ml of water if freezing. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging. Medium soil extracts should be analyzed using the water (unheated) calibration curve.

10.7.10 Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation. However, if the analyte is not detected, the non-detect may be reported and no further action is necessary.

10.7.11 All ICALs will be verified by a second source standard, as per QA Directive 99-1, before being used.

10.8 Continuing Calibration: The initial calibration must be verified every twelve hours.

10.8.1 Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 3 calibration standard is used as the continuing calibration.

10.8.2 The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in equation 4, Section 12.3.4.

10.8.3 The % drift or % deviation of the CCCs must be $\leq$ 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 11. In addition, the % drift or % deviation of all analytes must be $\leq$ 50% with allowance for up to six target analytes to have % drift or % deviation > 50%.

10.8.3.1 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.8.3.2 Cyclohexanone, one of the components of the Appendix IX standard, is unstable in the calibration solution, forming 1,1-dimethoxycyclohexane.

No calibration criteria are applied to cyclohexanone and quantitation is tentative. Cyclohexanone is included on the Universal Treatment Standard and FO-39 regulatory lists (but not on Appendix IX).

10.8.4 If the CCCs and or the SPCCs do not meet the criteria in Sections 10.5.3 and 10.5.4, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action such as a different type of column will require a new initial calibration.

10.8.5 Once the above criteria have been met, sample analysis may begin. **Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs.** Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 12 hours after the BFB is acceptable.)

11 PROCEDURE

11.4 Procedural Variations

11.4.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation shall be completely documented using a Nonconformance Memo and approved by a Supervisor or group leader and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.4.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.5 Preliminary Evaluation

11.5.1 Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.5.2 Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in volumetric flasks or in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 1 µL of sample then serial dilutions must be made in volumetric flasks.

11.5.2.1 The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.6 Sample Analysis Procedure

11.6.1 All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.6.2 All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, a LCS, and a method blank.

11.6.2.1 If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next tune period. However, if any re-tuning of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For medium level soils the batch is defined at the sample preparation stage.

11.6.2.2 Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

11.6.2.3 It is not necessary to reanalyze batch QC with reanalyses of samples. However, any reruns must be as part of a valid batch.

11.7 Water Samples

11.7.1 All samples and standard solutions must be at ambient temperature before analysis.

11.7.2 Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq$ 5 µL. Check and document the pH of the remaining sample.

11.7.3 Add 250 ng of each internal and surrogate standard (10 µL of a 25 µg/mL solution, refer to Tables 7 and 8). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 50 µg/L solution for a 5 mL sample, and a 10 µg/L solution for a 25 mL sample). Inject the sample into the purging chamber.

11.7.3.1 For TCLP samples use 0.5 mL of TCLP leachate with 4.5 mL reagent water and spike with 10 µL of the 25 µg/mL spiking solution. (Note that TCLP

reporting limits will be 10 times higher than the corresponding aqueous limits).

11.7.4 Purge the sample for eleven minutes (the trap must be ≤ 35°C).

11.7.5 After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 5-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.7.6 Desorb and bake time and temperature are optimized for the type of trap in use. The same conditions must be used for samples and standards.

11.8 Methanol Extract Soils

11.8.1 Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

11.9 Liquid wastes that are soluble in methanol and insoluble in water.

11.9.1 Pipet 1 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1 gram.

11.9.2 Quickly add 8 mL of methanol, then add 1 mL of surrogate spiking solution to bring the final volume to 10 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a MS/MSD or LCS, 7 mL of methanol, 1 mL of surrogate solution, and 1 mL of matrix spike solution is used.

11.9.3 Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

11.10 Aqueous and Low level Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

11.10.1 Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.10.2 If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.10.3 Soil samples must be quantitated against a curve prepared with standards containing about the same amount of sodium bisulfate as the samples (1 g in 5 mL).

11.10.4 Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.10.5 For aqueous samples, check the pH of the sample remaining in the VOA vial after analysis is completed.

11.11 Low-Level Solids Analysis using discrete autosamplers

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated sediment/soil sample mixed with sodium bisulfate solution containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.11.1 Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.11.2 Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method described in section 11.7.

11.11.3 Connect the purge vessel to the purge and trap device.

11.11.4 Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.). Add directly to the sample from 11.5.2.

11.11.5 The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.

11.11.6 Add the heater jacket or other heating device and start the purge and trap unit.

11.11.7 Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect.

11.12 Initial review and corrective actions

11.12.1 If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.12.2 If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.12.2.1 Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. If the change in sensitivity is a matrix effect confined to an individual sample reanalysis is not necessary. If the change in sensitivity is due to instrumental problems all affected samples must be reanalyzed after the problem is corrected.

11.12.3 The surrogate standard recoveries are evaluated to ensure that they are within limits. Corrective action for surrogates out of control will normally be to reanalyze the affected samples. However, if the surrogate standard response is out high and there are no target analytes or tentatively identified compounds, reanalysis may not be necessary. Out of control surrogate standard response may be a matrix effect. It is only necessary to reanalyze a sample once to demonstrate matrix effect, but reanalysis at a dilution should be considered.

11.13 Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.13.1 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement.

11.13.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

12.1.1 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

12.2 Tentatively Identified Compounds (TICs)

12.2.1 If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

12.2.1.1 Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

12.2.1.2 The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.1.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

12.2.1.5 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6 Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification.

12.3 Calculations.

12.3.1 Response factor (RF):

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specific internal standard

C_{is} = Concentration of the specific internal standard, ng

C_x = Concentration of the compound being measured, ng

12.3.2 Standard deviation (SD):

Equation 2

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(Xi - X)^2}{N - 1}}$$

X_i = Value of X at i through N

N = Number of points

X = Average value of X_i

12.3.3 Percent relative standard deviation (%RSD):

Equation 3

$$\%RSD = \frac{\text{Standard Deviation}}{\overline{RF_i}} \times 100$$

$\overline{RF_i}$ = **Mean of RF values in the curve**

12.3.4 Percent deviation between the initial calibration and the continuing calibration (%D):

Equation 4

$$\% \text{ Deviation} = \frac{RRF_{ic} - RRF_{cc}}{RRF_{ic}} \times 100$$

12.3.5 Percent drift between the initial calibration and the continuing calibration:

Equation 5

$$\textbf{\% Drift} = \frac{\mathbf{C_{expected} - C_{found}}}{\mathbf{C_{expected}}} \times \mathbf{100}$$

Where

$\mathbf{C_{expected}}$ = Known concentration in standard

$\mathbf{C_{found}}$ = Measured concentration using selected quantitation method

12.3.6 Target compound and surrogate concentrations:

Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is $\leq$ 15%.

12.3.6.1 Calculation of concentration using Average Response Factors

Equation 6

$$\textbf{Concentration } \mu\textbf{g / L} = \frac{\boldsymbol{x}}{\boldsymbol{RF}}$$

12.3.6.2 Calculation of concentration using Linear fit

Equation 7

$$\textbf{Concentration } \mu\textbf{g / L} = \boldsymbol{A} + \boldsymbol{Bx}$$

12.3.6.3 Calculation of concentration using Quadratic fit

Equation 8

$$\textbf{Concentration } \mu\textbf{g / L} = \boldsymbol{A} + \boldsymbol{Bx} + \boldsymbol{Cx}^2$$

$\boldsymbol{x}$ is defined in equations 8, 9 and 10

$\boldsymbol{A}$ is a constant defined by the intercept

$\boldsymbol{B}$ is the slope of the curve

$\boldsymbol{C}$ is the curvature

12.3.6.4 Calculation of ***x*** for Water and water-miscible waste:

Equation 9

$$x = \frac{(A_x)(I_s)(D_f)}{(A_{is})(V_o)}$$

Where:

$\mathbf{A_x}$ = Area of characteristic ion for the compound being measured (secondary ion quantitation is allowed only when there are sample interferences with the primary ion)

$\mathbf{A_{is}}$ = Area of the characteristic ion for the internal standard

$\mathbf{I_s}$ = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

$\mathbf{V_o}$ = Volume of water purged, mL

12.3.6.5 Calculation of ***x*** for Medium level soils:

Equation 10

$$x = \frac{(A_x)(I_s)(V_t)(1000)(D_f)}{(A_{is})(V_a)(W_s)(D)}$$

Where:

$\mathbf{A_x}$, $\mathbf{I_s}$, $\mathbf{D_f}$, $\mathbf{A_{is}}$, same as for water.

$\mathbf{V_t}$ = Volume of total extract, mL

$\mathbf{V_a}$ = Volume of extract added for purging, µL

$\mathbf{W_s}$ = Weight of sample extracted, g

$$\mathbf{D} = \frac{100 - \%\text{moisture}}{100}$$

12.3.6.6 Calculation of ***x*** for Low level soils:

Equation 11

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$

Where:

$\mathbf{A_x}$, $\mathbf{I_s}$, $\mathbf{A_{is}}$, same as for water.

D is as for medium level soils

$\mathbf{W_s}$ = Weight of sample added to the purge vessel, g

12.3.6.7 Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

$\mathbf{A_x}$ = Area in the total ion chromatogram for the compound being measured

$\mathbf{A_{is}}$ = Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

In other words, the concentration is equal to ***x*** as defined in equations 8, 9 and 10.

12.3.7 MS/MSD Recovery

Equation 12

$$\textbf{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result

SR = Sample result

SA = Spike added

12.3.8 Relative % Difference calculation for the MS/MSD

Equation 13

$$\mathbf{RPD} = \frac{\left|\mathbf{MSR - MSDR}\right|}{\frac{1}{2}\mathbf{(MSR + MSDR)}} \times \mathbf{100}$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

13 METHOD PERFORMANCE

13.1 Method Detection Limit

Generally, each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005. When non-standard compounds are analyzed at client request, lesser requirements are possible with client agreement. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method.

13.2 Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest. The QC check sample is made up at 20 µg/L. (Some compounds will be at higher levels, refer to the calibration standard levels for guidance.)

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. The %RSD should be $\leq$ 15% for each analyte, and the % recovery should be within 80-120% *for all controlled compounds.*

13.2.3 If any analyte does not meet the acceptance criteria, check the acceptance limits in the reference methods (Table 6 of Method 8260B). If the recovery or precision is outside the limits in the reference methods, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14 POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15 WASTE MANAGEMENT

15.1 Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

16 REFERENCES

16.1 SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260B, Update III, December 1996

17 MISCELLANEOUS

17.1 Modifications from the reference method

17.1.1 Ion 119 is used as the quantitation ion for chlorobenzene-d5.

17.1.2 A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.3 The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.1.4 SW-846 recommends that a curve be used for any analytes with %RSD of the response factors > 15%. However, some industry standard data systems and forms generation

software cannot report this data with the necessary information for data validation. In addition most software available does not allow weighting of the curve. Unweighted curves may exhibit serious errors in quantitation at the low end, resulting in possible false positives or false negatives. Therefore, this SOP allows use of average response factors if the average %RSD for all compounds is $\leq$ 15%.

17.2 Modifications from previous revision

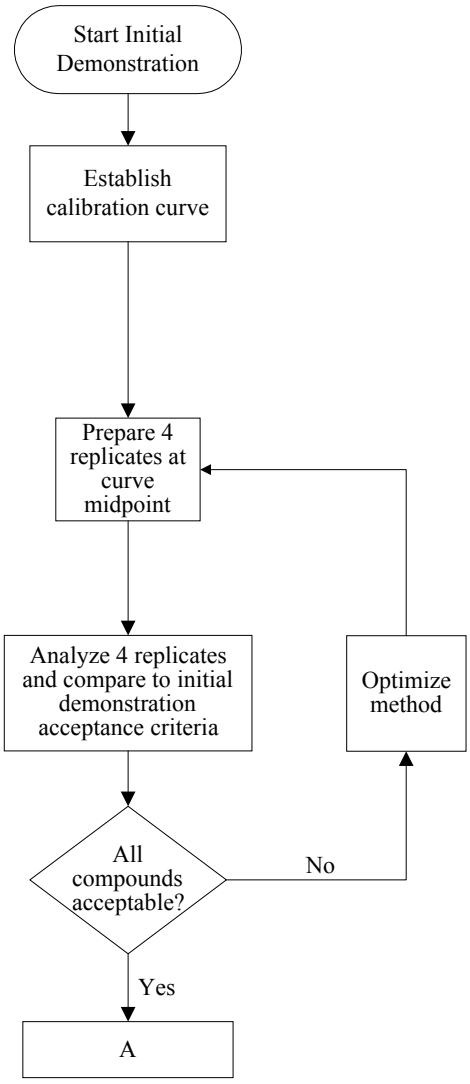
This SOP has been substantially revised to reflect the changes included in Update III to SW-846. Directions for method 524.2 and method 624 have also been added.

17.3 Facility specific SOPs

Each facility shall attach a list of facility-specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4 Flow diagrams

17.4.1 Initial Demonstration and MDL



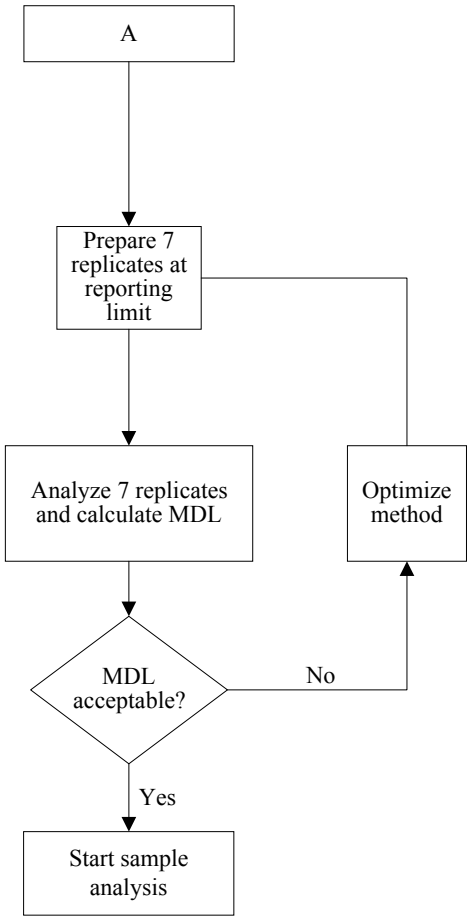


Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL Water µg/L	Low Levelwater µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	5	1	5	250
Chloromethane	74-87-3	5	1	5	250
Bromomethane	74-83-9	5	1	5	250
Vinyl chloride	75-01-4	5	1	5	250
Chloroethane	75-00-3	5	1	5	250
Trichlorofluoromethane	75-69-4	5	1	5	250
Acetone	67-64-1	20	10	20	1000
Trichlorotrifluoroethane	76-13-1	5	1	5	250
Iodomethane	74-88-4	5	1	5	250
Carbon disulfide	75-15-0	5	1	5	250
Methylene chloride	75-09-2	5	1	5	250
1,1-Dichloroethene	75-35-4	5	1	5	250
1,1-Dichloroethane	75-34-3	5	1	5	250
trans-1,2-Dichloroethene	156-60-5	5	1	5	250
Methyl *tert*-butyl ether (MTBE)	1634-04-4	20	5	20	1000
cis-1,2-Dichloroethene	156-59-2	5	1	5	250
1,2-Dichloroethene (Total)	540-59-0	5	1	5	250
Chloroform	67-66-3	5	1	5	250
1,2-Dichloroethane	107-06-2	5	1	5	250
Dibromomethane	74-95-3	5	1	5	250
2-Butanone	78-93-3	20	5	20	1000
1,1,1-Trichloroethane	71-55-6	5	1	5	250
Carbon tetrachloride	56-23-5	5	1	5	250
Bromodichloromethane	75-27-4	5	1	5	250
1,2-Dichloropropane	78-87-5	5	1	5	250
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250
Trichloroethene	79-01-6	5	1	5	250
Dibromochloromethane	124-48-1	5	1	5	250
1,2-Dibromoethane	106-93-4	5	1	5	250
1,2,3-Trichloropropane	96-18-4	5	1	5	250
1,1,2-Trichloroethane	79-00-5	5	1	5	250
Benzene	71-43-2	5	1	5	250
trans-1,3-Dichloropropene	10061-02-6	5	1	5	250
Bromoform	75-25-2	5	1	5	250
4-Methyl-2-pentanone	108-10-1	20	5	20	1000

Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL Water µg/L	Low Levelwater µg/L	Low soil µg/kg	Med. Soil µg/kg
2-Hexanone	591-78-6	20	5	20	1000
Tetrachloroethene	127-18-4	5	1	5	250
Toluene	108-88-3	5	1	5	250
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250
1,1,1,2-Tetrachloroethane	630-20-6	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	5	1	5	250
Chlorobenzene	108-90-7	5	1	5	250
Ethylbenzene	100-41-4	5	1	5	250
Styrene	100-42-5	5	1	5	250
m and p Xylenes		10	2	10	500
o-xylene	95-47-6	5	1	5	250
Total xylenes	1330-20-7	15	3	15	750
1,3-Dichlorobenzene	541-73-1	5	1	5	250
1,4-Dichlorobenzene	106-46-7	5	1	5	250
1,2-Dichlorobenzene	95-50-1	5	1	5	250

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

Table 2

STL Primary Standard Calibration Levels, 5 mL purge[1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichloroethane-d4 (Surrogate)	5	20	50	100	200
Toluene-d8 (Surrogate)	5	20	50	100	200
4-Bromofluorobenzene (Surrogate)	5	20	50	100	200
Dichlorodifluoromethane	5	20	50	100	200
Chloromethane	5	20	50	100	200
Bromomethane	5	20	50	100	200
Vinyl chloride	5	20	50	100	200
Chloroethane	5	20	50	100	200
Trichlorofluoromethane	5	20	50	100	200
Acetone	5	20	50	100	200
Carbon disulfide	5	20	50	100	200
Methylene chloride	5	20	50	100	200
Isopropylbenzene	5	20	50	100	200
1,1-Dichloroethene	5	20	50	100	200
1,1-Dichloroethane	5	20	50	100	200
trans-1,2-Dichloroethene	5	20	50	100	200
1,1,1,2 Tetrachloroethane	5	20	50	100	200
Methyl *tert*-butyl ether (MTBE)	5	20	50	100	200
1,2-Dibromo-3-chloropropane	5	20	50	100	200
cis-1,2-Dichloroethene	5	20	50	100	200
Chloroform	5	20	50	100	200
1,2-Dichloroethane	5	20	50	100	200
Dibromomethane	5	20	50	100	200
2-Butanone	5	20	50	100	200
1,1,1-Trichloroethane	5	20	50	100	200
Carbon tetrachloride	5	20	50	100	200
Bromodichloromethane	5	20	50	100	200
1,2-Dichloropropane	5	20	50	100	200
cis-1,3-Dichloropropene	5	20	50	100	200
Trichloroethene	5	20	50	100	200
Dibromochloromethane	5	20	50	100	200
1,2-Dibromoethane	5	20	50	100	200
1,2,3-Trichloropropane	5	20	50	100	200
1,1,2-Trichloroethane	5	20	50	100	200
Benzene	5	20	50	100	200
trans-1,3-Dichloropropene	5	20	50	100	200
Bromoform	5	20	50	100	200

Table 2

STL Primary Standard Calibration Levels, 5 mL purge[1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
4-Methyl-2-pentanone	5	20	50	100	200
2-Hexanone	5	20	50	100	200
Tetrachloroethene	5	20	50	100	200
Toluene	5	20	50	100	200
1,1,2,2-Tetrachloroethane	5	20	50	100	200
Chlorobenzene	5	20	50	100	200
Ethylbenzene	5	20	50	100	200
Styrene	5	20	50	100	200
m and p Xylenes	10	40	100	200	400
o-xylene	5	20	50	100	200
1,3-Dichlorobenzene	5	20	50	100	200
1,4-Dichlorobenzene	5	20	50	100	200
1,2-Dichlorobenzene	5	20	50	100	200

[1] **Levels for 25 mL purge are 5 times lower in all cases**

Table 3

STL Appendix IX Standard and Reporting Limits, 5 mL purge

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	Low level water µg/L	Low Soil µg/kg	Medium Soil µg/mL
Allyl Chloride	107-05-1	10	2	10	500
Acetonitrile	75-05-8	100	20	100	5000
Dichlorofluoromethane	75-43-4	10	2	10	500
Acrolein	107-02-8	100	20	100	5000
Chloroprene	126-99-8	5	1	5	250
Iodomethane	74-88-4	5	1	5	250
Propionitrile	107-12-0	20	4	20	1000
Methacrylonitrile	126-98-7	5	1	5	250
Isobutanol	78-83-1	400	100	400	20,000
Methyl methacrylate	80-62-6	5	1	5	250
Acrylonitrile	107-13-1	100	20	100	5000
Ethylmethacrylate	97-63-2	5	1	5	250
2-Chloroethyl vinyl ether[1]	110-75-8	10	2	50	1000
tert-Butyl Alcohol	75-65-0	200	50	200	10,000
Ethyl Acetate	141-78-6	20	4	20	1,000
1,4-Dioxane	123-91-1	500	200	500	25,000
Vinyl acetate	108-05-4	5	1	5	250
t-1,4-Dichloro-2-butene	110-57-6	5	1	5	250

[1] 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples.

Table 4

STL Appendix IX Standard Calibration Levels, µg/L

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Allyl Chloride	5	20	50	100	200
Acetonitrile	100	200	500	1,000	2,000
Dichlorofluoromethane	5	20	50	100	200
Chloroprene	5	20	50	100	200
Propionitrile	10	40	100	200	400
Methacrylonitrile	5	20	50	100	200
Isobutanol	200	400	1000	2000	4000
Methyl methacrylate	5	20	50	100	200
Acrolein	100	125	150	175	200
1,4-Dioxane	500	1000	2500	5000	10000
tert-Butyl alcohol	200	400	1000	2000	4000
Acrylonitrile	100	125	150	175	200
Ethylmethacrylate	5	20	50	100	200
2-Chloroethyl vinyl ether	10	40	100	200	400
Vinyl Acetate	5	20	50	100	200
Ethyl Acetate	10	40	100	200	400
t-1,4-Dichloro-2-butene	5	20	50	100	200

Table 5

Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Dichlorodifluoromethane	75-71-8				X	X
Chloromethane	74-87-3	X		X	X	X
Bromomethane	74-83-9	X		X	X	X
Vinyl chloride	75-01-4	X	X	X	X	X
Chloroethane	75-00-3	X		X	X	X
Trichlorofluoromethane	75-69-4				X	X
Acrolein	107-02-8				X	X
Acetone	67-64-1	X		X	X	X
Trichlorotrifluoroethane	76-13-1					X
Iodomethane	74-88-4				X	X
Carbon disulfide	75-15-0	X		X	X	X
Methylene chloride	75-09-2	X		X	X	X
tert-Butly alcohol	75-65-0					
1,1-Dichloroethene	75-35-4	X	X	X	X	X
1,1-Dichloroethane	75-34-3	X		X	X	X
trans-1,2-Dichloroethene	156-60-5	X		X	X	X
Total dichloroethene		X		X	X	X
Acrylonitrile	107-13-1				X	X
Methyl *tert*-butyl ether (MTBE)	1634-04-4					
cis-1,2-Dichloroethene	156-59-2	X		X		
Chloroform	67-66-3	X	X	X	X	X
1,2-Dichloroethane	107-06-2	X	X	X	X	X
Dibromomethane	74-95-3				X	X
2-Butanone	78-93-3	X	X	X	X	X
1,4-Dioxane	123-91-1				X	X
1,1,1-Trichloroethane	71-55-6	X		X	X	X
Carbon tetrachloride	56-23-5	X	X	X	X	X
Bromodichloromethane	75-27-4	X		X	X	X
1,2-Dichloropropane	78-87-5	X		X	X	X
cis-1,3-Dichloropropene	10061-01-5	X		X	X	X
Trichloroethene	79-01-6	X	X	X	X	X
Dibromochloromethane	124-48-1	X		X	X	X
1,2-Dibromoethane	106-93-4				X	X
1,2,3-Trichloropropane	96-18-4				X	X
1,1,2-Trichloroethane	79-00-5	X		X	X	X
Benzene	71-43-2	X	X	X	X	X

Table 5

Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Ethylmethacrylate	97-63-2				X	X
trans-1,3-Dichloropropene	10061-02-6	X		X	X	X
Bromoform	75-25-2	X		X	X	X
4-Methyl-2-pentanone	108-10-1	X		X	X	X
2-Hexanone	591-78-6	X		X	X	
Tetrachloroethene	127-18-4	X	X	X	X	X
Toluene	108-88-3	X		X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	X		X	X	X
2-Chloroethyl vinyl ether	110-75-8					
Vinyl acetate	108-05-4				X	
Chlorobenzene	108-90-7	X	X	X	X	X
Ethylbenzene	100-41-4	X		X	X	X
Styrene	100-42-5	X		X	X	
t-1,4-Dichloro-2-butene	110-57-6				X	
m and p Xylenes		X		X	X	X
o-xylene	95-47-6	X		X	X	X
Total xylenes	1330-20-7	X		X	X	X
1,3-Dichlorobenzene	541-73-1					
1,4-Dichlorobenzene	106-46-7					
1,2-Dichlorobenzene	95-50-1					

Table 6

Reportable Analytes for STL Standard Tests, Appendix IX standard

Compound	Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Allyl Chloride	107-05-1				X	
Acetonitrile	75-05-8				X	X
Chloroprene	126-99-8				X	
Propionitrile	107-12-0				X	
Methacrylonitrile	126-98-7				X	X
Isobutanol	78-83-1				X	X
Methyl methacrylate	80-62-6				X	X
1,1,1,2-Tetrachloroethane	630-20-6				X	X
1,2-Dibromo-3-chloropropane	96-12-8				X	X
Ethyl Acetate	141-78-6					X
Isopropylbenzene	98-82-8					

Table 7

Internal Standards

	Standard Concentration µg/mL	Quantitation ion (5 mL purge)	Quantitation ion (25 mL purge)
Fluorobenzene	25	96	96
Chlorobenzene-d5	25	*119*	119
1,4-Dichlorobenzene-d4	25	152	152

Notes:

1) 10 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L for a 5 mL purge or 10 µg/L for low level waters, Method 624 and Method 524.2.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 8

Surrogate Standards

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d_4	25
Dibromofluoromethane	25
Toluene-d_8	25
4-Bromofluorobenzene	25

Notes:

1) 10 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L for a 5 mL purge and 10 µg/L for low level SW846, Method 624 and Method 524.2.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

3) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 9

Matrix Spike / LCS Compounds

Compound	Standard Concentration µg /mL
1,1-Dichloroethene	25
Trichloroethene	25
Toluene	25
Benzene	25
Chlorobenzene	25

Notes:

1) 10 µL of the standard is added to the LCS or matrix spiked sample. This results in a concentration of each spike analyte in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a low level SW846, Method 624 and 524.2.

2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by the QA department.

Table 10

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 11

SPCC Compounds and Minimum Response Factors

Compound	8260B Min. RF
Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	>0.100
1,1,2,2-Tetrachloroethane	0.300
Chlorobenzene	0.300

Table 12

CCC compounds

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	≤30.0	≤20.0
1,1-Dichloroethene	≤30.0	≤20.0
Chloroform	≤30.0	≤20.0
1,2-Dichloropropane	≤30.0	≤20.0
Toluene	≤30.0	≤20.0
Ethylbenzene	≤30.0	≤20.0

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
1,2-Dichloroethane-d_4 (Surrogate)	65	102	
Dichlorodifluoromethane	85	87	50, 101,103
Chloromethane	50	52	49
Vinyl chloride	62	64	61
Bromomethane	94	96	79
Chloroethane	64	66	49
Trichlorofluoromethane	101	103	66
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Ethanol	45	46	
Acetone	43	58	
Methylene chloride	84	49	51, 86
tert-Butyl alcohol	59	74	
trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl *tert* butyl ether	73		
Hexane	57	43	
1,1-Dichloroethane	63	65	83
cis-1,2-Dichloroethene	96	61	98
2-Butanone	43	72**	
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121
Benzene	78	52	77
Trichloroethene	130	95	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d_8 (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone	43	58	57, 100
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
2-Hexanone	43	58	57, 100
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133
Allyl Chloride	76	41	78
Acetonitrile	40	41	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52
Isobutanol	41	43	74
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo-3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	

* The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.

** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

18 SUMMARY

This appendix lists modifications to the main body of the SOP that are necessary for analysis of drinking water by method 524.2.

18.1 A target analyte list based on the list in method 524.2 is frequently requested for analysis by method 8260B. STL's standard analyte list for this test, and the internal and surrogate standards used, are listed in Tables A-1 to A-2 below. In all other respects the method is as described in the main body of this SOP.

19 MODIFICATIONS REQUIRED FOR DRINKING WATER ANALYSIS BY METHOD 524.2

19.1 This method can be applied to surface water, ground water and drinking water.

19.2 Sample concentrations are calculated using initial calibration curve.

19.3 Three internal standards (see SW846) are used for this method.

19.4 A maximum of 25 ng of BFB is used for tuning for method 524.2

19.5 BFB tuning criteria for mass 75 are 30-80% of mass 95.

19.6 The recovery limits for the initial demonstration of capability are 80-120% with %RSD less than 20%.

19.7 Initial calibration curve requirements:

19.7.1 The number of calibration standards depends on the calibration range used. For a range of up to a factor of 20 (e.g. 1µg/L - 20µg/L) a minimum of three standards are necessary. For a factor of up to 50 four standards are necessary, and for a factor of up to 100 five standards are necessary.

19.7.2 All target compounds must have RSD ≤ 20%.

19.7.3 If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

19.8 Continuing calibration verification (CCV) requirements:

19.8.1 All target compounds must have %D ≤ 30%.

19.8.2 The internal standards in each CCV must be over 70% of the abundance found in the CCV analysis immediately preceding it *and* over 50% of the calibration point in the initial calibration curve whose concentration matches that of the CCV.

19.8.3 The same analysis run may be used to satisfy the requirements for an LCS (also known as a laboratory fortified blank, LFB) and a continuing calibration verification. The LCS/CCV does not need to be a second source standard.

19.9 Method clarifications, modifications and additions

19.9.1 Section 7.1 requires that the trap packing materials be Tenax GC, Methyl silicone, silica gel and coconut charcoal. STL routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

19.9.2 Section 7.8.2 of the source method requires that each calibration standard be prepared by diluting the appropriate volume of the working standard with organic-free water adjusted to pH < 2 in a volumetric flask. STL prepares calibration standards by diluting the the appropriate volume of the working standard with organic-free water in the gas-tight syringe that will be used to inject the sample into the purge and trap device.

19.9.3 Sections 9.8 and 9.9 of the source method require that duplicate spiked blanks and a second-source initial calibration verification standard be analyzed at least quarterly. Since some STL laboratories do not normally analyze drinking waters samples, these QC samples will be analyzed only during the conduct of projects that require this method.

19.9.4 If drinking water samples are to be analyzed, a 0.5 ppb standard will be run that day to confirm that this level can be seen by the instrument.

Table A-1

STL 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limit[2]	Reporting Limits[1]			
			5 mL water µg/L	Low level water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	1	5	1	5	500
Chloromethane	74-87-3	1	5	1	5	500
Bromomethane	74-83-9	1	5	1	5	500
Vinyl chloride	75-01-4	1	5	1	5	500
Chloroethane	75-00-3	1	5	1	5	500
Trichlorofluoromethane	75-69-4	1	5	1	5	500
Acetone[1]	67-64-1	10	20	10	20	1000
Methylene chloride	75-09-2	1	5	2	5	250
1,1-Dichloroethene	75-35-4	1	5	1	5	250
1,1-Dichloroethane	75-34-3	1	5	1	5	250
trans-1,2-Dichloroethene	156-60-5	1	5	1	5	250
Methyl *tert*-butyl ether (MTBE)[1]	1634-04-4	1	20	5	20	250
2,2-Dichloropropane	590-20-7	1	5	1	5	250
cis-1,2-Dichloroethene	156-59-2	1	5	1	5	250
1,2-Dichloroethene (Total)	540-59-0	1	5	1	5	250
Chloroform	67-66-3	1	5	1	5	250
Bromochloromethane	74-97-5	1	5	1	5	250
1,2-Dichloroethane	107-06-2	1	5	1	5	250
Dibromomethane	74-95-3	1	5	1	5	250
2-Butanone[1]	78-93-3	5	20	5	20	1000
1,1,1-Trichloroethane	71-55-6	1	5	1	5	250
Carbon tetrachloride	56-23-5	1	5	1	5	250
1,1-Dichloropropene	563-58-6	1	5	1	5	250
Bromodichloromethane	75-27-4	1	5	1	5	250
1,2-Dichloropropane	78-87-5	1	5	1	5	250
1,3-Dichloropropane	142-28-9	1	5	1	5	250
cis-1,3-Dichloropropene	10061-01-5	1	5	1	5	250
Trichloroethene	79-01-6	1	5	1	5	250
Dibromochloromethane	124-48-1	1	5	1	5	250
1,2-Dibromoethane	106-93-4	1	5	1	5	250
1,2,3-Trichloropropane	96-18-4	1	5	1	5	250
1,1,2-Trichloroethane	79-00-5	1	5	1	5	250
Benzene	71-43-2	1	5	1	5	250
trans-1,3-Dichloropropene	10061-02-6	1	5	1	5	250
Bromoform	75-25-2	1	5	1	5	250

Table A-1

STL 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limit[2]	Reporting Limits[1]			
			5 mL water µg/L	Low level water µg/L	Low soil µg/kg	Med. Soil µg/kg
4-Methyl-2-pentanone[1]	108-10-1	5	20	5	20	1000
2-Hexanone[1]	591-78-6	5	20	5	20	1000
Tetrachloroethene	127-18-4	1	5	1	5	250
Toluene	108-88-3	1	5	1	5	250
1,1,2,2-Tetrachloroethane	79-34-5	1	5	1	5	250
Chlorobenzene	108-90-7	1	5	1	5	250
1,1,1,2-Terrachloroethane	630-20-6	1	5	1	5	250
Ethylbenzene	100-41-4	1	5	1	5	250
Styrene	100-42-5	1	5	1	5	250
m and p Xylenes		2	10	2	10	500
o-xylene	95-47-6	1	5	1	5	250
Total xylenes	1330-20-7	3	15	3	15	750
Isopropylbenzene	98-82-8	1	5	1	5	250
Bromobenzene	108-86-1	1	5	1	5	250
n-Propylbenzene	103-65-1	1	5	1	5	250
2-Chlorotoluene	95-49-8	1	5	1	5	250
4-Chlorotoluene	106-43-4	1	5	1	5	250
1,3,5-Trimethylbenzene	108-67-8	1	5	1	5	250
tert-Butylbenzene	98-06-6	1	5	1	5	250
1,2,4-Trimethylbenzene	95-63-6	1	5	1	5	250
sec-butylbenzene	135-98-8	1	5	1	5	250
1,3-Dichlorobenzene	541-73-1	1	5	1	5	250
1,4-Dichlorobenzene	106-46-7	1	5	1	5	250
1,2-Dichlorobenzene	95-50-1	1	5	1	5	250
4-Isopropyltoluene	99-87-6	1	5	1	5	250
n-Butylbenzene	104-51-8	1	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	1	5	1	5	250
1,2,4-Trichlorobenzene	120-82-1	1	5	1	5	250
Napthalene	91-20-3	1	5	1	5	250
Hexachlorobutadiene	87-68-3	1	5	1	5	250
1,2,3-Trichlorobenzene	87-61-6	1	5	1	5	250

1 Not included on the method 524.2 analyte list, but included in the calibration standard as an add on frequently requested by method 8260B. These Reporting Limits are for Method 8260B.

2 These Reporting Limits are for Method 524.2.

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20 REQUIREMENTS FOR EPA 624

20.1 Method 624 is required for demonstration of compliance with NPDES wastewater discharge permits. This method can be applied only to aqueous matrices. The standard analyte list and reporting limits are listed in Table B-1.

20.2 The tune period for this method is defined as 24 hours.

20.3 The initial calibration curve for this method requires at least three points.

20.4 Sample concentrations are calculated using the average RRF from the initial calibration curve.

20.5 Each target analyte is assigned to the closest eluting internal standard.

20.6 Initial demonstration of Proficiency

20.6.1 The spiking level for the four replicate initial demonstration of proficiency is 20 μg/L. The acceptance criteria are listed in Table B-2

20.7 Initial calibration curve requirements:

20.7.1 Target compounds listed in Method 624 must have RSD ≤ 35%.

20.7.2 If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

20.7.3 For compounds not listed in Method 624, the average response factor will be used.

20.8 Continuing calibration verification requirements:

20.8.1 The continuing calibration standard is from a different source than the initial calibration standard. The acceptance criteria are listed in Table B-2.

20.9 MS/MSD and LCS requirements

20.9.1 The LCS, MS and MSD will be 10ppb for all compounds except, 2CEVE (20ppb), Acrolein (30ppb) and Acrylonitrile (30ppb). . The recovery limits for MS/MSD and LCS recovery are listed in Table B-2.

20.10 Method clarifications, modifications and additions

20.10.1 Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. STL routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

20.10.2 Section 5.3.2 of the source method describes a packed analytical column. STL routinely employs capillary columns when performing this method.

20.10.3 The source method provides a suggested list of compounds for internal and surrogate standards. STL uses the same internals and surrogates found in SW846 Method 8260B (See Tables 7 and 8).

Table B-1.

Method 624 Analytes and Reporting Limits

Analytes	µg/L
Benzene	1
Bromodichloromethane	1
Bromoform	1
Bromomethane	1
Carbon tetrachloride	1
Chlorobenzene	1
Chloroethane	1
2-Chloroethyl vinyl ether	2
Chloroform	1
Chloromethane	1
Dibromochloromethane	1
1,2-Dichlorobenzene	1
1,3-Dichlorobenzene	1
1,4-Dichlorobenzene	1
1,1-Dichloroethane	1
1,2-Dichloroethane	1
1,1-Dichloroethene	1
trans-1,2-Dichloroethene	1
1,2-Dichloropropane	1
cis-1,3-Dichloropropene	1
trans-1,3-Dichloropropene	1
Ethylbenzene	1
Methylene chloride	1
1,1,2,2-Tetrachloroethane	1
Tetrachloroethene	1
Toluene	1
1,1,1-Trichloroethane	1
1,1,2-Trichloroethane	1
Trichloroethene	1
Trichlorofluoromethane	1
Vinyl chloride	1

Table B-2.

Method 624 QC Acceptance Criteria

Analytes	Daily QC Chk acceptance criteria %Recovery	Mean recovery, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Standard deviation, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Matrix spike acceptance criteria (% Recovery)
Benzene	64-136	15.2-26.0	6.9	37-151
Bromodichloromethane	65-135	10.1-28.0	6.4	35-155
Bromoform	71-129	11.4-31.1	5.4	45-169
Bromomethane	14-186	D-41.2	17.9	D-242
Carbon tetrachloride	73-127	17.2-23.5	5.2	70-140
Chlorobenzene	66-134	16.4-27.4	6.3	37-160
Chloroethane	38-162	8.4-40.4	11.4	14-230
2-Chloroethyl vinyl ether	0-224	D-50.4	25.9	D-305
Chloroform	67-133	13.7-24.2	6.1	51-138
Chloromethane	0-204	D-45.9	19.8	D-273
Dibromochloromethane	67-133	13.8-26.6	6.1	53-149
1,2-Dichlorobenzene	63-137	11.8-34.7	7.1	18-190
1,3-Dichlorobenzene	73-127	17.0-28.8	5.5	59-156
1,4-Dichlorobenzene	63-137	11.8-34.7	7.1	18-190
1,1-Dichloroethane	72-128	14.2-28.5	5.1	59-155
1,2-Dichloroethane	68-132	14.3-27.4	6.0	49-155
1,1-Dichloroethene	50-150	3.7-42.3	9.1	D-234
trans-1,2-Dichloroethene	69-131	13.6-28.5	5.7	54-156
1,2-Dichloropropane	34-166	3.8-36.2	13.8	D-210
cis-1,3-Dichloropropene	24-176	1.0-39.0	15.8	D-227
trans-1,3-Dichloropropene	50-150	7.6-32.4	10.4	17-183
Ethylbenzene	59-141	17.4-26.7	7.5	37-162
Methylene chloride	60-140	D-41.0	7.4	D-221
1,1,2,2-Tetrachloroethane	60-140	13.5-27.2	7.4	46-157
Tetrachloroethene	73-127	17.0-26.6	5.0	64-148
Toluene	74-126	16.6-26.7	4.8	47-150
1,1,1-Trichloroethane	75-125	13.7-30.1	4.6	52-162
1,1,2-Trichloroethane	71-129	14.3-27.1	5.5	52-150
Trichloroethene	66-134	18.6-27.6	6.6	71-157
Trichlorofluoromethane	48-152	8.9-31.5	10.0	17-181
Vinyl chloride	4-196	D-43.5	20.0	D-251

APPENDIX 23

STL STANDARD OPERATING PROCEDURE

TITLE: GC/MS ANALYSIS BASED ON METHODS 8270C AND 625

(SUPERSEDES: Revision 2.1)

Prepared by: Patrick Conlon

Reviewed by: _____ 4/25/02
Technical Review

Approved by: _____ 4/25/02
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____ 4/25/02
Management

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1. SCOPE AND APPLICATION

1.1. This method is based upon SW846 8270C, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. The modifications presented in Attachment A may be followed for analysis of wastewater following method 625. Direct injection of a sample may be used in limited applications. Refer to Tables 1, 2, 3 and 4 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in section 13 before sample analysis.

1.2. The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- Hexachlorophene is not amenable to analysis by this method.
- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method.

1.3. The standard reporting limit (SRL) of this method for determining an individual compound is approximately 0.33 mg/kg (wet weight) for soil/sediment samples, 1 - 200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. Some compounds have higher reporting limits. Refer to Tables 1 and 2 for specific SRLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

2. SUMMARY OF METHOD

2.1. Aqueous samples are extracted with methylene chloride using a separatory funnel, a continuous extractor or Accelerated One-Step™. Solid samples are extracted with methylene chloride / acetone using sonication, soxhlet, accelerated soxhlet or pressurized fluid extraction. Waste dilution is used for samples that are miscible with the solvent. The extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Extraction procedures are detailed in SOP# CORP-OP-0001. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3. DEFINITIONS

3.1. CCC (Calibration Check Compounds) - A subset of target compounds used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCC's is specified for calibration acceptance.

3.2. SPCC (System Performance Check Compounds) - Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factors are specified for acceptable performance.

3.3. Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

3.4. Method Blank - An analytical control consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and

reagent contamination.

3.5. LCS (Laboratory Control Sample) - A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.6. MS (Matrix Spike)- aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.7. MSD (Matrix Spike Duplicate)- a second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference is detected it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2. The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.3. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4.4. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5. Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5. SAFETY PRECAUTIONS

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates. The following requirements must be met:

5.1.1. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.1.2. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.1.3. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine. Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in a hood.

5.1.4. Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made.

5.1.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported immediately to a laboratory supervisor.

5.1.6.

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph/Mass Spectrometer System: An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.2. Column: 30 m x 0.32 mm I.D. (or 0.25 mm I.D.) 0.5-µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3. Mass Spectrometer: Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization

mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when 50 ng of the GC/MS tuning standard is injected through the GC.

6.4. GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5. Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.6. Syringe: 10 µL Hamilton Laboratory grade syringes or equivalent.

6.7. Carrier gas: Ultra high purity helium.

7. REAGENTS AND STANDARDS

7.1. A minimum five point calibration curve is prepared. The low point should be at or below the reporting limit. Refer to Tables 12 and 13 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2. An Internal Standard solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.2.1. Internal Standards are added to all standards and extracts to result in 40ng injected onto the column. For example, if the volume of an extract used was 200 µL, 20 µL of a 400 µg/mL internal standard solution would be added for a 1 µL injection.

7.3. Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 11.

7.4. GC/MS Tuning Standard: A methylene chloride solution containing 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT, should also be included in the Tuning Standard at 50 µg/mL.

7.5. Laboratory Control Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. LCS compounds and levels are listed in Tables 9 and 10.

7.6. Matrix Spike Solution: Prepare as indicated in the preparative methods. See preparation SOP. The matrix spike compounds and levels are the same as the LCS compounds.

7.7. The standards listed in 7.1 to 7.6 should be refrigerated at $\leq 6^{o}C$ when not in use. Refrigeration at $-10^{o}C$ to $-20^{o}C$ may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. The continuing calibration standard must be replaced every week and is stored at $\leq 6^{o}C$.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Reference appropriate facility SOP for sample bottle preservation and storage.

8.2. Samples are stored at $4 \pm 2^{o}C$. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. (Extracts will normally be stored for 30 days after invoicing.)

8.3. Water samples are extracted within seven days of sampling and the extracts are analyzed within forty days of extraction. Solids, sludges, and organic liquids are extracted within fourteen days of sampling and the extracts are analyzed within forty days of extraction.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin. Refer to the flow chart in section 17.4.1.

9.1.2. For non-standard analytes an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes,

and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, MS and LCSPrecision limits for matrix spikes / matrix spike duplicates are mean relative percent difference +/- 3 standard deviations.

9.2.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.2.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.3. Refer to the QC program document (QA-003) for further details of control limits.

9.3. Method Blank

A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water for aqueous samples, and sodium sulfate for soil samples (Refer to SOP No. CORP-OP-0001 for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the RL. Such action must be taken in consultation with the client.

- Reanalysis of any samples with reportable concentrations of analytes found in the method blank is required unless other actions are agreed with the client.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.3.1. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.3.2. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

9.3.3. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.3.4. Sample results are NOT blank subtracted unless specific requests and arrangements have been made with a client or agency.

9.4. Instrument Blank

9.4.1. Instruments must be evaluated for contamination during each 12 hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated in the same way as the method blank.

9.5. Laboratory Control Sample (LCS)

9.5.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All analytes must be within established control limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless specified by a client or agency. The compounds must be spiked at a concentration equivalent to 100 or 150 ng on-column depending on the analyte.

9.5.2. If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS).

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5.3. Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same subset of analytes as the LCS (See Tables 9 and 10). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7. Surrogates

9.7.1. Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. Surrogate compounds must be spiked at either 100 or 150 ng on-column, depending on the surrogate. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 11.

9.7.2. If any surrogates are outside limits the following corrective actions must take place (except for dilutions):

- Check all calculations for error.

- Ensure that instrument performance is acceptable.

- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Re-extract and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.7.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the MSD do not require reanalysis as this phenomenon would indicate a possible matrix problem.

9.7.4. If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable, then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate.)

9.7.5. If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.8. Nonconformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

9.9. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10. STL QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective

actions.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is tuned for DFTPP, calibrated initially with a five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 5.

10.2. All standards and extracts are allowed to warm to room temperature before injecting.

10.3. Instrument Tuning

At the beginning of every twelve hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table 6) is achieved for DFTPP (decafluorotriphenylphosphine).

10.3.1. Inject 50 ng of the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 6 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.2. The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Benzidine and pentachlorophenol should not exhibit excessive tailing. If DDT is an analyte of interest, it must be included in the tuning standard, and its breakdown must be < 20%. Refer to section 12 for the appropriate calculations.

10.4. Initial Calibration

10.4.1. Internal Standard Calibration Procedure: Internal standards are listed in Table 7. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.4.2. Compounds should be assigned to the IS with the closest retention time.

10.4.3. Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Six standards must be used for a quadratic least squares calibration. It may also be useful to analyze six calibration

levels and use the lower five for most analytes and the upper five for analytes that have poor response. Add the internal standard mixture to result in 40 ng on column. (For example, if the volume of the calibration standard used is 1 mL, add 100 µL of the 400 µg/mL internal standard solution for a 1 µL injection). The concentrations of all analytes are listed in tables 12 and 13.

10.4.4. Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in section 12 and verify that the CCC and SPCC criteria in section 10.4.5 and 10.4.6 are met. **No sample analysis may be performed unless these criteria are met.**

10.4.5. System Performance Check Compounds (SPCCs): The minimum average RF for semivolatile SPCCs is 0.050. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

SPCC Compounds:

N-nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4-Nitrophenol

10.4.6. Calibration Check Compounds (CCCs): The %RSD of the response factors for each CCC in the initial calibration must be less than 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could affect this criterion.

10.4.6.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.6.2. CCC Compounds:

Phenol
Acenaphthene
1,4-Dichlorobenzene
N-nitrosodiphenylamine

2-Nitrophenol
Pentachlorophenol
2,4-Dichlorophenol
Fluoranthene
Hexachlorobutadiene
Di-n-octylphthalate
4-Chloro-3-methylphenol
Benzo(a)pyrene
2,4,6-Trichlorophenol

10.4.7. If the average of all %RSDs in the initial calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

10.4.7.1. If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation.

10.4.7.2. If the average of all the %RSDs in the initial calibration is > 15%, then calibration on a curve must be used for those analytes with %RSD > 15%. Linear or quadratic curve fits may be used. Use of $1/Concentration^2$ weighting is recommended to improve the accuracy of quantitation at the low end of the curve. The analyst should consider instrument maintenance to improve the linearity of response. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient (coefficient of determination for non-linear curves) must be $\geq$ 0.990.

10.4.8. Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.9. If time remains in the 12 hour period initiated by the DFTPP injection before

the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.10. **Quantitation is performed using the calibration curve or average response factor form the initial curve, not the continuing calibration.**

10.5. Continuing Calibration

10.5.1. At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 6.

10.5.2. Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration.

10.5.3. The following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of ≥ 0.05.
- The percent difference or drift of the CCC compounds from the initial calibration must be $\leq 20\%$. (see section 12 for calculations) In addition, the percent difference or drift of all analytes must be $\leq 50\%$, with allowance being made for up to six target compounds to have percent drift greater than 50%.
- The internal standard response must be within 50-200% of the response in the mid level of the initial calibration.
- The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.

10.5.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.5.4. Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed. (A sample *injected* less than 12 hours after the DFTPP is acceptable.)

11. PROCEDURE

11.1. Sample Preparation

Samples are prepared following SOP CORP-OP-0001.

11.2. Sample Analysis Procedure

11.2.1. Calibrate the instrument as described in section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2. All samples must be analyzed using the same instrument conditions as the preceeding continuing calibration standard.

11.2.3. Add internal standard to the extract to result in 40 ng injected on column (for example, 1 µL of a 2000µL/mL internal standard solution in 100 µL of extract for a 2 µL injection). Mix thoroughly before injection into the instrument.

11.2.4. Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.2.5. The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.6. Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system.

11.2.7. Target compounds identified by the data system are evaluated using the criteria listed in section 12.1.

11.2.8. Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client. They are evaluated using the criteria in section 12.3. At least 20 TICs will be generated.

11.3. Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the

appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

11.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4. Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at $4 \pm 2^{o}C$, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

11.5. Retention time criteria for samples

If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.5.1. If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceeding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

11.6. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to the facility specific SOP for determination of percent moisture.

11.7. Procedural Variations

11.7.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in

sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.8. Troubleshooting Guide

11.8.1. Daily Instrument Maintenance

In addition to the checks listed in the instrument maintenance schedule in the STL QAMP, the following daily maintenance should be performed.

11.8.1.1.Clip Column as necessary.

11.8.1.2.Install new or cleaned injection port liner as necessary.

11.8.1.3.Install new septum as necessary.

11.8.1.4.Perform mass calibration as necessary.

11.8.2. Major Maintenance

11.8.2.1.A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the ion volume or repeller, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the

retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.1. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2. Mass chromatogram searches.

Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte a mass chromatogram search is made.

12.2.1. Hexachlorophene

Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

12.3. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30%and 70%.)

- Molecular ions present in the reference spectrum should be present in the sample spectrum.

- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.

- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

- Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

12.4. Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol

4,6-Dinitro-2-methylphenol

Manually checking the integrations would be appropriate for these compounds.

12.5. Calculations

12.5.1. Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

RF = Mean of RFs from intial caibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

RFi = RF for each of the calibration levels

N = Number of RF values

12.5.2. Continuing calibration percent drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.5.3. Concentration in the extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.3.1.Average response factor

If the average of all the %RSDs of the response factors in the initial calibration is $\leq$ 15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is}\overline{RF}}$$

12.5.3.2.Linear fit

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

C_{ex}= Concentration in extract, µg/mL

R_x= Response for analyte

R_{is}= Response for internal standard

C_{is}= Concentration of internal standard

A= Intercept

B= Slope

12.5.3.3.Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)$$

C= Curvature

12.5.4. The concentration in the sample is then calculated.

12.5.4.1. Aqueous Calculation

$$\text{Concentration, } \mu g / L = \frac{C_{ex} V_t}{V_o}$$

Where:

V_t = Volume of total extract, µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, V_t = 2,000.)

V_o = Volume of water extracted (mL)

12.5.5. Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis:

$$\text{Concentration, } \mu g / kg = \frac{C_{ex} V_t}{W_s D}$$

W_s = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry weight basis or 1 for a wet weight basis

12.6. MS/MSD percent recovery calculation.

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

S_{SR} = Spike sample result

S_R=Sample result

S_A = Spike added

12.7. Relative % Difference calculation for the MS/MSD

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

RPD = Relative percent difference

MS_R = Matrix spike result

MSD_R = Matrix spike duplicate result

12.8. Relative response factor calculation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

A_x=Area of the characteristic ion for the compound being measured

A_{is}=Area of the characteristic ion for the specific internal standard

C_x=Concentration of the compound being measured (µg/L)

C_{is} =Concentration of the specific internal standard (µg/L)

12.9. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x=Area of the total ion chromatogram for the compound being measured

A_{is}=Area of the total ion chromatogram for the nearest internal standard without interference

RF=1

12.10. Percent DDT breakdown

$$\% \text{ DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDarea}}$$

The total ion current areas are used for this calculation

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to the level 4 calibration standard.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in table 14.

13.2.3. If any analyte does not meet the acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Non-standard analytes

For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

13.4. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.5. Data Quality Objectives (DQO). Refer to project-specific Quality Assurance plans for DQO information.

14. POLLUTION PREVENTION

14.1. This section is not applicable to this procedure.

15. WASTE MANAGEMENT

15.1. Waste generated during aliquotting and from used vials must be disposed of in accordance with the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update II, October 1994, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270B.

16.2. J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975)

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.2. Modifications from Previous Revision

17.2.1. This SOP has been substantially revised to meet the requirements of method 8270C.

17.2.2. Directions for analysis be method 625 have been added as an attachment.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if

applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Tables

Table 1

STL Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Pyridine	110-86-1	20	660
N-nitrosodimethylamine	62-75-9	10	330
Aniline	62-53-3	10	330
Phenol	108-95-2	10	330
Bis(2-chloroethyl)ether	111-44-4	10	330
2-Chlorophenol	95-57-8	10	330
1,3-Dichlorobenzene	541-73-1	10	330
1,4-Dichlorobenzene	106-46-7	10	330
Benzyl alcohol	100-51-6	10	330
1,2-Dichlorobenzene	95-50-1	10	330
2-Methylphenol	95-48-7	10	330
2,2'-oxybis(1-chloropropane)[2]	108-60-1	10	330
4-Methylphenol	106-44-5	10	330
N-Nitroso-di-n-propylamine	621-64-7	10	330
Hexachloroethane	67-72-1	10	330
Nitrobenzene	98-95-3	10	330
Isophorone	78-59-1	10	330
2-Nitrophenol	88-75-5	10	330
2,4-Dimethylphenol	105-67-9	10	330
Benzoic acid	65-85-0	50	1600
Bis(2-chloroethoxy)methane	111-91-1	10	330
2,4-Dichlorophenol	120-83-2	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
Naphthalene	91-20-3	10	330
4-Chloroaniline	106-47-8	10	330
Hexachlorobutadiene	87-68-3	10	330
4-Chloro-3-methylphenol	59-50-7	10	330
2-Methylnaphthalene	91-57-6	10	330
Hexachlorocyclopentadiene	77-47-4	50	1600
2,4,6-Trichlorophenol	88-06-2	10	330
2,4,5-Trichlorophenol	95-95-4	10	330
2-Chloronaphthalene	91-58-7	10	330
2-Nitroaniline	88-74-4	50	1600
Dimethyl phthalate	131-11-3	10	330
Acenaphthylene	208-96-8	10	330
3-Nitroaniline	99-09-2	50	1600
Acenaphthene	83-32-9	10	330
2,4-Dinitrophenol	51-28-5	50	1600
4-Nitrophenol	100-02-7	50	1600
Dibenzofuran	132-64-9	10	330
2,4-Dinitrotoluene	121-14-2	10	330

Table 1

STL Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2,6-Dinitrotoluene	606-20-2	10	330
Diethylphthalate	84-66-2	10	330
4-Chlorophenyl phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	10	330
4-Nitroaniline	100-01-6	50	1600
4,6-Dinitro-2-methylphenol	534-52-1	50	1600
N-Nitrosodiphenylamine	86-30-6	10	330
Azobenzene	103-33-3	10	330
4-Bromophenyl phenyl ether	101-55-3	10	330
Hexachlorobenzene	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	10	330
Anthracene	120-12-7	10	330
Carbazole	86-74-8	10	330
Di-n-butyl phthalate	84-74-2	10	330
Fluoranthene	206-44-0	10	330
Benzidine	92-87-5	100	3300
Pyrene	129-00-0	10	330
Butyl benzyl phthalate	85-68-7	10	330
3,3'-Dichlorobenzidine	91-94-1	50	1600
Benzo(a)anthracene	56-55-3	10	330
Bis(2-ethylhexyl)phthalate	117-81-7	10	330
Chrysene	218-01-9	10	330
Di-n-octylphthalate	117-84-0	10	330
Benzo(b)fluoranthene	205-99-2	10	330
Benzo(k)fluoranthene	207-08-9	10	330
Benzo(a)pyrene	50-32-8	10	330
Indeno(1,2,3-cd)pyrene	193-39-5	10	330
Dibenz(a,h)anthracene	53-70-3	10	330
Benzo(g,h,i)perylene	191-24-2	10	330

[1] The STL primary standard is the standard normally used at STL. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

[2] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

Table 2

STL Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2-Picoline	109-06-8	20	660
N-Nitrosomethylethylamine	10595-95-6	10	330
Methyl methanesulfonate	66-27-3	10	330
N-Nitrosodiethylamine	55-18-5	10	330
Ethyl methanesulfonate	62-50-0	10	330
Pentachloroethane	76-01-7	50	1600
Acetophenone	98-86-2	10	330
N-Nitrosopyrrolidine	930-55-2	10	330
N-Nitrosomorpholine	59-89-2	10	330
o-Toluidine	95-53-4	20	660
3-Methylphenol	108-39-4	10	330
N-Nitrosopiperidine	100-75-4	10	330
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1	50	1600
a,a-Dimethyl-phenethylamine	122-09-8	50	1600
2,6-Dichlorophenol	87-65-0	10	330
Hexachloropropene	1888-71-7	100	3300
p-Phenylenediamine	106-50-3	100	3300
n-Nitrosodi-n-butylamine	924-16-3	10	330
Safrole	94-59-7	20	660
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330
Isosafrole	120-58-1	20	660
1,4-Dinitrobenzene	100-25-4	10	330
1,4-Naphthoquinone	130-15-4	50	1600
1,3-Dinitrobenzene	99-65-0	10	330
Pentachlorobenzene	608-93-5	10	330
1-Naphthylamine	134-32-7	10	330
2-Naphthylamine	91-59-8	10	330
2,3,4,6-Tetrachlorophenol	58-90-2	50	1600
5-Nitro-o-toluidine	99-55-8	20	660
Thionazin[2]	297-97-2	50	1600
1,3,5-Trinitrobenzene	99-35-4	50	1600
Sulfotepp[2]	3689-24-5	50	1600
Phorate[2]	298-02-2	50	1600
Phenacetin	62-44-2	20	660
Diallate[3]	2303-16-4	20	660
Dimethoate[2]	60-51-5	20	660
4-Aminobiphenyl	92-67-1	50	1600
Pentachloronitrobenzene	82-68-8	50	1600
Pronamide	23950-58-5	20	660
Disulfoton[2]	298-04-4	50	1600
2-secbutyl-4,6-dinitrophenol (Dinoseb)	88-85-7	20	660
Methyl Parathion[2]	298-00-0	50	1600
4-Nitroquinoline-1-oxide	56-57-5	100	3300

Table 2

STL Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Parathion[2]	56-38-2	50	1600
Methapyrilene	91-80-5	50	1600
Aramite	140-57-8	20	660
Isodrin[3]	465-73-6	10	330
Kepone[2]	143-50-0	100	3300
Famphur[3]	52-85-7	100	3300
p-(Dimethylamino)azobenzene	60-11-7	20	660
p-Chlorobenzilate[3]	510-15-6	10	330
3,3'-Dimethylbenzidine	119-93-7	50	1600
2-Acetylaminofluorene	53-96-3	100	3300
Dibenz(a,j)acridine	224-42-0	20	660
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660
3-Methylcholanthrene	56-49-5	20	660

[1] The Appendix IX standard contains additional analytes required for the Appendix IX list. The STL primary standard must also be analyzed to include all of the Appendix IX list.

[2] May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

[3] May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

Table 3

Reportable Analytes for STL Standard Tests, Primary Standard

Analyte	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
Pyridine	110-86-1		X		X
N-nitrosodimethylamine	62-75-9				X
Aniline	62-53-3				X
Phenol	108-95-2	X		X	X
Bis(2-chloroethyl)ether	111-44-4	X		X	X
2-Chlorophenol	95-57-8	X		X	X
1,3-Dichlorobenzene	541-73-1	X		X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X
Benzyl alcohol	100-51-6				X
1,2-Dichlorobenzene	95-50-1	X		X	X
2-Methylphenol	95-48-7	X	X	X	X
2,2'-oxybis(1-chloropropane)[1]	180-60-1	X		X	X
4-Methylphenol	106-44-5	X	X	X	X
N-Nitroso-di-n-propylamine	621-64-7	X		X	X
Hexachloroethane	67-72-1	X	X	X	X
Nitrobenzene	98-95-3	X	X	X	X
Isophorone	78-59-1	X		X	X
2-Nitrophenol	88-75-5	X		X	X
2,4-Dimethylphenol	105-67-9	X		X	X
Benzoic acid	65-85-0				
Bis(2-chloroethoxy)methane	111-91-1	X		X	X
2,4-Dichlorophenol	120-83-2	X		X	X
1,2,4-Trichlorobenzene	120-82-1	X		X	X
Naphthalene	91-20-3	X		X	X
4-Chloroaniline	106-47-8	X		X	X
Hexachlorobutadiene	87-68-3	X	X	X	X
4-Chloro-3-methylphenol	59-50-7	X		X	X
2-Methylnaphthalene	91-57-6	X		X	X
Hexachlorocyclopentadiene	77-47-4	X		X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	X	X
2-Chloronaphthalene	91-58-7	X		X	X
2-Nitroaniline	88-74-4	X		X	X
Dimethyl phthalate	131-11-3	X		X	X
Acenaphthylene	208-96-8	X		X	X
3-Nitroaniline	99-09-2	X		X	X
Acenaphthene	83-32-9	X		X	X
2,4-Dinitrophenol	51-28-5	X		X	X
4-Nitrophenol	100-02-7	X		X	X
Dibenzofuran	132-64-9	X		X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X		X	X
Diethylphthalate	84-66-2	X		X	X
4-Chlorophenyl phenyl ether	7005-72-3	X		X	X

Table 3

Reportable Analytes for STL Standard Tests, Primary Standard

Analyte	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
Fluorene	86-73-7	X		X	X
4-Nitroaniline	100-01-6	X		X	X
4,6-Dinitro-2-methylphenol	534-52-1	X		X	X
N-Nitrosodiphenylamine	86-30-6	X		X	X
Azobenzene[4]	103-33-3				
4-Bromophenyl phenyl ether	101-55-3	X		X	X
Hexachlorobenzene	118-74-1	X	X	X	X
Pentachlorophenol	87-86-5	X	X	X	X
Phenanthrene	85-01-8	X		X	X
Anthracene	120-12-7	X		X	X
Carbazole	86-74-8	X		X	
Di-n-butyl phthalate	84-74-2	X		X	X
Fluoranthene	206-44-0	X		X	X
Benzidine	92-87-5				
Pyrene	129-00-0	X		X	X
Butyl benzyl phthalate	85-68-7	X		X	X
3,3'-Dichlorobenzidine	91-94-1	X		X	X
Benzo(a)anthracene	56-55-3	X		X	X
Bis(2-ethylhexyl)phthalate	117-81-7	X		X	X
Chrysene	218-01-9	X		X	X
Di-n-octylphthalate	117-84-0	X		X	X
Benzo(b)fluoranthene	205-99-2	X		X	X
Benzo(k)fluoranthene	207-08-9	X		X	X
Benzo(a)pyrene	50-32-8	X		X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X		X	X
Dibenz(a,h)anthracene	53-70-3	X		X	X
Benzo(g,h,i)perylene	191-24-2	X		X	X

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2] Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 4

Reportable analytes for STL Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
2-Picoline	109-06-8				X
N-Nitrosomethylethylamine	10595-95-6				X
Methyl methanesulfonate	66-27-3				X
N-Nitrosodiethylamine	55-18-5				X
Ethyl methanesulfonate	62-50-0				X
Pentachloroethane	76-01-7				X
Acetophenone	98-86-2				X
N-Nitrosopyrrolidine	930-55-2				X
N-Nitrosomorpholine	59-89-2				X
o-Toluidine	95-53-4				X
3-Methylphenol	108-39-4				X
N-Nitrosopiperidine	100-75-4				X
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1				X
a,a-Dimethyl-phenethylamine	122-09-8				X
2,6-Dichlorophenol	87-65-0				X
Hexachloropropene	1888-71-7				X
p-Phenylenediamine	106-50-3				X
n-Nitrosodi-n-butylamine	924-16-3				X
Safrole	94-59-7				X
1,2,4,5-Tetrachlorobenzene	95-94-3				X
Isosafrole	120-58-1				X
1,4-Dinitrobenzene	100-25-4				
1,4-Naphthoquinone	130-15-4				X
1,3-Dinitrobenzene	99-65-0				X
Pentachlorobenzene	608-93-5				X
1-Naphthylamine	134-32-7				X
2-Naphthylamine	91-59-8				X
2,3,4,6-Tetrachlorophenol	58-90-2				X
5-Nitro-o-toluidine	99-55-8				X
Thionazin[2]	297-97-2				X
1,3,5-Trinitrobenzene	99-35-4				X
Sulfotepp[2]	3689-24-5				X
Phorate[2]	298-02-2				X
Phenacetin	62-44-2				X
Diallate	2303-16-4				X
Dimethoate[2]	60-51-5				X
4-Aminobiphenyl	92-67-1				X
Pentachloronitrobenzene	82-68-8				X
Pronamide	23950-58-5				X
Disulfoton[2]	298-04-4				X
2-secbutyl-4,6-dinitrophenol (Dinoseb)[2]	88-85-7				X
Methyl parathion[2]	298-00-0				X
4-Nitroquinoline-1-oxide	56-57-5				X

Table 4

Reportable analytes for STL Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
Parathion[2]	56-38-2				X
Isodrin[3]	465-73-6				X
Kepone [2]	143-50-0				X
Famphur[2]	52-85-7				X
Methapyrilene	91-80-5				X
Aramite	140-57-8				X
p-(Dimethylamino)azobenzene	60-11-7				X
p-Chlorobenzilate[3]	510-15-6				X
3,3'-Dimethylbenzidine	119-93-7				X
2-Acetylaminofluorene	53-96-3				X
Dibenz(a,j)acridine	224-42-0				
7,12-Dimethylbenz(a)anthracene	57-97-6				X
3-Methylcholanthrene	56-49-5				X
Hexachlorophene[4]	70-30-4				X
Diphenylamine[5]	122-39-4				X

[2] May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

[3] May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

[4] Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram. (See section 12.2.1)

[5] Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

Table 5

Suggested Instrumental Conditions

Mass Range	35-500 amu
Scan Time	≤1 second/scan
Initial Column Temperature/Hold Time	40°C for 2 minutes
Column Temperature Program	40 - 320°C at 11.5°C/min
Final Column Temperature/Hold Time	320°C (until at least one minute after benzo(g,h,i)perylene has eluted)
Injector Temperature	250 - 300°C
Transfer Line Temperature	250 - 300°C
Source Temperature	According to manufacturer's specifications
Injector	Grob-type, split / splitless
Sample Volume	1 or 2 µl
Carrier Gas	Helium at 30 cm/sec

Table 6

DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17 - 23% of mass 442

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
N-nitrosodimethylamine	74	42	
Pyridine	79	52	
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d5 (Surrogate Standard)	99	42	71
Aniline	93	66	
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	111
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	115
1,4-Dichlorobenzene	146	148	111
Benzyl Alcohol	108	79	77
1,2-Dichlorobenzene	146	148	111
2-Methylphenol	108	107	79
2,2'-oxybis(1-chloropropane)[1]	45	77	121
4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	42	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d5 (Surrogate Standard)	82	128	54
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
Benzoic Acid	122	105	77
Bis(2-chloroethoxy)methane	93	95	123
2,4-Dichlorophenol	162	164	98
1,2,4-Trichlorobenzene	180	182	145
Naphthalene-d8 (Internal Standard)	136	68	54
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
Hexachlorobutadiene	225	223	227
4-Chloro-3-methylphenol	107	144	142
2-Methylnaphthalene	142	141	115
Hexachlorocyclopentadiene	237	235	272
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164
Acenaphthylene	152	151	153
2,6-Dinitrotoluene	165	89	63

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
Acenaphthene-d10 (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	139	109	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	51	105
N-Nitrosodiphenylamine	169	168	167
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Pentachlorophenol	266	264	268
Phenanthrene-d10 (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Carbazole	167	166	168
Di-n-butylphthalate	149	150	104
Fluoranthene	202	101	203
Benzidine	184	92	185
Pyrene	202	200	203
Terphenyl-d14 (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d12 (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d12 (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	
3-Methylphenol	108	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
2,6-Dichlorophenol	162	164	63
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
1,2,4,5-Tetrachlorobenzene	216	214	218
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
1,3-Dinitrobenzene	168	75	76
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	
2-Naphthylamine	143	115	
2,3,4,6-Tetrachlorophenol	232	230	131
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	121	75	260
Phenacetin	108	179	109
Diallate	86	234	
Dimethoate	87	93	125
4-Aminobiphenyl	169		
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160
Parathion	109	97	291

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
Isodrin	193	66	195
Kepone	272	274	237
Famphur	218	125	93
Methapyrilene	97	58	
Aramite 1	185	319	
Aramite 2	185	319	
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	106	
2-Acetylaminofluorene	181	180	223
Dibenz(a,j)acridine	279	280	
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 9

8270C LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract[1]
1,2,4-Trichlorobenzene	100
Acenaphthene	100
2,4-Dinitrotoluene	100
Pyrene	100
N-Nitroso-di-n-propylamine	100
1,4-Dichlorobenzene	100
Pentachlorophenol	150
Phenol	150
2-Chlorophenol	150
4-Chloro-3-methylphenol	150
4-Nitrophenol	150

[1] Levels are 50 and 75 ng/µL if 2 µL injection is used

Table 10

TCLP LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract[1]
1,4-Dichlorobenzene	100
2,4-Dinitrotoluene	100
Hexachlorobenzene	100
Hexachlorobutadiene	100
Hexachloroethane	100
2-Methylphenol	100
3-Methylphenol	100
4-Methylphenol	100
Nitrobenzene	100
Pentachlorophenol	100
Pyridine	100
2,4,5-Trichlorophenol	100
2,4,6-Trichlorophenol	100

[1] Levels are 50 ng/µL if 2 µL injection is used

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA department.

Table 11

8270C Surrogate Compounds

Surrogate Compounds	Spiking Level, ng/µL in extract[2]
Nitrobenzene-d5	100
2-Fluorobiphenyl	100
Terphenyl-d14	100
1,2-Dichlorobenzene-d4[1]	100
Phenol-d5	150
2-Fluorophenol	150
2,4,6-Tribromophenol	150
2-Chlorophenol-d4[1]	150

[1] Included in standard mix, but not routinely evaluated for method 8270B

[2] Levels are 50 and 75 ng/µL if 2 µL injection is used

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 12

Calibration Levels, Primary Standard, ug/ml (for 2ul injection)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
Pyridine	10	25	40	60	80
N-nitrosodimethylamine	10	25	40	600	800
Aniline	10	25	400	600	800
Phenol	10	25	40	60	80
Bis(2-chloroethyl)ether	10	25	40	60	80
2-Chlorophenol	10	25	40	60	80
1,3-Dichlorobenzene	10	25	40	60	80
1,4-Dichlorobenzene	10	25	40	60	80
Benzyl alcohol	10	25	40	60	80
1,2-Dichlorobenzene	10	25	40	60	80
2-Methylphenol	10	25	40	60	80
2,2'-oxybis(1-chloropropane)[1]	10	25	40	60	80
4-Methylphenol	10	25	40	60	80
N-Nitroso-di-n-propylamine	10	25	40	60	80
Hexachloroethane	10	25	40	60	80
Nitrobenzene	10	25	40	60	80
Isophorone	10	25	40	60	80
2-Nitrophenol	10	25	40	60	80
2,4-Dimethylphenol	10	25	40	60	80
Benzoic acid	20	50	80	120	160
Bis(2-chloroethoxy)methane	10	25	40	60	80
2,4-Dichlorophenol	10	25	40	60	80
1,2,4-Trichlorobenzene	10	25	40	60	80
Naphthalene	10	25	40	60	80
4-Chloroaniline	10	25	40	60	80
Hexachlorobutadiene	10	25	40	60	80
4-Chloro-3-methylphenol	10	25	40	60	80
2-Methylnaphthalene	10	25	40	60	80
Hexachlorocyclopentadiene	10	25	40	60	80
2,4,6-Trichlorophenol	10	25	40	60	80
2,4,5-Trichlorophenol	10	25	40	60	80
2-Chloronaphthalene	10	25	40	60	80
2-Nitroaniline	20	50	80	120	160
Dimethyl phthalate	10	25	40	60	80
Acenaphthylene	10	25	40	60	80
3-Nitroaniline	20	50	80	120	160
Acenaphthene	10	25	40	60	80
2,4-Dinitrophenol	20	50	80	120	160
4-Nitrophenol	20	50	80	120	160
Dibenzofuran	10	25	40	60	80
2,4-Dinitrotoluene	10	25	40	60	80
2,6-Dinitrotoluene	10	25	40	60	80
Diethylphthalate	10	25	40	60	80
4-Chlorophenyl phenyl ether	10	25	40	60	80
Fluorene	10	25	40	60	80

Table 12

Calibration Levels, Primary Standard, ug/ml (for 2ul injection)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
4-Nitroaniline	10	25	40	60	80
4,6-Dinitro-2-methylphenol	20	50	80	120	160
N-Nitrosodiphenylamine	10	25	40	60	80
Azobenzene[2]	10	25	40	60	80
4-Bromophenyl phenyl ether	10	25	40	60	80
Hexachlorobenzene	10	25	40	60	80
Pentachlorophenol	20	50	80	120	160
Phenanthrene	10	25	40	60	80
Anthracene	10	25	40	60	80
Carbazole	10	25	40	60	80
Di-n-butyl phthalate	10	25	40	60	80
Fluoranthene	10	25	40	60	80
Benzidine	20	50	80	120	160
Pyrene	10	25	40	60	80
Butyl benzyl phthalate	10	25	40	60	80
3,3'-Dichlorobenzidine	20	50	80	120	160
Benzo(a)anthracene	10	25	40	60	80
Bis(2-ethylhexyl)phthalate	10	25	40	60	80
Chrysene	10	25	40	60	80
Di-n-octylphthalate	10	25	40	60	80
Benzo(b)fluoranthene	10	25	40	60	80
Benzo(k)fluoranthene	10	25	40	60	80
Benzo(a)pyrene	10	25	40	60	80
Indeno(1,2,3-cd)pyrene	10	25	40	60	80
Dibenz(a,h)anthracene	10	25	40	60	80
Benzo(g,h,i)perylene	10	25	40	60	80

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2]Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 13
Calibration Levels, Appendix IX Standard, µg/mL (for 2ul injection)

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
2-Picoline	10	25	40	60	80
N-Nitrosomethylethylamine	10	25	40	60	80
Methyl methanesulfonate	10	25	40	60	80
N-Nitrosodiethylamine	10	25	40	60	80
Ethyl methanesulfonate	10	25	40	60	80
Pentachloroethane	10	25	40	60	80
Acetophenone	10	25	40	60	80
N-Nitrosopyrrolidine	10	25	40	60	80
N-Nitrosomorpholine	10	25	40	60	80
o-Toluidine	10	25	40	60	80
3-Methylphenol	10	25	40	60	80
N-Nitrosopiperidine	10	25	40	60	80
o,o,o-Triethyl-Phosphorothioate	20	50	80	120	160
a,a-Dimethyl-phenethylamine	10	25	40	60	80
2,6-Dichlorophenol	10	25	40	60	80
Hexachloropropene	20	50	80	120	160
p-Phenylenediamine	10	25	40	60	80
n-Nitrosodi-n-butylamine	10	25	40	60	80
Safrole	10	25	40	60	80
1,2,4,5-Tetrachlorobenzene	10	25	40	60	80
Isosafrole 1 + 2	20	50	80	120	160
1,4-Dinitrobenzene	10	25	40	60	80
1,4-Naphthoquinone	10	25	40	60	80
1,3-Dinitrobenzene	10	25	40	60	80
Pentachlorobenzene	10	25	40	60	80
1-Naphthylamine	10	25	40	60	80
2-Naphthylamine	10	25	40	60	80
2,3,4,6-Tetrachlorophenol	10	25	40	60	80
5-Nitro-o-toluidine	10	25	40	60	80
Thionazin	10	25	40	60	80
1,3,5-Trinitrobenzene	20	50	80	120	160
Sulfotepp	10	25	40	60	80
Phorate	10	25	40	60	80
Phenacetin	10	25	40	60	80
Diallate 1 + 2	20	50	80	120	160
Dimethoate	10	25	40	60	80
4-Aminobiphenyl	10	25	40	60	80
Pentachloronitrobenzene	20	50	80	120	160
Pronamide	10	25	40	60	80
Disulfoton	10	25	40	60	80
2-secbutyl-4,6-dinitrophenol (Dinoseb)	20	50	80	120	160
Methyl parathion	10	25	40	60	80
4-Nitroquinoline-1-oxide	20	50	80	120	160
Parathion	10	25	40	60	80
Isodrin	10	25	40	60	80
Kepone	20	50	80	120	160

Table 13
Calibration Levels, Appendix IX Standard, µg/mL (for 2ul injection)

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
Famphur	20	50	80	120	160
Methapyrilene	10	25	40	60	80
Aramite 1 and 2	20	50	80	120	160
p-(Dimethylamino)azobenzene	10	25	40	60	80
p-Chlorobenzilate	10	25	40	60	80
3,3'-Dimethylbenzidine	10	25	40	60	80
2-Acetylaminofluorene	10	25	40	60	80
Dibenz (a,j)acridine	10	25	40	60	80
7,12-Dimethylbenz(a)anthracene	10	25	40	60	80
3-Methylcholanthrene	10	25	40	60	80

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
Acenaphthene	50	27.6	60.1-132.3
Acenaphthylene	50	40.0	53.5-126.0
Aldrin[1]	50	39.0	7.2-152.2
Anthracene	50	32.0	43.4-118.0
Benz(a)anthracene	50	27.6	41.8-133.0
Benzo(b)fluoranthene	50	38.8	42.0-140.4
Benzo(k)fluoranthene	50	32.3	25.2-145.7
Benzo(a)pyrene	50	39.0	31.7-148.0
Benzo(ghi)perylene	50	58.9	D-195.0
Benzylbutyl phthalate	50	23.4	D-139.9
B-BHC[1]	50	31.5	41.5-130.6
d-BHC[1]	50	21.6	D-100.0
Bis(2-chloroethyl) ether	50	55.0	42.9-126.0
Bis(2-chloroethoxy)methane	50	34.5	49.2-164.7
Bis(2-chloroisopropyl) ether	50	46.3	62.8-138.6
Bis(2-ethylhexyl) phthalate	50	41.1	28.9-136.8
4-Bromophenyl phenyl ether	50	23.0	64.9-114.4
2-Chloronaphthalene	50	13.0	64.5-113.5
4-Chlorophenyl phenyl ether	50	33.4	38.4-144.7
Chrysene	50	48.3	44.1-139.9
4,4'-DDD[1]	50	31.0	D-134.5
4,4'-DDE[1]	50	32.0	19.2-119.7
4,4'-DDT[1]	50	61.6	D-170.6
Dibenzo(a,h)anthracene	50	70.0	D-199.7
Di-n-butyl phthalate	50	16.7	8.4-111.0
1,2-Dichlorobenzene	50	30.9	48.6-112.0
1,3-Dichlorobenzene	50	41.7	16.7-153.9

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
1,4-Dichlorobenzene	50	32.1	37.3-105.7
3,3'-Dichlorobenzidine	50	71.4	8.2-212.5
Dieldrin[1]	50	30.7	44.3-119.3
Diethyl phthalate	50	26.5	D-100.0
Dimethyl phthalate	50	23.2	D-100.0
2,4-Dinitrotoluene	50	21.8	47.5-126.9
2,6-Dinitrotoluene	50	29.6	68.1-136.7
Di-n-octylphthalate	50	31.4	18.6-131.8
Endosulfan sulfate[1]	50	16.7	D-103.5
Endrin aldehyde	50	32.5	D-188.8
Fluoranthene	50	32.8	42.9-121.3
Fluorene	50	20.7	71.6-108.4
Heptachlor[1]	50	37.2	D-172.2
Heptachlor epoxide[1]	50	54.7	70.9-109.4
Hexachlorobenzene	50	24.9	7.8-141.5
Hexachlorobutadiene	50	26.3	37.8-102.2
Hexachloroethane	50	24.5	55.2-100.0
Indeno(1,2,3-cd)pyrene	50	44.6	D-150.9
Isophorone	50	63.3	46.6-180.2
Naphthalene	50	30.1	35.6-119.6
Nitrobenzene	50	39.3	54.3-157.6
N-Nitrosodi-n-propylamine	50	55.4	13.6-197.9
PCB-1260[1]	50	54.2	19.3-121.0
Phenanthrene	50	20.6	65.2-108.7
Pyrene	50	25.2	69.6-100.0
1,2,4-Trichlorobenzene	50	28.1	57.3-129.2
4-Chloro-3-methylphenol	50	37.2	40.8-127.9
2-Chlorophenol	50	28.7	36.2-120.4
2,4-Chlorophenol	50	26.4	52.5-121.7
2,4-Dimethylphenol	50	26.1	41.8-109.0
2,4-Dinitrophenol	50	49.8	D-172.9
2-Methyl-4,6-dinitrophenol	50	93.2	53.0-100.0
2-Nitrophenol	50	35.2	45.0-166.7
4-Nitrophenol	50	47.2	13.0-106.5
Pentachlorophenol	50	48.9	38.1-151.8
Phenol	50	22.6	16.6-100.0
2,4,6-Trichlorophenol	50	31.7	52.4-129.2

[1]Since the organochlorine pesticides and PCBs are normally determined by method 8080 at STL, they will not be included in the initial demonstration of capability for method 8270B.

ATTACHMENT A

MODIFICATIONS REQUIRED FOR ANALYSIS OF WASTEWATER FOLLOWING METHOD 625

18. REQUIREMENTS FOR METHOD 625

18.1. Method 625 is required for demonstration of compliance with NPDES wastewater discharge permits. The standard analyte list and reporting limits are listed in Table A-1.

18.2. This method can be applied only to aqueous matrices.

18.3. The tune period for this method is defined as 24 hours.

18.4. Initial calibration curve requirements:

18.4.1. The initial calibration curve for this method requires at least three points.

18.4.2. Target compounds must have RSD ≤ 35%.

18.4.3. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds.

18.5. Continuing calibration verification requirements: All target compounds must have %D ≤ 20%.

18.6. Matrix Spike and LCS requirements:

18.6.1. A full analyte spike is required for method 625. The spiking levels are given in Table A-2.

Table A-1. STL Method 625 standard reporting list and reporting limits.

Analytes	CAS Number	Aqueous µg/L
Phenol	108-95-2	10
Bis(2-chloroethyl)ether	111-44-4	10
2-Chlorophenol	95-57-8	10
1,3-Dichlorobenzene	541-73-1	10
1,4-Dichlorobenzene	106-46-7	10
1,2-Dichlorobenzene	95-50-1	10
2,2'-oxybis(1-chloropropane)	108-60-1	10
N-Nitroso-di-n-propylamine	621-64-7	10
Hexachloroethane	67-72-1	10
Nitrobenzene	98-95-3	10
Isophorone	78-59-1	10
2-Nitrophenol	88-75-5	10
2,4-Dimethylphenol	105-67-9	10
Bis(2-chloroethoxy)methane	111-91-1	10
2,4-Dichlorophenol	120-83-2	10
1,2,4-Trichlorobenzene	120-82-1	10
Naphthalene	91-20-3	10
Hexachlorobutadiene	87-68-3	10
4-Chloro-3-methylphenol	59-50-7	10
Hexachlorocyclopentadiene	77-47-4	50
2,4,6-Trichlorophenol	88-06-2	10
2-Chloronaphthalene	91-58-7	10
Dimethyl phthalate	131-11-3	10
Acenaphthylene	208-96-8	10
Acenaphthene	83-32-9	10
2,4-Dinitrophenol	51-28-5	50
4-Nitrophenol	100-02-7	50
2,4-Dinitrotoluene	121-14-2	10
2,6-Dinitrotoluene	606-20-2	10
Diethylphthalate	84-66-2	10
4-Chlorophenyl phenyl ether	7005-72-3	10
Fluorene	86-73-7	10
4,6-Dinitro-2-methylphenol	534-52-1	50
N-Nitrosodiphenylamine	86-30-6	10
4-Bromophenyl phenyl ether	101-55-3	10
Hexachlorobenzene	118-74-1	10
Pentachlorophenol	87-86-5	50
Phenanthrene	85-01-8	10
Anthracene	120-12-7	10
Di-n-butyl phthalate	84-74-2	10
Fluoranthene	206-44-0	10
Benzidine	92-87-5	100
Pyrene	129-00-0	10
Butyl benzyl phthalate	85-68-7	10

Analytes	CAS Number	Aqueous µg/L
3,3'-Dichlorobenzidine	91-94-1	50
Benzo(a)anthracene	56-55-3	10
Bis(2-ethylhexyl)phthalate	117-81-7	10
Chrysene	218-01-9	10
Di-n-octylphthalate	117-84-0	10
Benzo(b)fluoranthene	205-99-2	10
Benzo(k)fluoranthene	207-08-9	10
Benzo(a)pyrene	50-32-8	10
Indeno(1,2,3-cd)pyrene	193-39-5	10
Dibenz(a,h)anthracene	53-70-3	10
Benzo(g,h,i)perylene	191-24-2	10

Table A-2. Method 625 LCS and MS compounds and spike concentrations.

LCS Compounds	Spiking Level, ng/µL in extract[1]
Phenol	100
Bis(2-chloroethyl)ether	100
2-Chlorophenol	100
1,3-Dichlorobenzene	100
1,4-Dichlorobenzene	100
1,2-Dichlorobenzene	100
2,2'-oxybis(1-chloropropane)	100
N-Nitroso-di-n-propylamine	100
Hexachloroethane	100
Nitrobenzene	100
Isophorone	100
2-Nitrophenol	100
2,4-Dimethylphenol	100
Bis(2-chloroethoxy)methane	100
2,4-Dichlorophenol	100
1,2,4-Trichlorobenzene	100
Naphthalene	100
Hexachlorobutadiene	100
4-Chloro-3-methylphenol	100
Hexachlorocyclopentadiene	100
2,4,6-Trichlorophenol	100
2-Chloronaphthalene	100
Dimethyl phthalate	100
Acenaphthylene	100
Acenaphthene	100
2,4-Dinitrophenol	100
4-Nitrophenol	100
2,4-Dinitrotoluene	100
2,6-Dinitrotoluene	100
Diethylphthalate	100
4-Chlorophenyl phenyl ether	100
Fluorene	100
4,6-Dinitro-2-methylphenol	100
N-Nitrosodiphenylamine	100
4-Bromophenyl phenyl ether	100
Hexachlorobenzene	100
Pentachlorophenol	100
Phenanthrene	100
Anthracene	100
Di-n-butyl phthalate	100
Fluoranthene	100
Benzidine	100
Pyrene	100
Butyl benzyl phthalate	100
3,3'-Dichlorobenzidine	100

LCS Compounds	Spiking Level, ng/µL in extract[1]
Benzo(a)anthracene	100
Bis(2-ethylhexyl)phthalate	100
Chrysene	100
Di-n-octylphthalate	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Benzo(a)pyrene	100
Indeno(1,2,3-cd)pyrene	100
Dibenz(a,h)anthracene	100
Benzo(g,h,i)perylene	100

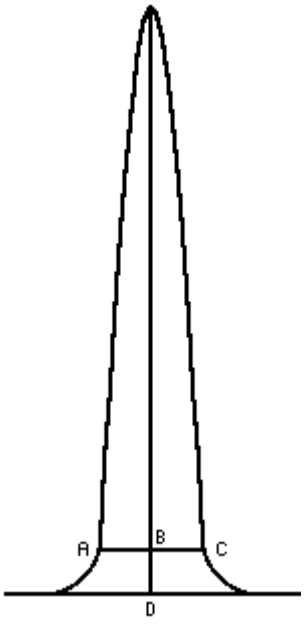
[1] Levels are 50 and 75 ng/µL if 2 µL injection is used

TUNING CRITERIA FOR BENZIDINE & PENTACHLOROPHENOL

At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP. Each day that benzidine is to be determined, the tailing factor must be less than 3.0. Each day that acids are to be determined, the tailing factor for pentachlorophenol must be less than 5.0. Calculation of the Tailing Factor is illustrated below:

$$\frac{BC}{AB} = \text{Tailing Factor}$$

Where:
BD = 10% peak height



APPENDIX 24

(The attached SOP from STL Pittsburgh included Appendices for several analyses that are not required for this QAPP or that are included with QAPP Appendix 25. Therefore, this QAPP Appendix 24 only contains STL Pittsburgh SOP No. C-GC-0001 with Appendix B - Analysis of Organochlorine Pesticides based on Method 8081A.)

STL STANDARD OPERATING PROCEDURE

TITLE: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000B, SW-846 8081A, 8082 8141A, 8151A and 8310

(SUPERSEDES: Revision 5.2)

Prepared by: _____

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. SCOPE AND APPLICATION

This SOP describes procedures for analysis of organic analytes by Gas Chromatography (GC). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA). Individual analytes and methods are described in the appendices. Currently, Method SW8021B is not run by STL – Pittsburgh, however other laboratories within STL do run this method.

2. SUMMARY OF METHOD

In general, semivolatile analytes in aqueous samples are prepared for analysis using continuous or separatory funnel liquid / liquid extraction or solid phase extraction (SOP # CORP-OP-0001) Solid samples are prepared using sonication, Soxhlet or pressurized fluid extraction (SOP # CORP-OP-0001).

After the initial preparation step, the sample is introduced to the GC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Internal or external standardization procedures are used as specified in the method appendices.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. In addition, some purge and trap autosamplers are susceptible to port specific contamination. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. In particular, this is a problem with non-selective detectors such as the Flame Ionization Detector (FID). See the appendices for interferences specific to individual tests and suggested corrective actions.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates. The following requirements must be met:

Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately. Refer to the STL Chemical Hygiene plan for a complete description of personal protection equipment.

The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. Specific hazards are covered in the appendices.

5.1.1. Opened containers of neat standards will be handled in a fume hood.

5.2. Sample extracts and standards which are in a flammable solvent shall be stored in an explosion-proof refrigerator.

5.3. When using hydrogen gas as a carrier, all precautions listed in the CHP shall be observed.

5.4. Standard preparation and dilution shall be performed inside an operating fume hood.

6. EQUIPMENT AND SUPPLIES

An analytical system complete with a gas chromatograph is required. A data system capable of measuring peak area and/or height is required. Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from pure solutions. Semivolatile stock standard solutions are stored at $\leq 6^{o}C$. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

Semivolatile stock standard solutions must be replaced after one year. Stock standards of gases must be replaced at least every week, unless the acceptability of the standard is demonstrated (Less than 20% drift from the initial is an acceptable demonstration). Other volatile stock standards must be replaced every 6 months or sooner, if comparison with check standards prepared from an independent source indicates a problem.

7.1.1. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If a vendor supplied standard has an earlier expiration date then that date is used.

7.2. Calibration Standards

7.2.1. Congener Calibration Standards

The procedure for preparation of PCB Congener standards is given in Appendix A.

7.2.2. Semivolatile Calibration Standards

Semivolatile calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method appendices. Semivolatile calibration solutions must be refrigerated at $\leq 6^{o}C$ and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.3. Gases for carrier and make-up: Hydrogen, Helium, Nitrogen, Argon/Methane.

7.4. Quality control (QC) Standards

QC standards (matrix spiking and LCS standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE PRESERVATION AND STORAGE

Semivolatile extracts must be refrigerated at $\leq 6^{o}C$ and analyzed within 40 days of the end of the extraction.

9. QUALITY CONTROL

9.1. Refer to the STL Pittsburgh QC Program document (QA-003) for further details on criteria and corrective actions. Refer to “Project Checklist” for project specific requirements.

9.2. Initial Demonstration of Capability

9.2.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin.

9.2.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.3. Batch Definition

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

9.3.1. Quality Control Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD a LCSD may be substituted.

9.4. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be verified at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Refer to policy QA-003 for more details.

9.4.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.4.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.4.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.5. Surrogates

All methods must use surrogates to the extent possible. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem. Repreparation is not necessary is there is obvious chromatographic interference.
- The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.5.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.5.2. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then repreparation or flagging of the data is required.

9.5.3. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.6. Method Blanks

9.6.1. For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous semivolatiles samples, and sodium sulfate for semivolatiles soils tests (Refer to SOP No. CORP-OP-0001 for details).

9.6.2. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher. Wherever blank contamination is greater than 1/10 the concentrations found in the samples and/or 1/10 of the regulatory limit it is potentially at a level of concern and should be handled as a non-conformance. Blank contamination should always be assessed against project specific requirements (See associated project checklist).

9.6.3. If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone, phthalate esters) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

9.6.4. Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

9.6.5. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.7. Instrument Blanks

9.7.1. An instrument blank must be analyzed during any 12 hour period of analysis that does not contain a method blank.

9.7.2. An instrument blank consists of the appropriate solvent with internal standards added. If internal standards are not used the surrogates should be added.

9.7.3. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.8. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. The LCS may also contain the full set of analytes. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch; however, if the matrix spike and matrix spike duplicate are within limits, the batch may be acceptable.

9.8.1. Refer to the STL QC Program document (QA-003) for further details of the corrective action.

9.8.2. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.8.3. LCS compound lists are included in the appendices.

9.8.4. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client.

9.9. Matrix Spikes

- For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific historically generated limits.
- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed.
- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed.
- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.9.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.11. STL QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

Internal or external calibration may be used. Internal calibration is recommended unless the sample matrix is likely to interfere with the quantitation of the internal standard. In either event prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.

10.1. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, changing PID lamps or FID jets or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance.

10.2. With the exception of 10.3 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points. Third order calibrations require at least seven points.

10.3. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial or no purge run. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.4. External standard calibration

Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

$$Calibration\ Factor\ (CF) = \frac{Area\ or\ Height\ of\ Peak}{Mass\ Injected\ (ng)}$$

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. It is also possible to use the concentration of the standard rather than the mass injected. (This would require changes in the equations used to calculate the sample concentrations). Use of peak area or height must be consistent. However, if matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute.

10.5. Internal standard calibration

10.5.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. To use this approach, select one or more internal standard(s) that are similar in analytical behavior to the compounds of interest. Recommended internal standards are given in the appendices. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. If the sample matrix interferes with quantitation of the internal standard, then the external standard approach must be used instead. In this event use the response factors from the

previous continuing calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.5.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

10.6. Calibration curve fits

Average response factor, linear regression, or quadratic curves may be used to fit the data. Average response factor may be used if the average % RSD of the response factors or calibration factors of all the analytes in the calibration standard taken together is $\leq$ 20%. The average %RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes.

10.6.1. In general, for environmental analysis, average response factors are the most appropriate calibration model. Linear or curved regression fits should only be used if the analyst has reason to believe that the average RF model does not fit the normal concentration/response behavior of the detector.

10.6.2. Average response factor

The average response factor may be used if the average percent relative standard deviation (%RSD) of all the response factors taken together is $\leq$ 20%.

The equation for average response factor is:

$$\text{Average response factor} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where: n = Number of calibration levels

$\sum_{i=1}^{n} RF_i$ = Sum of response factors for each calibration level

10.6.3. Linear regression

The linear fit uses the following functions:

10.6.3.1. External Standard

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.6.3.2. Internal Standard

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$

Where: C_s = Concentration in the sample
A_s = Area of target peak in the sample
A_{is} = Area of internal standard in the sample
C_{is} = Concentration of the internal standard

10.6.4. Quadratic curve

The quadratic curve uses the following functions:

10.6.4.1. External standard

$$y = ax + cx^2 + b$$

Where c is the curvature

10.6.4.2. Internal Standard

$$y = a\left(\frac{A_s \times C_{is}}{A_{is}}\right) + c\left(\frac{A_s \times C_{is}}{A_{is}}\right)^2 + b$$

10.7. Evaluation of calibration curves

10.7.1. The percent relative standard error (%RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.7.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard error is calculated as follows:

$$\%\ RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where:
N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_i = True concentration for level i
PC_i = Predicted concentration for level i

Note that when average response factors are used, %RSE is equivalent to %RSD.

10.8. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response must be less than $\pm$ the reporting limit for the analyte.
- The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be $\leq$ 20%.
- Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (r) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on r. As a result a curve may have a very good correlation coefficient (>0.995), while also having > 100% error at the low point.

10.9. Weighting of data points

10.9.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.10. Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation.

10.11. Calibration Verification

10.11.1. 12 hour Calibration

The working calibration curve or RF must be verified by the analysis of a mid point calibration standard at the beginning, after every 12 hours, and at the end of the analysis sequence. The center of each retention time window is updated with each 12 hour calibration. The CCV is varied periodically to check for linearity, this occurs when MDL's are performed.

10.11.2. Calibration Verification

It may be appropriate to analyze a mid point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12 hour calibration with the exception that retention times are not updated.

10.11.3. Any individual compounds with $\%D \leq 15\%$ meet the calibration criteria. The calibration verification is also acceptable if the average of the %D for all the analytes is $\leq 15\%$. This average is calculated by summing all the absolute %D results in the calibration (including surrogates) and dividing by the number of analytes.

10.11.4. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.11.5. Samples quantitated by external standard methods must be bracketed by calibration verification standards that meet the criteria listed above. Bracketing is not necessary for internal standard methods.

10.11.6. If the analyst notes that a CCV has failed and can document the reason for failure (e.g. no purge, broken vial, carryover from the previous sample etc.) then a second CCV may be analyzed without any adjustments to the instrument. If this CCV meets criteria then the preceding samples have been successfully bracketed. If adjustments to the instrument are performed before the repeat CCV then the preceding samples have not been successfully bracketed but analysis may continue.

10.11.7. In general, it is not advisable to analyze repeat CCVs on unattended runs. If repeat CCVs are analyzed then the first will serve as the bracketing standard for the preceding samples and the last will serve as the CCV for the following samples.

10.11.8. A mult-level calibration verification should be done periodically to verify stability of the intrument over the calibration range. This will be done at a minimum on an annual basis along with the MDLs.

10.11.9. If highly contaminated samples are expected it is acceptable to analyze blanks or primers at any point in the run.

10.11.10. % Difference calculation

% Difference for internal and external methods is calculated as follows

Internal Standard:

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

External standard:

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where RF_c and CF_c are the response and calibration factors from the continuing calibration

$\overline{RF}$ and $\overline{CF}$ are the average response and calibration factors from the initial calibration

10.11.11. % Drift calculation

% Drift is used for comparing the continuing calibration to a linear or quadratic curve. The criteria for % drift are the same as for % difference

$$\%\ Drift = \frac{Calculated\ Conc. - Theoretical\ Conc.}{Theoretical\ Conc.} \times 100\%$$

10.11.12. Corrective Actions for Continuing Calibration

If the overall average %D of all analytes is greater than $\pm$ 15% corrective action must be taken. This may include clipping the column, changing the liner or other minor instrument adjustments, followed by reanalyzing the standard. If the overall average %D still varies by more than $\pm$ 15%, a new calibration curve must be prepared.

10.11.13. Corrective Action for Samples

For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be reinjected.

For external standard methods, any samples injected after the last good continuing calibration standard must be reinjected.

If the average %D for all the analytes in the calibration is over 15%, but all of the analytes requested for a particular sample have %D $\leq$ 15%, then the analysis is acceptable for that sample.

10.11.14. Each initial calibration will be verified with the analysis of a second source standard. These must be from lots independent of the sources used for the primary calibration standard. This second source standard must at a minimum pass CCV criteria for the compounds being reported from the curve.

11. PROCEDURE

11.1. Extraction

Extraction procedures are referenced in the appendices.

11.2. Cleanup

Cleanup procedures are referenced in the appendices.

11.3. Gas Chromatography

Chromatographic conditions for individual methods are presented in the appendices.

11.4. Sample Introduction

Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5. Analytical Sequence

An analytical sequence starts with an initial calibration or a daily calibration. Refer to the individual method appendices for method specific details of daily calibrations and analytical sequences.

11.5.1. The daily calibration includes analysis of standards containing all single response analytes and updating the retention time windows.

11.5.2. If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration.

11.6. Retention Time Windows

11.6.1. Retention time windows must be specified for all analytes. *A Fixed retention time windows (± .05 minutes) will be used for all GC methods. Alternatively, if it is determined through calculation that wider limits are necessary, the limits will be developed as follows:* Make an injection of all analytes of interest each day over a three day period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). For multiresponse analytes (e.g., Aroclors) use the retention time of major peaks. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The center of the retention time window is the retention time from the last of the three standards. The centers of the windows are updated with the mid point of the initial calibration and each 12 hour calibration. The widths of the windows will remain the same until new windows are generated following the installation of a new column.

11.6.3. *Where calculated limits are being used, if* the retention time window as calculated above is less than +/- 0.05 minutes, use +/- 0.05 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.4. *Where calculated limits are being used, t*he laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.5. Corrective Action for Retention Times

The retention times of all compounds in each continuing calibration must be within the retention time windows established by the 12 hour calibration. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

The retention time of that compound in the standard must be within a retention time range equal to twice the original window.

No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Daily Retention Time Windows

The center of the retention time windows determined in section 11.6 are adjusted to the retention time of each analyte as determined in the 12 hour calibration standards. (See the method 8081A and 8082 appendices for exceptions for multi-response components.) The retention time windows must be updated at the beginning of each analytical sequence and with each 12 hour calibration, but not for any other calibration verification standards.

11.8. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP CORP-OP-0001 for determination of percent moisture.

11.9. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a supervisor and QA/QC manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Normally confirmation is required on a second column, but if the detector is sufficiently specific or if the sample matrix is well enough defined, single column analysis may be adequate. In some cases GC/MS confirmation may be required. Client specific requirements may also define the need for second column confirmation and / or GC/MS confirmation. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (MDL if J flag confirmation required).

12.1.2. Dual column quantitation

- For confirmed results, two approaches are available to the analyst;

A) The primary column approach
Or
B) The better result approach

Both are acceptable to avoid the reporting of erroneous or unconfirmed data. The approach used is based on the project requirements.

12.1.2.1. Primary column approach (may be used where indicated as a project requirement)

The result from the primary column is normally reported. The result from the secondary column is reported if any of the following three bulleted possibilities are true.

- There is obvious chromatographic interference on the primary column
- The result on the primary column is > 40% greater than the result on the secondary column
- Continuing or bracketing standard fails on the primary column but is acceptable on the secondary column. (If the primary column result is > 40% higher than the secondary and the primary column calibration fails, then the sample must be evaluated for reanalysis.)

12.1.2.2. Better result approach (default practice of laboratory subject to project requirements)

The lower of the two results is normally reported. The lower result is considered better because the higher result is generally higher because of chromatographic interference. The higher result is reported if any of the following two bulleted possibilities are true.

- There is obvious chromatographic interference on the column with the lower result
- The continuing or bracketing calibration on the column with the lower result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for reanalysis.)
- This rule may be reversed to favor reporting of the higher value or the higher value where the results differ by 40% when indicated as a project requirement by the PM.

12.1.3. If the Relative percent difference (RPD) between the response on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{R1 - R2}{\frac{1}{2}(R1 + R2)} x\,100$$

Where R=Result

12.1.4. Multi-response Analytes

For multi-response analytes, the analyst should use the retention time window, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

12.1.5. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.1.6 The Lab reports the lower of the two values. If requested by the client, the higher of the two values will be reported.

12.2. Calibration Range

If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most

concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions

Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and only minor matrix peaks are, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgement is required to determine the most concentrated dilution that will not result in instrument contamination.

12.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4. Interferences

If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Internal Standard Criteria for Continuing Calibration

If internal standard calibration is used, then the internal standard response in a continuing calibration standard must be within 50 to 150% of the response in the mid level of the initial calibration.

12.6. Calculations

Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.6.1. External Standard Calculations

12.6.1.1. Aqueous samples

$$Concentration\ (mg/L) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times V_s)}$$

Where:

A_x = Response for the analyte in the sample
V_i = Volume of extract injected, µL
D_f = Dilution factor
V_t = Volume of total extract, µL
V_s = Volume of sample extracted or purged, mL
CF = Calibration factor, area or height/ng, Section 10.1

12.6.1.2. Non-aqueous Samples

$$Concentration\ (mg/kg) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times W \times D)}$$

Where:

W = Weight of sample extracted or purged, g

$$D = \frac{100 - \%\ Moisture}{100}$$ (D = 1 if wet weight is required)

12.6.2. Internal Standard Calculations

12.6.2.1. Aqueous Samples

$$Concentration\ (mg/L) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times V_s)}$$

Where:

C_{is} = Amount of internal standard added, ng
A_{is} = Response of the internal standard
RF = Response factor for analyte

12.6.2.2. Non-aqueous Samples

$$Concentration\ (mg/kg) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times W \times D)}$$

12.6.3. Surrogate Recovery

Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation:

$$\%\ \text{Recovery} = \frac{Concentration\ (or\ amount)\ found}{Concentration\ (or\ amount)\ spiked} \times 100$$

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.2.4. The CCV will be varied perodically to demonstrate verification of linearity of the curve.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Section 8000B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the Method Detection Limit. This SOP states that the Method Blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed to be up to 5 times the reporting limit in the blank following consultation with the client.

17.2. Modifications from Previous Revision

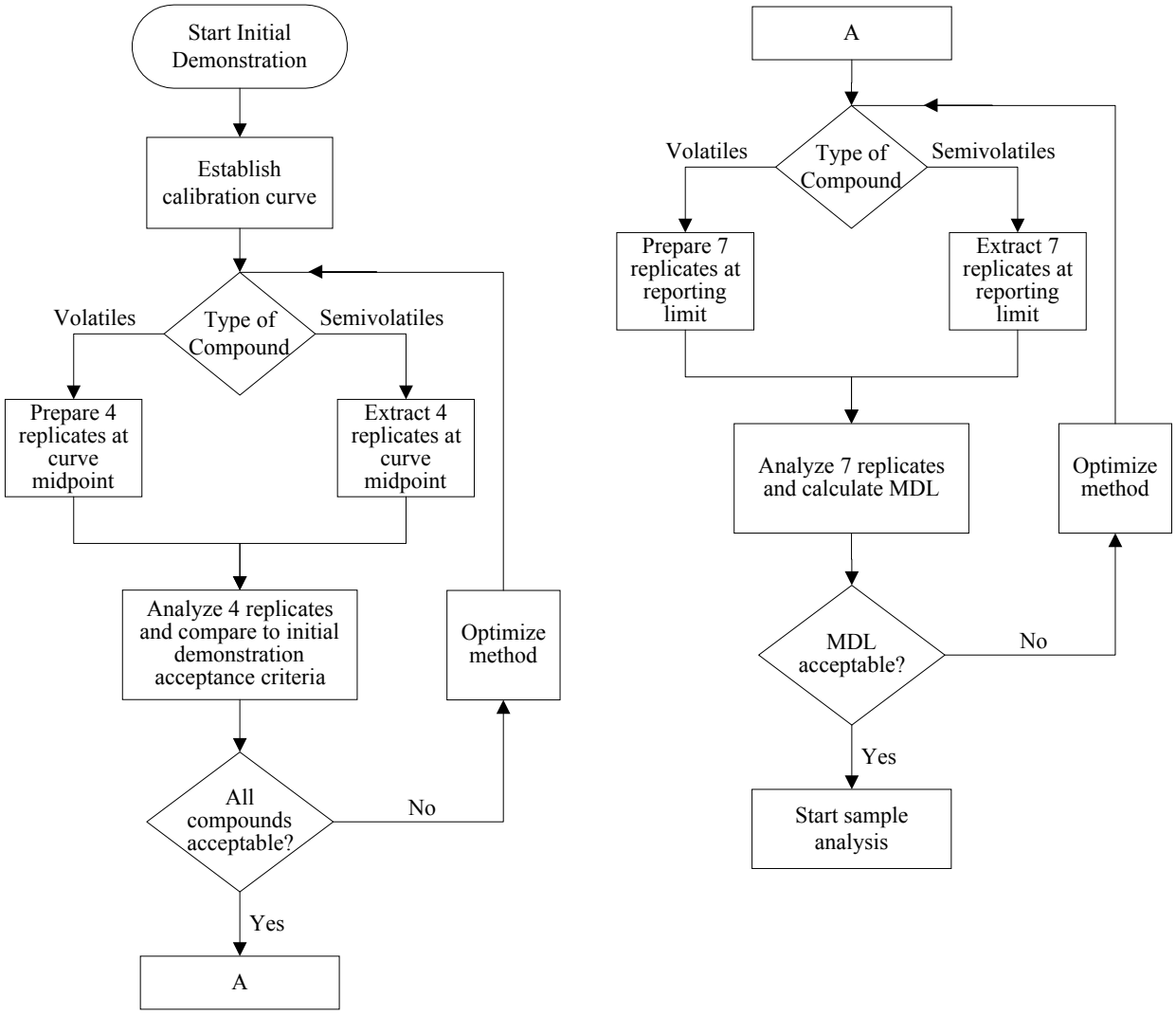
The calibration criteria in section 10.11 have been rewritten to improve consistency with SW-846 and to improve clarity.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

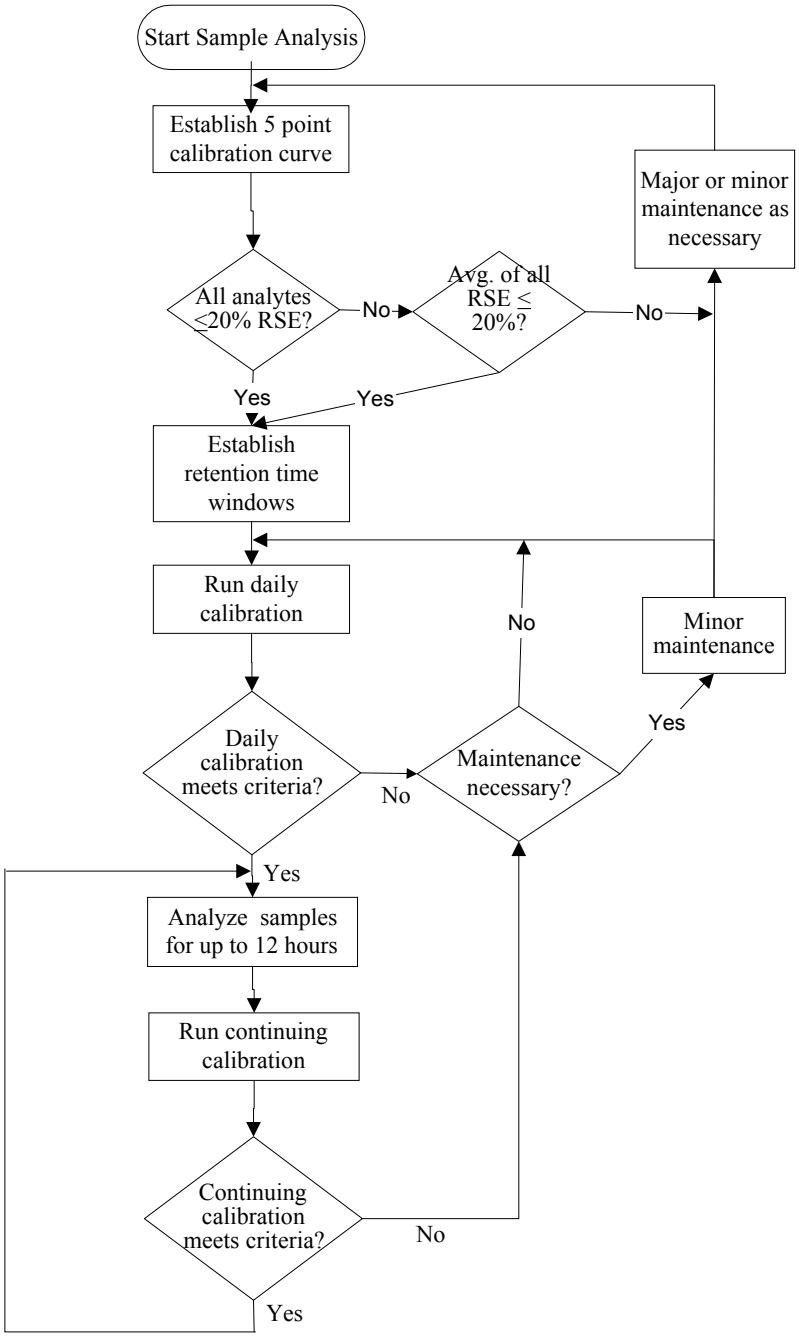
17.4. Flow Diagrams

17.4.1. Initial demonstration and MDL[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

17.4.2. Sample Analysis[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8081A is applied to the analysis of organochlorine pesticides by GC/ECD. This Appendix may also to be applied when discontinued SW-846 Method 8080A is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001)

Table B-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

At client request, this method may also be used for the analysis of PCBs (Arochlors) in combination with pesticides, although these are normally analyzed following method 8082, as described in Appendix C of this SOP. In any event, if samples for PCB analysis do not need the acid clean up procedure, then the same injection may be used for method 8081B and 8082, assuming all calibration and QC requirements for both methods are met. Extracts that have been acid cleaned may not be analyzed for pesticides, since several of the pesticides will be degraded.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of organochlorine pesticides. The pesticides are injected onto the column and separated and detected by electron capture detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001. Use or hexane / acetone as the extraction solvent (rather than hexane / methylene chloride) will reduce the amount of interferences extracted.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

7.4. Column Degradation Evaluation Mix

A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates. Refer to Table B-4 for details of the column degradation evaluation mix.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both columns. Closely eluting pairs are DDE and Dieldrin on the Rtx-5 or DB-5 column and Endosulfan II and DDD on the 1701 column.

10.3. Column Degradation Evaluation

Before any calibration runs, either initial or 12 hour, The column evaluation mix must be injected before each initial or daily calibration. The degradation of DDT and endrin must be calculated (see equations 9 and 10) and each shown to be less than 15% before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.
- Replacing the GC column.

10.4. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.4.1. Refer to Table B-8 for the initial calibration analytical sequence.

10.4.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4.3. The surrogate calibration curve is calculated from the Individual AB mix. Surrogates in the other calibration standards are used only as retention time markers. If there are resolution problems, then the A and B mixes may be analyzed separately.

10.4.4. For multi-component pesticides:

Single point calibration is used for multicomponent pesticides (typically toxaphene and technical chlordane). Two options are possible; the same quantitation option must be used for standards and samples. Refer to section 12.3 for guidance on which option to use.

10.4.5. For multicomponent analytes, the mid level standard must be analyzed as part of the initial calibration. This single point calibration is used to quantitate multicomponent analytes.

10.4.6. The analyst may include a full 5 point calibration for any of the multicomponent analytes with the initial calibration.

10.5. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.5.1. At a minimum, the 12 hour calibration includes analysis of the breakdown mix followed by mid level standards of any single and multicomponent analytes.

10.5.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.6. Continuing Calibration

The AB calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. The continuing calibration standard need not include multicomponent analytes. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.6.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-8.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Identification of Multicomponent Analytes

Retention time windows are also used for identification of multi-component analytes, but the "fingerprint" produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.3. Quantitation of Multicomponent Analytes

Use 3-10 major peaks or total area for quantitation as described in section 10.4.4, initial calibration of multicomponent analytes.

12.3.1. If there are no interfering peaks within the envelope of the multicomponent analyte, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.3.1.1. Multiple peak option

This option is particularly valuable if toxaphene is identified but interferences make quantitation based on total area difficult. Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

Chlordane may be quantitated either using the multiple peak option (12.3.1.1) total area option (12.3.1.2.) or by quantitation of the major components, α-chlordane, γ-chlordane and heptachlor.

12.3.1.2. Total area option

The total area of the standards and samples may be used for quantitation of multicomponent analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multicomponent pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

12.4. Second column confirmation multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) unless it is determined that sample interference has adversely affected the quantitation of that surrogate. Tetrachloro-m-xylene (TCMX) recovery is reported in lieu of DCB in samples having the interference, and also may be used in samples in which DCB recovery is low. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

12.6. Calculation of Column Degradation/% Breakdown (%B)

$$DDT\ \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} x\ 100$$

where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

$$Endrin\ \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} x\ 100$$

where:
A_{EK}, A_{EA}, and A_E = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are presented in Table B-7. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

SW846, Update III, December 1996, Method 8081A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aldrin	0.05	1.7	50
α-BHC	0.05	1.7	50
β-BHC	0.05	1.7	50
δ-BHC	0.05	1.7	50
γ-BHC (Lindane)	0.05	1.7	50
α-Chlordane	0.05	1.7	50
γ-Chlordane	0.05	1.7	50
Chlordane (technical)	0.5	17	500
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1.7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3.3	100
Toxaphene	2.0	67	2000
APPENDIX IX ADD ONs			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzillate	0.1	3.3	100
Kepone[1]	1.0	33	1000

[1] Kepone is sometimes requested for analysis by method 8081A. However kepone may produce peaks with broad tails that elute later than the standard by up to a minute (presumably due to hemi-acetal formation). As a result kepone analysis by 8081A is unreliable and not recommended. Analysis by method 8270C is a possible alternative. Note: alpha chlordane, gamma chlordane, and endrin ketone are not required for some projects.

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	120°C for 1 min, 8.5°C/min to 285°C, , 6 min hold
Column 1	Rtx-CLPesticides 30m x 0.32mm id, 0.5µm
Column 2	Rtx-35 30m x 0.32 mm id, 0.5µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table B-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[2]
Individual Mix AB[1]						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	10	20	50	100	200	400
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
α-Chlordane [3]	5	10	25	50	100	200
γ-Chlordane [3]	5	10	25	50	100	200
Multicomponent Standards						
Chlordane (Technical)			250[4]			
Toxaphene			1000[5]			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.
[2] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.
[3] Compounds may be used in lieu of running a daily technical Chlordane standard for samples that are non-detect for technical Chlordane.
[4] This standard may be used for quantitation of technical chlordane between 50 and 1000 ng/mL. If the chlordane is more concentrated, the extract must be diluted and reanalyzed.
[5] This standard may be used for quantitation of toxaphene between 200 and 4000 ng/mL. If the toxaphene is more concentrated, the extract must be diluted and reanalyzed.

Table B-4	
Column Degradation Evaluation Mix ng/mL	
Component	Concentration
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

Table B-5			
LCS/Matrix Spike and Surrogate Spike levels μg/L or μg/kg			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	0.20	6.67	200
Aldrin	0.20	6.67	200
Heptachlor	0.20	6.67	200
Dieldrin	0.50	16.7	500
Endrin	0.50	16.7	500
4,4'DDT	0.50	16.7	500
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table B-6		
LCS/Matrix Spike and Surrogate Spike levels for TCLP μg/L or μg/kg		
	Aqueous	Waste
Heptachlor	5	500
Heptachlor epoxide	5	500
Lindane	5	500
Endrin	5	500
Methoxychlor	10	1000

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)	
Breakdown Mix	
Individual mix AB	All levels
Technical Chlordane	Level 3[1]
Toxaphene	Level 3[1]
Solvent blank	
Up to 20 samples unless 12 hours comes first)	
Solvent blank (optional)	
Individual mix AB	Mid level (Continuing calibration)
Samples	
After 12 hours:	
Breakdown mix	
Individual mix AB	
Any other single component analytes	
Any multicomponent analytes	

[1] A five point curve for any of the multicomponent analytes may be included
If Arochlors are included, a 5 point calibration for Arochlor 1016/1260 should be included with the initial calibration and a single point for the other Arochlors. The mid point 1016/1260 mix is included with the daily calibration (every 12 hours).

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB, and the breakdown mix must be run before the continuing calibration.

Table B-8		
Performance limits, four replicate initial demonstration of capability		
Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
Aldrin	46-112	21
alpha-BHC	51-122	24
beta-BHC	61-120	32
delta-BHC	49.5-118.5	36
gamma-BHC	57-116	23
Chlordane	44.8-108.6	20
4,4'-DDD	52-126	28
4,4'-DDE	46-120	27.5
4,4'-DDT	54-137	36
Dieldrin	42.5-124.5	38
Endosulfan I	43-141	24.5
Endosulfan II	78-171	61
Endosulfan Sulfate	62-132	27
Endrin	49-126	37
Heptachlor	57-100	20
Heptachlor Epoxide	43.5-131.5	25.4
Toxaphene	44.4-111.2	20

APPENDIX 25

(The attached SOP from STL Pittsburgh included Appendices for several analyses that are not required for this QAPP or that are included with QAPP Appendix 24. Therefore, this QAPP Appendix 25 only contains STL Pittsburgh SOP No. C-GC-0001 with Appendix D - Analysis of Phenoxy Acid Herbicides based on Method 8151A.)

STL STANDARD OPERATING PROCEDURE

TITLE: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000B, SW-846 8081A, 8082 8141A, 8151A and 8310

(SUPERSEDES: Revision 5.2)

Prepared by: _____

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. SCOPE AND APPLICATION

This SOP describes procedures for analysis of organic analytes by Gas Chromatography (GC). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA). Individual analytes and methods are described in the appendices. Currently, Method SW8021B is not run by STL – Pittsburgh, however other laboratories within STL do run this method.

2. SUMMARY OF METHOD

In general, semivolatile analytes in aqueous samples are prepared for analysis using continuous or separatory funnel liquid / liquid extraction or solid phase extraction (SOP # CORP-OP-0001) Solid samples are prepared using sonication, Soxhlet or pressurized fluid extraction (SOP # CORP-OP-0001).

After the initial preparation step, the sample is introduced to the GC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Internal or external standardization procedures are used as specified in the method appendices.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. In addition, some purge and trap autosamplers are susceptible to port specific contamination. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. In particular, this is a problem with non-selective detectors such as the Flame Ionization Detector (FID). See the appendices for interferences specific to individual tests and suggested corrective actions.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates. The following requirements must be met:

Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately. Refer to the STL Chemical Hygiene plan for a complete description of personal protection equipment.

The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. Specific hazards are covered in the appendices.

5.1.1. Opened containers of neat standards will be handled in a fume hood.

5.2. Sample extracts and standards which are in a flammable solvent shall be stored in an explosion-proof refrigerator.

5.3. When using hydrogen gas as a carrier, all precautions listed in the CHP shall be observed.

5.4. Standard preparation and dilution shall be performed inside an operating fume hood.

6. EQUIPMENT AND SUPPLIES

An analytical system complete with a gas chromatograph is required. A data system capable of measuring peak area and/or height is required. Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from pure solutions. Semivolatile stock standard solutions are stored at $\leq 6^{o}C$. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

Semivolatile stock standard solutions must be replaced after one year. Stock standards of gases must be replaced at least every week, unless the acceptability of the standard is demonstrated (Less than 20% drift from the initial is an acceptable demonstration). Other volatile stock standards must be replaced every 6 months or sooner, if comparison with check standards prepared from an independent source indicates a problem.

7.1.1. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If a vendor supplied standard has an earlier expiration date then that date is used.

7.2. Calibration Standards

7.2.1. Congener Calibration Standards

The procedure for preparation of PCB Congener standards is given in Appendix A.

7.2.2. Semivolatile Calibration Standards

Semivolatile calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method appendices. Semivolatile calibration solutions must be refrigerated at $\leq 6^{o}C$ and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.3. Gases for carrier and make-up: Hydrogen, Helium, Nitrogen, Argon/Methane.

7.4. Quality control (QC) Standards

QC standards (matrix spiking and LCS standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE PRESERVATION AND STORAGE

Semivolatile extracts must be refrigerated at $\leq 6^{o}C$ and analyzed within 40 days of the end of the extraction.

9. QUALITY CONTROL

9.1. Refer to the STL Pittsburgh QC Program document (QA-003) for further details on criteria and corrective actions. Refer to “Project Checklist” for project specific requirements.

9.2. Initial Demonstration of Capability

9.2.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin.

9.2.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.3. Batch Definition

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

9.3.1. Quality Control Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD a LCSD may be substituted.

9.4. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be verified at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Refer to policy QA-003 for more details.

9.4.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.4.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.4.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.5. Surrogates

All methods must use surrogates to the extent possible. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem. Repreparation is not necessary is there is obvious chromatographic interference.
- The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.5.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.5.2. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then repreparation or flagging of the data is required.

9.5.3. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.6. Method Blanks

9.6.1. For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous semivolatiles samples, and sodium sulfate for semivolatiles soils tests (Refer to SOP No. CORP-OP-0001 for details).

9.6.2. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher. Wherever blank contamination is greater than 1/10 the concentrations found in the samples and/or 1/10 of the regulatory limit it is potentially at a level of concern and should be handled as a non-conformance. Blank contamination should always be assessed against project specific requirements (See associated project checklist).

9.6.3. If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone, phthalate esters) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

9.6.4. Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

9.6.5. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.7. Instrument Blanks

9.7.1. An instrument blank must be analyzed during any 12 hour period of analysis that does not contain a method blank.

9.7.2. An instrument blank consists of the appropriate solvent with internal standards added. If internal standards are not used the surrogates should be added.

9.7.3. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.8. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. The LCS may also contain the full set of analytes. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch; however, if the matrix spike and matrix spike duplicate are within limits, the batch may be acceptable.

9.8.1. Refer to the STL QC Program document (QA-003) for further details of the corrective action.

9.8.2. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.8.3. LCS compound lists are included in the appendices.

9.8.4. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client.

9.9. Matrix Spikes

- For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific historically generated limits.
- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed.
- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed.
- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.9.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.11. STL QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

Internal or external calibration may be used. Internal calibration is recommended unless the sample matrix is likely to interfere with the quantitation of the internal standard. In either event prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.

10.1. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, changing PID lamps or FID jets or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance.

10.2. With the exception of 10.3 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points. Third order calibrations require at least seven points.

10.3. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial or no purge run. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.4. External standard calibration

Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

$$Calibration\ Factor\ (CF) = \frac{Area\ or\ Height\ of\ Peak}{Mass\ Injected\ (ng)}$$

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. It is also possible to use the concentration of the standard rather than the mass injected. (This would require changes in the equations used to calculate the sample concentrations). Use of peak area or height must be consistent. However, if matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute.

10.5. Internal standard calibration

10.5.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. To use this approach, select one or more internal standard(s) that are similar in analytical behavior to the compounds of interest. Recommended internal standards are given in the appendices. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. If the sample matrix interferes with quantitation of the internal standard, then the external standard approach must be used instead. In this event use the response factors from the

previous continuing calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.5.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

10.6. Calibration curve fits

Average response factor, linear regression, or quadratic curves may be used to fit the data. Average response factor may be used if the average % RSD of the response factors or calibration factors of all the analytes in the calibration standard taken together is $\leq$ 20%. The average %RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes.

10.6.1. In general, for environmental analysis, average response factors are the most appropriate calibration model. Linear or curved regression fits should only be used if the analyst has reason to believe that the average RF model does not fit the normal concentration/response behavior of the detector.

10.6.2. Average response factor

The average response factor may be used if the average percent relative standard deviation (%RSD) of all the response factors taken together is $\leq$ 20%.

The equation for average response factor is:

$$\text{Average response factor} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where: n = Number of calibration levels

$\sum_{i=1}^{n} RF_i$ = Sum of response factors for each calibration level

10.6.3. Linear regression

The linear fit uses the following functions:

10.6.3.1. External Standard

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.6.3.2. Internal Standard

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$

Where: C_s = Concentration in the sample
A_s = Area of target peak in the sample
A_{is} = Area of internal standard in the sample
C_{is} = Concentration of the internal standard

10.6.4. Quadratic curve

The quadratic curve uses the following functions:

10.6.4.1. External standard

$$y = ax + cx^2 + b$$

Where c is the curvature

10.6.4.2. Internal Standard

$$y = a\left(\frac{A_s \times C_{is}}{A_{is}}\right) + c\left(\frac{A_s \times C_{is}}{A_{is}}\right)^2 + b$$

10.7. Evaluation of calibration curves

10.7.1. The percent relative standard error (%RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.7.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard error is calculated as follows:

$$\%\ RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where:
N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_i = True concentration for level i
PC_i = Predicted concentration for level i

Note that when average response factors are used, %RSE is equivalent to %RSD.

10.8. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response must be less than $\pm$ the reporting limit for the analyte.
- The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be $\leq$ 20%.
- Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (r) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on r. As a result a curve may have a very good correlation coefficient (>0.995), while also having > 100% error at the low point.

10.9. Weighting of data points

10.9.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.10. Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation.

10.11. Calibration Verification

10.11.1. 12 hour Calibration

The working calibration curve or RF must be verified by the analysis of a mid point calibration standard at the beginning, after every 12 hours, and at the end of the analysis sequence. The center of each retention time window is updated with each 12 hour calibration. The CCV is varied periodically to check for linearity, this occurs when MDL's are performed.

10.11.2. Calibration Verification

It may be appropriate to analyze a mid point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12 hour calibration with the exception that retention times are not updated.

10.11.3. Any individual compounds with $\%D \leq 15\%$ meet the calibration criteria. The calibration verification is also acceptable if the average of the %D for all the analytes is $\leq 15\%$. This average is calculated by summing all the absolute %D results in the calibration (including surrogates) and dividing by the number of analytes.

10.11.4. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.11.5. Samples quantitated by external standard methods must be bracketed by calibration verification standards that meet the criteria listed above. Bracketing is not necessary for internal standard methods.

10.11.6. If the analyst notes that a CCV has failed and can document the reason for failure (e.g. no purge, broken vial, carryover from the previous sample etc.) then a second CCV may be analyzed without any adjustments to the instrument. If this CCV meets criteria then the preceding samples have been successfully bracketed. If adjustments to the instrument are performed before the repeat CCV then the preceding samples have not been successfully bracketed but analysis may continue.

10.11.7. In general, it is not advisable to analyze repeat CCVs on unattended runs. If repeat CCVs are analyzed then the first will serve as the bracketing standard for the preceding samples and the last will serve as the CCV for the following samples.

10.11.8. A mult-level calibration verification should be done periodically to verify stability of the intrument over the calibration range. This will be done at a minimum on an annual basis along with the MDLs.

10.11.9. If highly contaminated samples are expected it is acceptable to analyze blanks or primers at any point in the run.

10.11.10. % Difference calculation

% Difference for internal and external methods is calculated as follows

Internal Standard:

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

External standard:

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where RF_c and CF_c are the response and calibration factors from the continuing calibration

$\overline{RF}$ and $\overline{CF}$ are the average response and calibration factors from the initial calibration

10.11.11. % Drift calculation

% Drift is used for comparing the continuing calibration to a linear or quadratic curve. The criteria for % drift are the same as for % difference

$$\%\ Drift = \frac{Calculated\ Conc. - Theoretical\ Conc.}{Theoretical\ Conc.} \times 100\%$$

10.11.12. Corrective Actions for Continuing Calibration

If the overall average %D of all analytes is greater than $\pm$ 15% corrective action must be taken. This may include clipping the column, changing the liner or other minor instrument adjustments, followed by reanalyzing the standard. If the overall average %D still varies by more than $\pm$ 15%, a new calibration curve must be prepared.

10.11.13. Corrective Action for Samples

For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be reinjected.

For external standard methods, any samples injected after the last good continuing calibration standard must be reinjected.

If the average %D for all the analytes in the calibration is over 15%, but all of the analytes requested for a particular sample have %D $\leq$ 15%, then the analysis is acceptable for that sample.

10.11.14. Each initial calibration will be verified with the analysis of a second source standard. These must be from lots independent of the sources used for the primary calibration standard. This second source standard must at a minimum pass CCV criteria for the compounds being reported from the curve.

11. PROCEDURE

11.1. Extraction

Extraction procedures are referenced in the appendices.

11.2. Cleanup

Cleanup procedures are referenced in the appendices.

11.3. Gas Chromatography

Chromatographic conditions for individual methods are presented in the appendices.

11.4. Sample Introduction

Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5. Analytical Sequence

An analytical sequence starts with an initial calibration or a daily calibration. Refer to the individual method appendices for method specific details of daily calibrations and analytical sequences.

11.5.1. The daily calibration includes analysis of standards containing all single response analytes and updating the retention time windows.

11.5.2. If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration.

11.6. Retention Time Windows

11.6.1. Retention time windows must be specified for all analytes. *A Fixed retention time windows (± .05 minutes) will be used for all GC methods. Alternatively, if it is determined through calculation that wider limits are necessary, the limits will be developed as follows:* Make an injection of all analytes of interest each day over a three day period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). For multiresponse analytes (e.g., Aroclors) use the retention time of major peaks. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The center of the retention time window is the retention time from the last of the three standards. The centers of the windows are updated with the mid point of the initial calibration and each 12 hour calibration. The widths of the windows will remain the same until new windows are generated following the installation of a new column.

11.6.3. *Where calculated limits are being used, if* the retention time window as calculated above is less than +/- 0.05 minutes, use +/- 0.05 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.4. *Where calculated limits are being used, t*he laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.5. Corrective Action for Retention Times

The retention times of all compounds in each continuing calibration must be within the retention time windows established by the 12 hour calibration. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

The retention time of that compound in the standard must be within a retention time range equal to twice the original window.

No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Daily Retention Time Windows

The center of the retention time windows determined in section 11.6 are adjusted to the retention time of each analyte as determined in the 12 hour calibration standards. (See the method 8081A and 8082 appendices for exceptions for multi-response components.) The retention time windows must be updated at the beginning of each analytical sequence and with each 12 hour calibration, but not for any other calibration verification standards.

11.8. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP CORP-OP-0001 for determination of percent moisture.

11.9. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a supervisor and QA/QC manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Normally confirmation is required on a second column, but if the detector is sufficiently specific or if the sample matrix is well enough defined, single column analysis may be adequate. In some cases GC/MS confirmation may be required. Client specific requirements may also define the need for second column confirmation and / or GC/MS confirmation. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (MDL if J flag confirmation required).

12.1.2. Dual column quantitation

- For confirmed results, two approaches are available to the analyst;

A) The primary column approach
Or
B) The better result approach

Both are acceptable to avoid the reporting of erroneous or unconfirmed data. The approach used is based on the project requirements.

12.1.2.1. Primary column approach (may be used where indicated as a project requirement)

The result from the primary column is normally reported. The result from the secondary column is reported if any of the following three bulleted possibilities are true.

- There is obvious chromatographic interference on the primary column
- The result on the primary column is > 40% greater than the result on the secondary column
- Continuing or bracketing standard fails on the primary column but is acceptable on the secondary column. (If the primary column result is > 40% higher than the secondary and the primary column calibration fails, then the sample must be evaluated for reanalysis.)

12.1.2.2. Better result approach (default practice of laboratory subject to project requirements)

The lower of the two results is normally reported. The lower result is considered better because the higher result is generally higher because of chromatographic interference. The higher result is reported if any of the following two bulleted possibilities are true.

- There is obvious chromatographic interference on the column with the lower result
- The continuing or bracketing calibration on the column with the lower result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for reanalysis.)
- This rule may be reversed to favor reporting of the higher value or the higher value where the results differ by 40% when indicated as a project requirement by the PM.

12.1.3. If the Relative percent difference (RPD) between the response on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{R1 - R2}{\frac{1}{2}(R1 + R2)} x\,100$$

Where R=Result

12.1.4. Multi-response Analytes

For multi-response analytes, the analyst should use the retention time window, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

12.1.5. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.1.6 The Lab reports the lower of the two values. If requested by the client, the higher of the two values will be reported.

12.2. Calibration Range

If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most

concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions

Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and only minor matrix peaks are, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgement is required to determine the most concentrated dilution that will not result in instrument contamination.

12.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4. Interferences

If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Internal Standard Criteria for Continuing Calibration

If internal standard calibration is used, then the internal standard response in a continuing calibration standard must be within 50 to 150% of the response in the mid level of the initial calibration.

12.6. Calculations

Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.6.1. External Standard Calculations

12.6.1.1. Aqueous samples

$$Concentration\ (mg/L) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times V_s)}$$

Where:

A_x = Response for the analyte in the sample
V_i = Volume of extract injected, µL
D_f = Dilution factor
V_t = Volume of total extract, µL
V_s = Volume of sample extracted or purged, mL
CF = Calibration factor, area or height/ng, Section 10.1

12.6.1.2. Non-aqueous Samples

$$Concentration\ (mg/kg) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times W \times D)}$$

Where:

W = Weight of sample extracted or purged, g

$$D = \frac{100 - \%\ Moisture}{100}$$ (D = 1 if wet weight is required)

12.6.2. Internal Standard Calculations

12.6.2.1. Aqueous Samples

$$Concentration\ (mg/L) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times V_s)}$$

Where:

C_{is} = Amount of internal standard added, ng
A_{is} = Response of the internal standard
RF = Response factor for analyte

12.6.2.2. Non-aqueous Samples

$$Concentration\ (mg/kg) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times W \times D)}$$

12.6.3. Surrogate Recovery

Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation:

$$\%\ \text{Recovery} = \frac{Concentration\ (or\ amount)\ found}{Concentration\ (or\ amount)\ spiked} \times 100$$

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.2.4. The CCV will be varied perodically to demonstrate verification of linearity of the curve.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Section 8000B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the Method Detection Limit. This SOP states that the Method Blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed to be up to 5 times the reporting limit in the blank following consultation with the client.

17.2. Modifications from Previous Revision

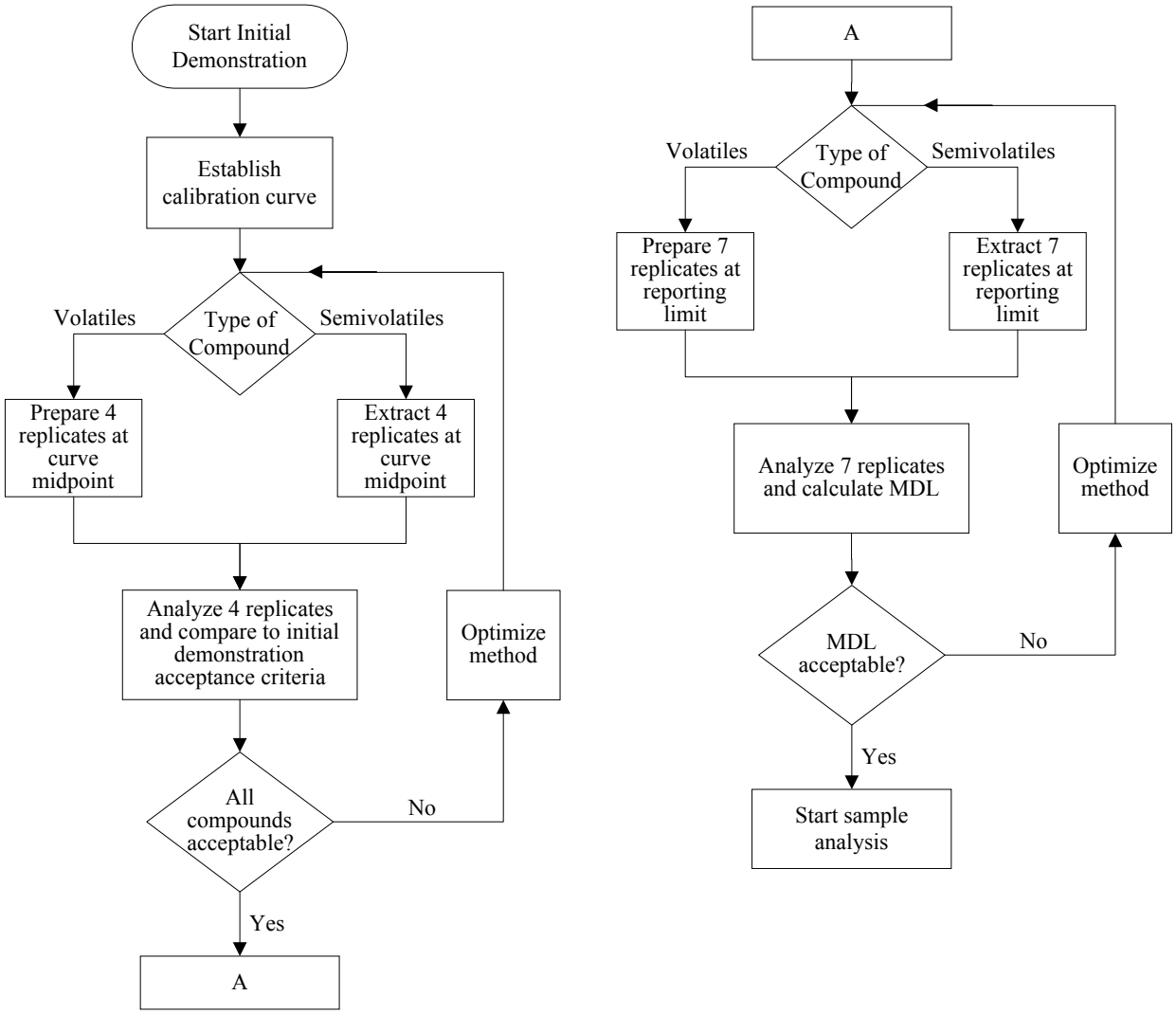
The calibration criteria in section 10.11 have been rewritten to improve consistency with SW-846 and to improve clarity.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

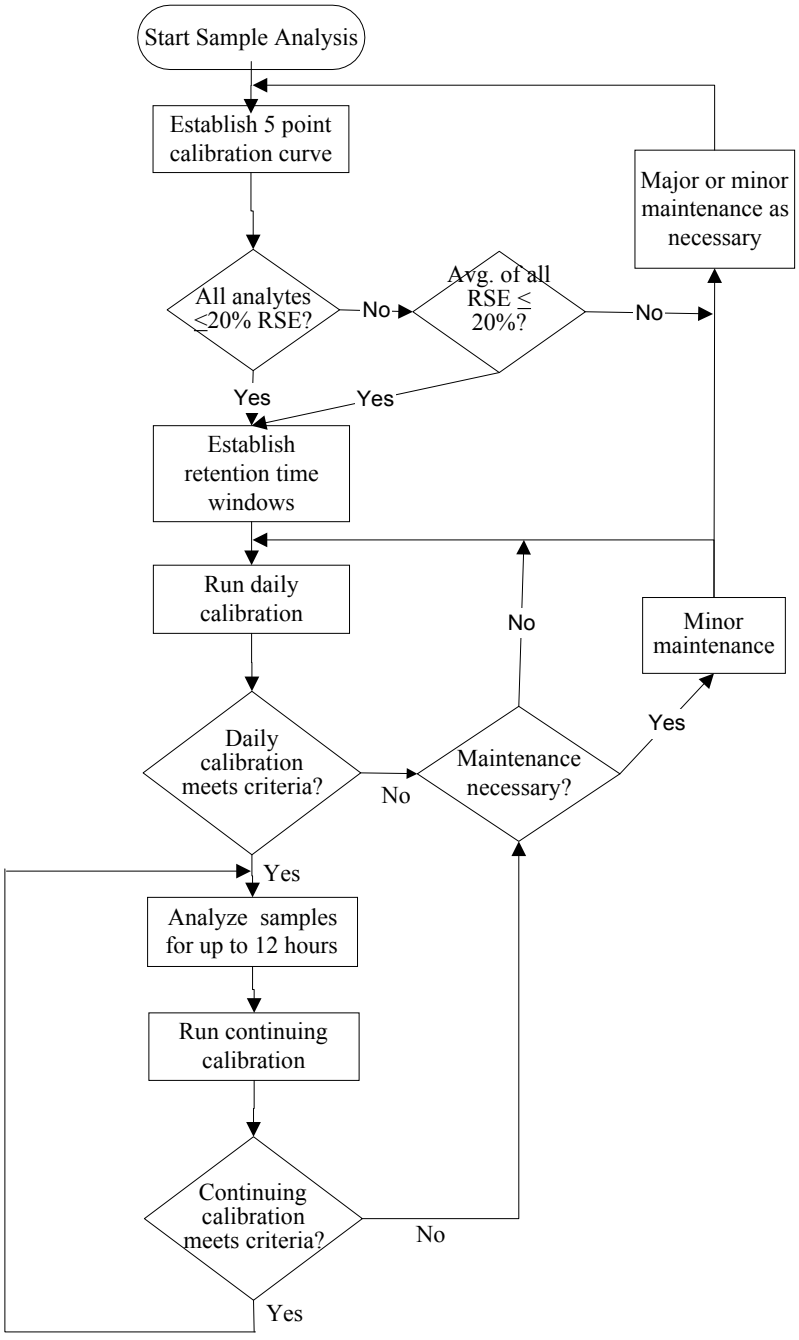
17.4. Flow Diagrams

17.4.1. Initial demonstration and MDL[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

17.4.2. Sample Analysis[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

1. SCOPE AND APPLICATION

This method is applicable to the gas chromatographic determination of Chlorinated phenoxy acid herbicides in extracts prepared by SOP CORP-OP-0001. The herbicides listed in Table D1 are routinely analyzed. Other chlorinated acids may be analyzed by this method if the quality control criteria in section 9 and the initial demonstration of method performance in section 13 are met.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of phenoxy acid herbicides by gas chromatography. The herbicides, as their methyl esters, are injected onto the column, separated, and detected by electron capture detectors. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

4.2. Chlorinated acids and phenols cause the most direct interference with this method.

4.3. Sulfur may interfere and may be removed by the procedure described in SOP#CORP-OP-0001.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A Ni_{63} electron capture detector is required.

6.2. Refer to Table D2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to section 7 of the 8000B section of this SOP for general information on reagents and standards.

7.2. Refer to Table D-3 and D-4 for details of calibration and other standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

Refer to section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table D-5 for minimum performance criteria for the initial demonstration of capability.

9.3. Refer to Table D-4 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Calibration standards are made up from the free acids, and then esterified using the same process as for samples (See SOP Corp-OP-0001)

10.3. The low level standard must be at or below the laboratory reporting limit. Other standards are chosen to bracket the expected range of concentrations found in samples, without saturating the detector or leading to excessive carryover.

10.4. Refer to Table D-2, for details of GC operating conditions.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP #CORP-OP-0001.

11.3. Cleanup

The alkaline hydrolysis and subsequent extraction of the basic solution described in the extraction procedure provides an effective cleanup.

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

11.4.2. The daily calibration consists of mid level standards of all analytes of interest. Retention time windows must be updated with the daily calibration.

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

11.5. Gas Chromatography

Chromatographic conditions are listed in Table D-2.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. The herbicides are analyzed as their methyl esters, but reported as the free acid. For this reason it is necessary to correct the results for the molecular weight of the ester versus the free acid. This is achieved through the concentrations of the calibration standards. For example the 20µg/L calibration standard for 2,4-D contains 21.3 µg/L of the methyl ester. No further correction is necessary.

Standard Analyte list
Weight Corrections

Compound	*CAS Number*	*Molecular weight(g/mol)*	
		Acid	*Methyl Ester*
2,4-D	*94-75-7*	*221.0*	*235.1*
2,4-DB	*94-82-6*	*249.1*	*263.1*
2,4,5-TP (Silvex)	*93-72-1*	*269.5*	*283.5*
2,4,5-T	*93-76-5*	*255.5*	*269.5*
Dalapon	*75-99-0*	*143.0*	*157.0*
Dicamba	*1918-00-9*	*221.0*	*235.1*
Dichloroprop	*120-36-5*	*235.1*	*249.1*
Dinoseb	*88-85-7*	*240.2*	*254.2*
MCPA	*94-74-6*	*200.6*	*214.6*
MCPP	*7085-19-0*	*214.6*	*228.6*

13. METHOD PERFORMANCE

13.1. Multiple laboratory performance data has not been published by the EPA for this method. Table D-5 lists minimum performance standards required by STL for the four replicate initial demonstration or capability (required by Section 13.2 of the 8000B part of this SOP) for this method. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

Method 8151A, SW-846, Update III, December 1996

17. MISCELLANEOUS

17.1. Modifications from Reference Method

Refer to the method 8000B section of this SOP for modifications from the reference method.

17.2. Modifications from Previous Revision

The calibration procedure has been changed to require esterification of the calibration standards

17.3. Tables

Table D-1					
Standard Analyte list					
Compound	CAS Number	Reporting Limit, µg/L or µg/kg			
		Aqueous	Soil	Waste	TCLP
2,4-D	94-75-7	4	80	4000	500
2,4-DB	94-82-6	4	80	4000	---
2,4,5-TP (Silvex)	93-72-1	1	20	1000	500
2,4,5-T	93-76-5	1	20	1000	---
Dalapon	75-99-0	2	40	2000	---
Dicamba	1918-00-9	2	40	2000	---
Dichloroprop	120-36-5	4	80	4000	---
Dinoseb	88-85-7	0.6	12	600	---
MCPA	94-74-6	400	8000	400,000	---
MCPP	93-65-2	400	8000	400,000	---

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.	Dilution Factor
Ground water	1000 mL	10 mL	20
Low-level Soil without GPC	50 g	10 mL	20
High-level soil / waste	1 g	10 mL	20

Specific reporting limits are highly matrix dependent. The reporting limits listed above are provided for guidance only and may not always be achievable. For special projects, the extracts may be analyzed without any dilution, resulting in reporting limits 20 times lower than those in Table D-1.

Table D-2	
Instrumental Conditions	
PARAMETER	Recommended conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	80,2/30/170,0/1/180,1
Column 1	DB-5MS or RTX 5 30x0.32, 0.5um
Column 2	DB-1701 or Rtx-1701
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Recommended conditions should result in resolution of all analytes listed in Table D-1.

The reporting limits listed in Table D-1 will be achieved with these calibration levels and a 20 fold dilution of the sample extract. Lower reporting limits can be achieved with lesser dilutions of the sample extract.

Table D-3				
LCS/Matrix Spike and Surrogate Spike levels μg/L or μg/kg[1]				
	Aqueous	Soil	Waste	TCLP
2,4-D	16	800	16000	6ug/L ; 120ug/kg
Silvex	4	200	4000	6ug/L ; 120ug/kg
2,4,5-T	4	200	4000	6ug/L ; 120ug/kg
2,4-DB	16	800	16000	---
Dalapon	8	400	8000	---
DCAA (surrogate)	16	800	16000	10ug/L;500ug/kg

[1] LCS, MS and SS spikes are as the free acid.

Table D-4		
Performance limits, four replicate initial demonstration of capability		
Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
2,4-D	50-150	25
2,4-DB	50-150	25
2,4,5-TP (Silvex)	50-150	25
2,4,5-T	50-150	25
Dalapon	50-150	25
Dicamba	50-150	25
Dichloroprop	50-150	25
Dinoseb	25-120	40
MCPA	50-150	25
MCPP	50-150	25

Table D-5					
Calibration Levels					
Compound	Concentration levels in ug/ml				
2,4-D	0.0211	0.0425	0.0851	0.1700	0.3400
DCAA	0.0213	0.0425	0.0851	0.1700	0.3400
2,4-DB	0.0211	0.0422	0.0845	0.1690	0.3380
2,4,5-TP (Silvex)	0.0053	0.0105	0.0211	0.0421	0.0840
2,4,5-T	0.0053	0.0105	0.0211	0.0422	0.0844
Pentachlorophenol	0.0027	0.0053	0.0106	0.0213	0.0425
Dalapon	0.0110	0.0220	0.0439	0.0878	0.1760
Dicamba	0.0106	0.0213	0.0425	0.0851	0.1700
Dichloroprop	0.0212	0.0424	0.0848	0.1700	0.3390
MCPP	2.120	4.260	8.520	17.00	34.10
Dinoseb	0.0032	0.0063	0.0127	0.0254	0.0508
MCPA	2.140	4.280	8.560	17.10	34.00

APPENDIX 26

STL STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 AND MCAWW 200 SERIES METHODS

(SUPERSEDES: REVISION 0)

Prepared by: Kurt Ill and Richard Burrows

Reviewed by: _____
Technical Specialist

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption (FLAA) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) using the MCAWW 200 series methods (NPDES) and SW846 Methods 3005A, 3010A, 3020A and 7060A/7740 (RCRA).

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II (Appendix A) and the applicable determinative methods are illustrated by Figures 6 and 7 (Section 17). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, solids, sludges, wastes, sediments, air sampling media, biological tissue and leachates/extracts.

1.4. SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by FLAA, ICP and GFAA (antimony only).

1.5. MCAWW Method 200.7 Section 9.4 is used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by ICP.

1.6. SW-846 Method 3010A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by FLAA or ICP.

1.7. MCAWW Method 200.7 Section 9.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by ICP.

1.8. SW-846 Method 3020A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals by GFAA.

1.9. MCAWW Method 200.0 Section 4.1.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by GFAA.

1.10. MCAWW Method 200.0 Section 4.1.4 is used to surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by GFAA.

1.11. SW-846 Methods 7060A and 7740, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.12. MCAWW Methods 206.2 and 270.2, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.13. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples and this must be clarified before project initiation.

2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP Spectroscopy

A representative aliquot of sample is heated with nitric and hydrochloric acids and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy

A representative aliquot of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary) and brought up to volume.

2.3. Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals for Analysis by GFAA Spectroscopy

A representative aliquot of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. After the digestate has been reduced to a low volume, it is cooled, filtered (if necessary) and brought up to volume.

2.4. Methods 7060A/206.2 and Methods 7740/270.2 - Preparation for Arsenic/Selenium Analysis by GFAA

A representative aliquot of sample is heated with nitric acid and peroxide until the digestion is complete or until the volume is reduced by one-half. The sample is cooled, filtered (if necessary) and brought up to volume.

2.5. Method 200.0 Section 4.1.4 - Total Recoverable GFAA Preparation (NPDES)

A representative aliquot of sample is heated with nitric acid until the volume is reduced to 15 - 20 mL. The sample is cooled, filtered (if necessary) and brought up to volume.

3. DEFINITIONS

Additional definitions of terms used in this SOP may be found in the glossary of the QAMP.

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix D for additional contamination control guidelines.

4.3. Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals . If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.7. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample.

4.8. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. All sample digestions, including cooling of digestates, must be carried out in a fume hood.

5.4. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.11. Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block or other adjustable heating source capable of maintaining a temperature of 90 - 95°C.

6.2. Thermometer that covers a temperature range of 0-200°C.

6.3. Griffin beakers of assorted sizes or equivalent.

6.4. Watch glasses, ribbed or equivalent.

6.5. Whatman No. 41 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 50 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repipetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipet tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic digestate storage bottles.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: The ICP LCS/MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS spike solution by diluting the custom stock solution (7.2) 100x. The working spike solution must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working GFAA LCS solution must be made fresh every three months.

7.5. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.6. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.7. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables II and III (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.9. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.11. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids <u>always</u> add acid to water. If the water is added to the acid a violent reaction may occur.

7.12. 30% Hydrogen peroxide (H_2O_2), reagent grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. For dissolved metals analysis, the samples should be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field or within 24 hours of collection.

Note: If a sample being analyzed for dissolved metals is found to contain sediment the analyst should contact their supervisor or group leader. The client should be notified of the problem to decide how to treat the sample.

9. QUALITY CONTROL

Table VI (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using any method contained within this SOP the following requirements must be met:

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDL's must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in STL QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS) are not included in the sample count for determining the size of a preparation batch. MS/MSD are not included in the sample count unless there are multiple sets of MS/MSD per batch. In other words, the first MS/MSD are not counted; all additional MS and MSDs are counted as samples.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the

acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.4.1. Aqueous method blanks are prepared by taking 50 mL or 50 g of reagent water through the appropriate procedure as described in Section 11.

9.4.2. TCLP method blanks are prepared by taking 50 mL or 50 g of leachate fluid through the appropriate procedure as described in Section 11.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Refer to Section 7.3 and 7.4 for instructions on preparation of the aqueous LCS spike solution.

9.5.1. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 0.5 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed through the appropriate procedure as described in Section 11.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred.

9.6.1. The aqueous matrix spike sample is prepared by spiking a 50 mL aliquot of a sample with 0.5 mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in Section 11.

9.6.2. The TCLP matrix spike sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (7.5). The matrix spike sample is then processed as described in Section 11.

NOTE: The TCLP matrix spike must be added prior to preservation of the leachate.

9.6.3. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. CALIBRATION AND STANDARDIZATION

10.1 Hotplate temperature must be verified daily for each hotplate used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. All preparation procedures must be carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. In most cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be measured out and processed at the same time.

11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.10. The following procedure must be followed for all aqueous sample preparations:

11.10.1. Measure and record sample pH with pH paper on a separate aliquot of sample.

Note: If the sample pH is > 2 pH units, the client must be notified of the anomaly.

Note: If sample pH has already been verified and documented in sample receipt this step may be omitted.

11.10.2. Mix sample by shaking the container.

11.10.3. Measure and transfer 50 mL or 50 g of the sample into a beaker.

Note: This SOP allows for samples to be weighed instead of measured volumetrically (See Section 17.1.1.2).

11.10.4. Measure two extra aliquots of sample selected for the MS/MSD analysis. Spike each aliquot with 0.5 mL of spiking solution (7.3 or 7.4).

11.10.5. Measure and transfer 50 mL of reagent water into a beaker for the method blank.

11.10.6. Measure and transfer 50 mL of reagent water into a beaker for the LCS and add 0.5 mL of spiking solution (7.3 or 7.4)

11.11. Proceed to the appropriate Section for the desired method as follows:

Method 3005A or Method 200.7 Section 9.4	11.12
Method 3010A or Method 200.7 Section 9.3	11.13
Method 3020A or Method 200.0 Section 4.1.3	11.14
Method 7060A/7740 or Method 206.2/270.2	11.15
Method 200.0 Section 4.1.4	11.16

11.12. **Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP (See Figures 1, 6 and 7)**

11.12.1. To the sample beaker, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

11.12.2. Cover with ribbed watch glass.

11.12.3. Heat at 90 - 95°C until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.12.4. Cool the beaker in a fume hood.

11.12.5. Wash down beaker walls and watch glass with reagent water.

11.12.6. Filter sample, if insoluble materials are present, though Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid.

Note: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing , may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.12.7. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.12.8. Add 1.5 mL concentrated HNO_3 and adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis

11.13. **Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy (See Figures 2, 6 and 7)**

11.13.1. To the sample beaker, add 1.5 mL of concentrated HNO_3 .

11.13.2. Cover with ribbed watch glass.

11.13.3. Place beaker on hotplate (90-95 °C) and evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.13.4. Cool the beaker in a fume hood.

11.13.5. Add another 1.5 mL portion of concentrated HNO_3 and re-cover the beaker.

11.13.6. Continue refluxing until the digestion is complete.

Note: Digestion is complete when the digestate is light in color or does not change in appearance. For most samples the addition of two nitric acid aliquots is sufficient, additional aliquots of nitric acid may be added if necessary.

11.13.7. Evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

11.13.8. Cool the beaker in a fume hood.

11.13.9. Add 5 mL of 1:1 HCl.

11.13.10. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue.

11.13.11. Wash down beaker walls and watch glass with reagent water.

11.13.12. Filter sample, if insoluble materials are present, through Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid (1%).

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing , may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.13.13. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.13.14. Adjust final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

11.14. **Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals Analysis by GFAA (See Figures 3, 6 and 7)**

11.14.1. To the sample beaker, add 1.5 mL of concentrated HNO_3 .

11.14.2. Cover with ribbed watch glass.

11.14.3. Place beaker on hotplate (90-95 °C) and evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.14.4. Cool the beaker in the fume hood.

11.14.5. Add another 1.5 mL portion of concentrated HNO_3.

11.14.6. Recover with watch glass.

11.14.7. Continue refluxing and adding acid as necessary until digestion is complete.

Note: Digestion is complete when the digestate is light in color or does not change in appearance. For most samples the addition of two nitric acid aliquots is sufficient, additional aliquots of nitric acid may be added if necessary.

11.14.8. After the digestion is complete evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

11.14.9. Cool the beaker in the fume hood.

11.14.10. Add 10 mL of reagent water and mix sample.

11.14.11. Heat sample for 10 to 15 minutes more to dissolve any residue.

11.14.12. Cool the beaker in the fume hood.

11.14.13. Wash down beaker walls and watch glass with reagent water.

11.14.14. Filter sample, if insoluble materials are present, though Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid (1%).

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing , may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.14.15. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.14.16. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.15. **Method 7060A/7740 and Method 206.2/270.2 - Preparation for Arsenic and Selenium Analysis by GFAA (See Figures 4, 6 and 7)**

11.15.1. To the sample beaker, add 1 mL of 30 % H_2O_2 and 0.5 mL of concentrated HNO_3.

11.15.2. Heat, until the digestion is complete, at 90 - 95°C or until the volume has been reduced to slightly less than 25 mL.

11.15.3. Cool beaker.

11.15.4. Filter sample, if insoluble materials are present, though Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing , may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.15.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.15.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.16. **Method 200.0 Section 4.1.4 - Preparation for Total Recoverable GFAA Analyses. (See Figures 5 and 7)**

11.16.1. To the sample beaker, add 0.5 mL of concentrated HNO_3.

11.16.2. Heat, until the digestion is complete, at 90 - 95°C or until the volume has been reduced to 15 - 20 mL.

11.16.3. Cool beaker.

11.16.4. Filter sample, if insoluble materials are present, though Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing , may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.16.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.16.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The facility EH & S coordinator should be contacted if additional information is required.

15.2. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A, 3010A, 3020A, 7060A and 7740A.

16.2. Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983.

16.3. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010A and Method 200.7.

16.4. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.5. QA-003, STL QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference methods.

17.1.1. Modifications applicable to SW-846 reference methods.

17.1.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.1.2. This SOP allows for aqueous samples to be weighed instead of measured volumetrically. This assumes the density of the sample is close to 1.0 g/mL. Samples with large amounts of sediment or suspended solids, sludges, non-aqueous liquids must be processed volumetrically. Weighing samples directly into the digestion vessel minimizes the potential for cross contamination, offers improved accuracy over the use of graduated cylinders (comparable

to volumetric flask accuracy), uses less glassware and is more efficient.

17.1.1.3. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "..flexibility to alter digestion volumes is addressed and "allowed" by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Olliver Fordham stated " As a "representative sample" can be assured, scaling causes no loss of precision and accuracy in the analysis."

17.1.2. Modifications Specific to Method 3005A

17.1.2.1. In order to matrix match the digestate to the ICP calibration standards, Section 11.12.8 requires the addition of 1.5 mL of concentrated nitric acid to the digestate prior to dilution to final volume. This step ensures that bias due to differences in acid matrix will not be a factor in the analytical determination. Since this step is performed post-digestion it does not impact the digestion recoveries. This approach to matrix matching was discussed with Olliver Fordham of OSW who indicated that it was an acceptable practice.

17.1.3. Modifications Specific to Method 3010A

17.1.3.1. Section 11.13.7 of this SOP requires the sample be reduced to a volume of 5 - 10 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.3.2. The scope of 3010A has been expanded to include silver based on comparison studies with 7760A. Method 3010A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water and TCLP leachate) up to a concentration of 1 ppm silver.

17.1.4. Modifications Specific to Method 3020A

17.1.4.1. Section 11.14.8 of this SOP requires the sample be reduced to a volume of 5 - 10 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.5. Modifications Specific to Method 7060A/7740

17.1.5.1. Methods 7060A and 7740A incorporate the use of a two step dilution to accommodate the addition of a nickel nitrate modifier. This SOP performs the dilution directly in one step and omits the addition of the modifier. The modifier is added automatically at the instrument by direct injection into the furnace.

17.1.6. Modifications Specific to MCAWW Methods

It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP as described in Section 11.0. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness vs. an exact volume).

17.2. Modifications from previous SOP

None.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be

attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst name, matrix, prep type (ICP or GFAA), SOP reference.
- Sample ID, initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.
- Reviewer's Signature and date.

Figure 1. **Method 3005A / Method 200.7 Section 9.4 (Section 11.12)**

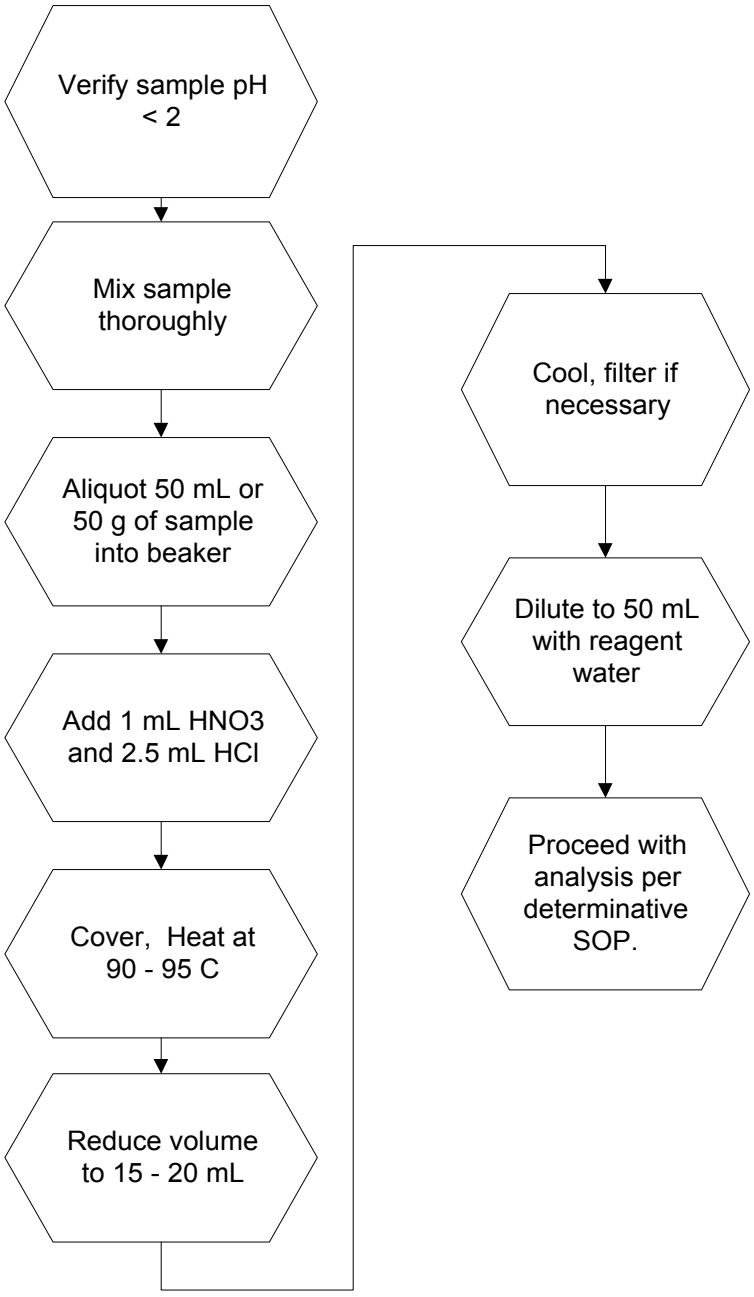


Figure 2. **Method 3010A / Method 200.7 Section 9.3 (Section 11.13)**

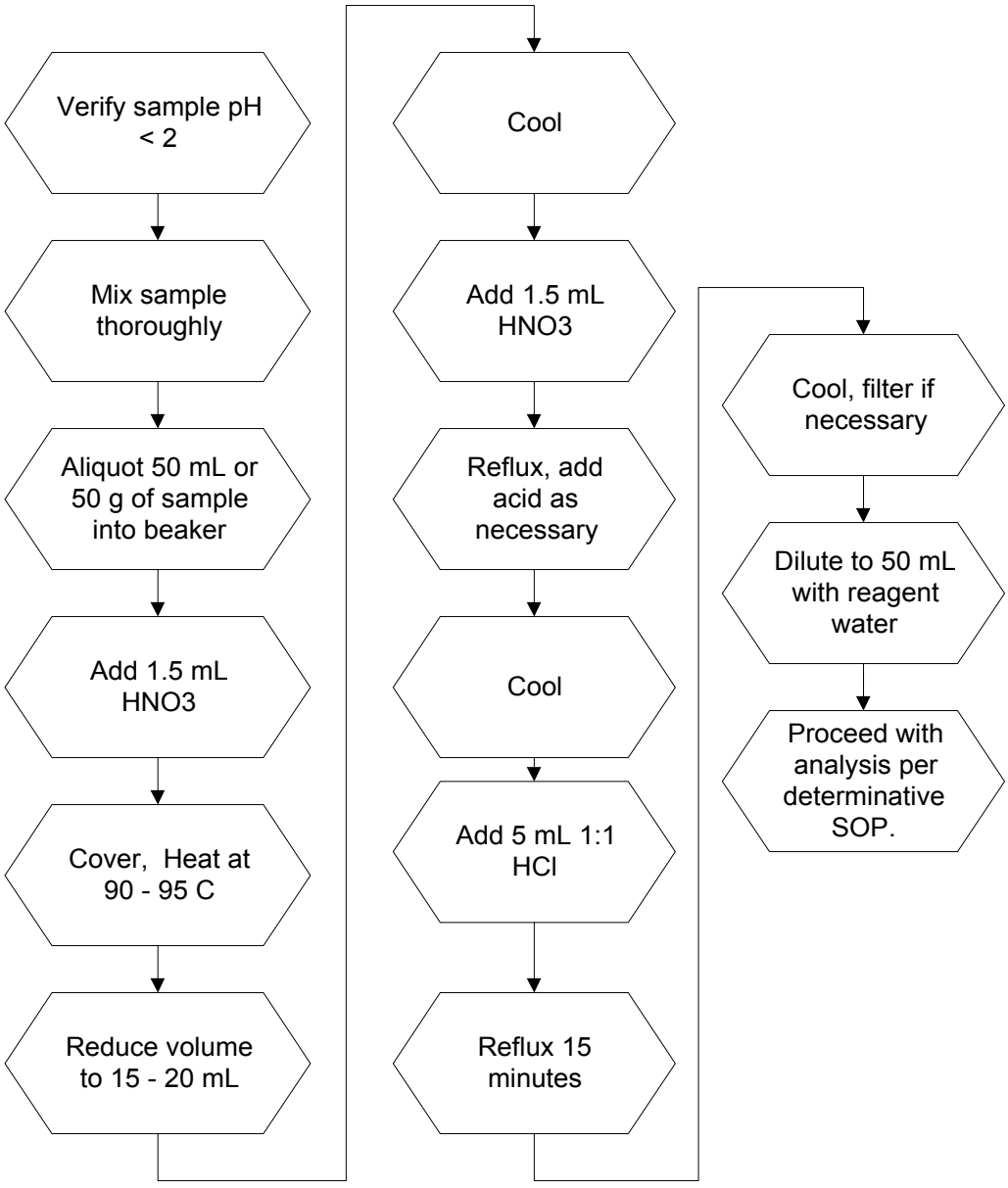


Figure 3. **Method 3020A / Method 200.0 Section 4.1.3 (Section 11.14)**

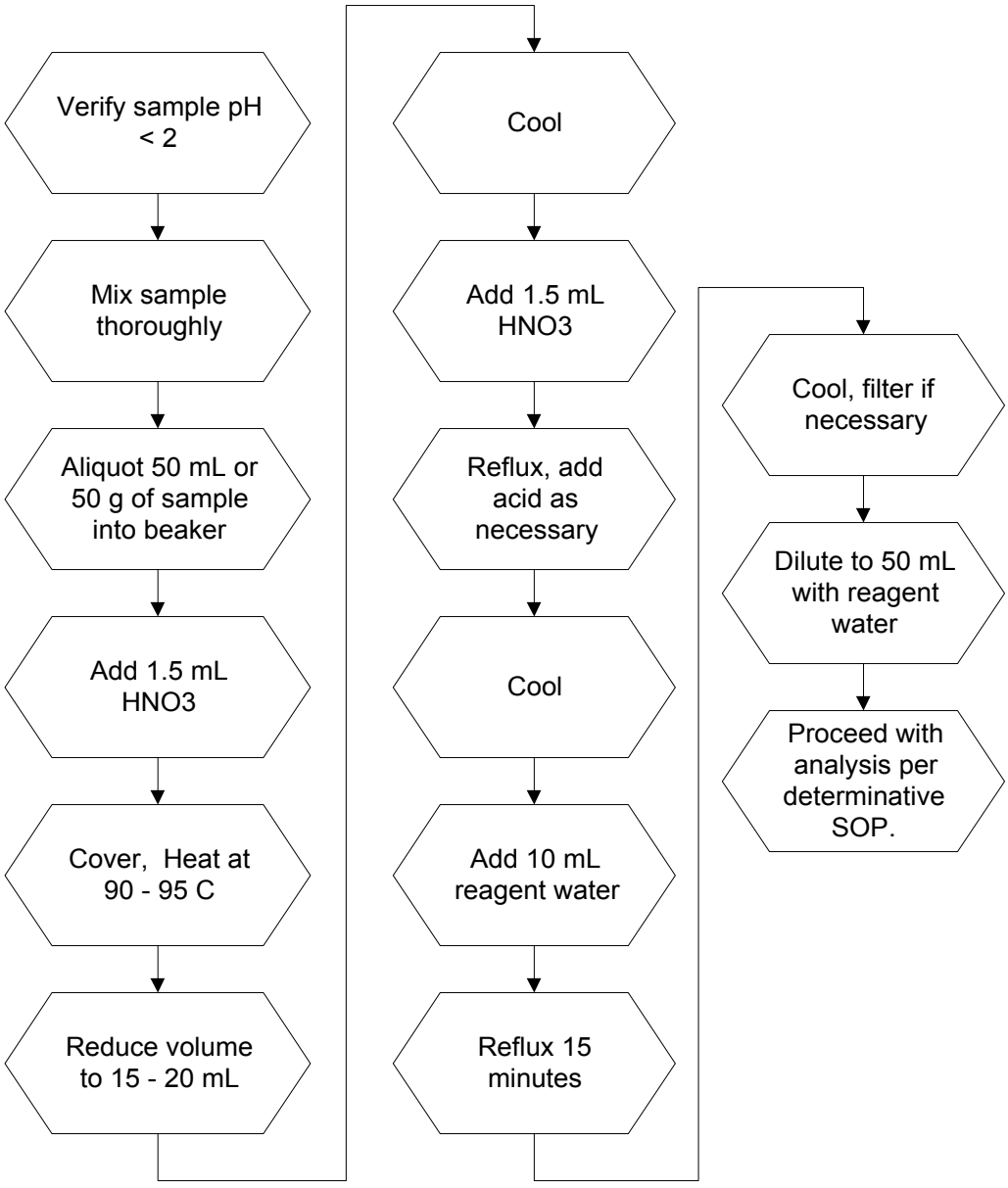


Figure 4. **Method 7060A/7740A and Method 206.2/270.2 (Section 11.15)**

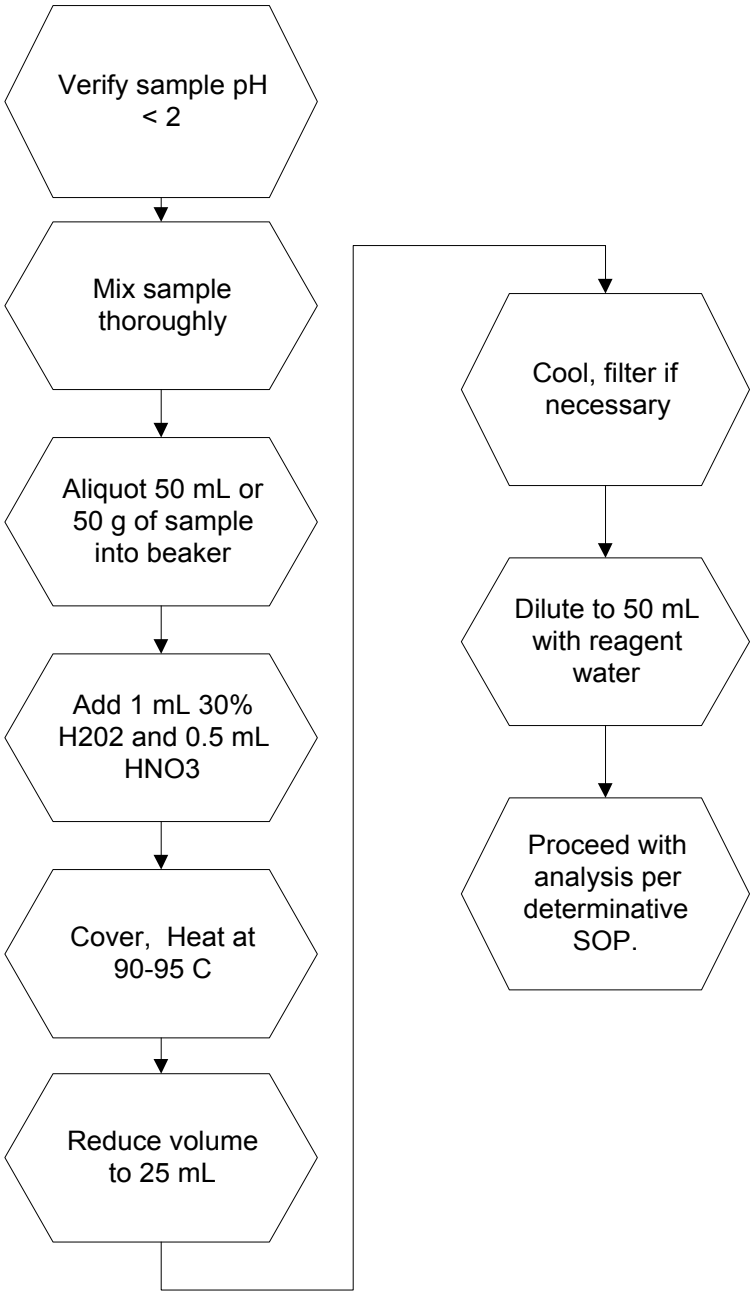


Figure 5. **Method 200.0 Section 4.1.4 (Section 11.16)**

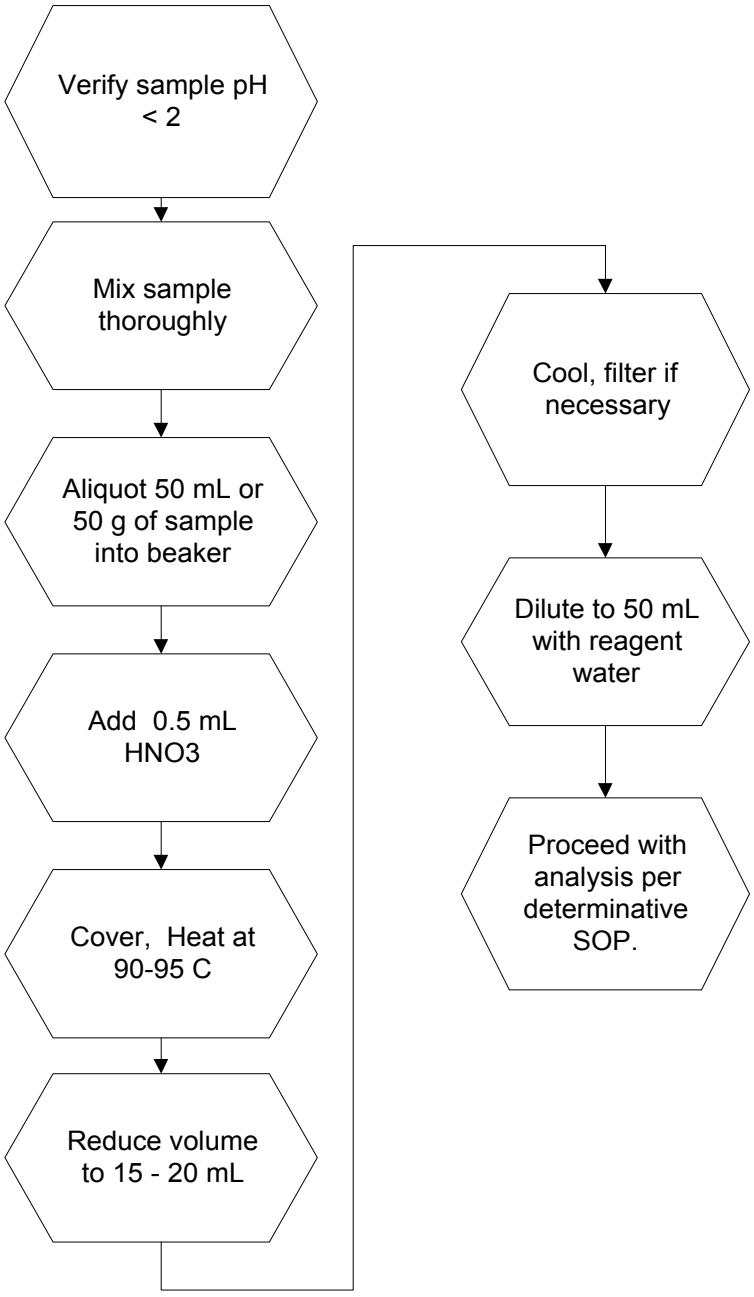
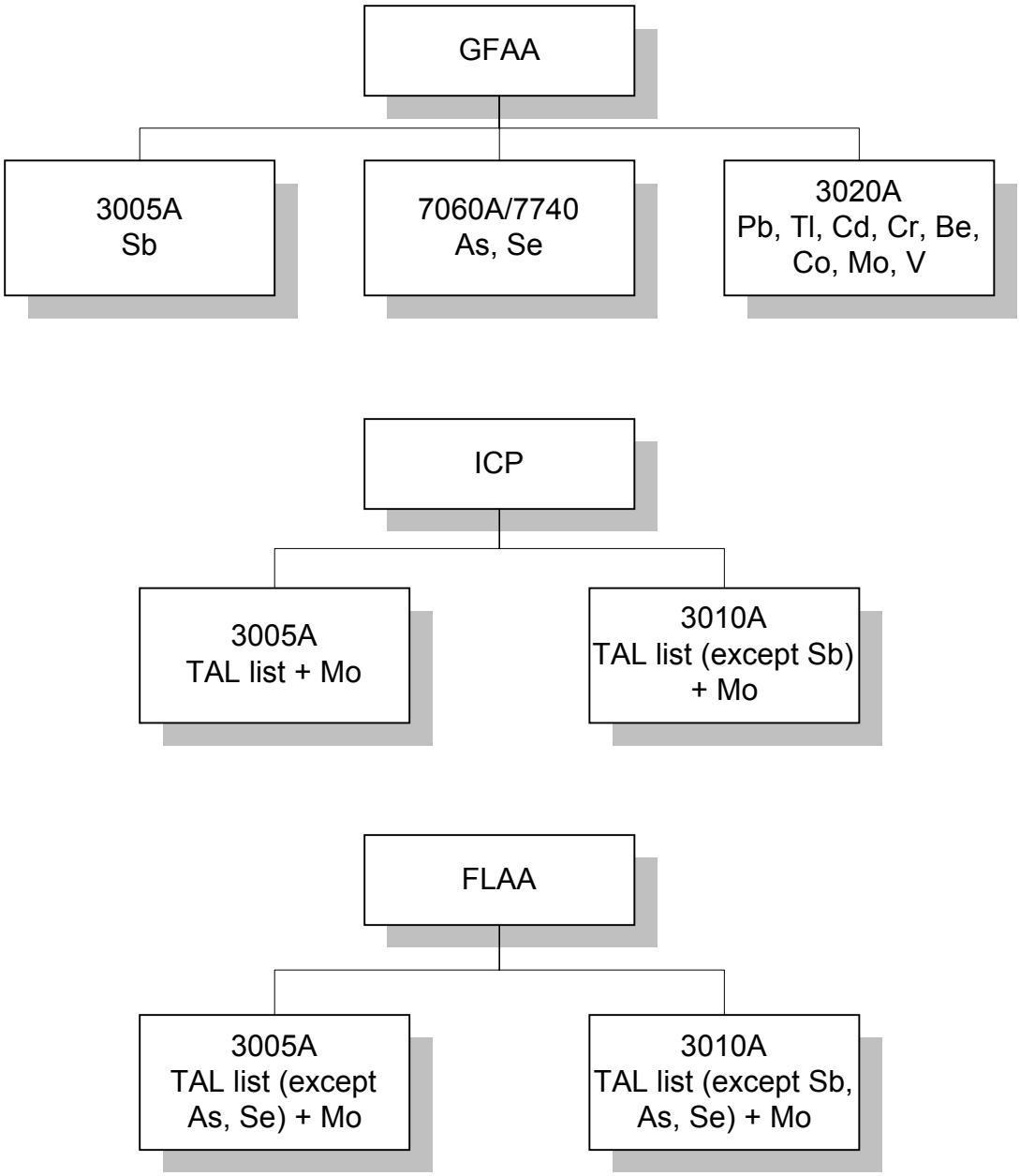
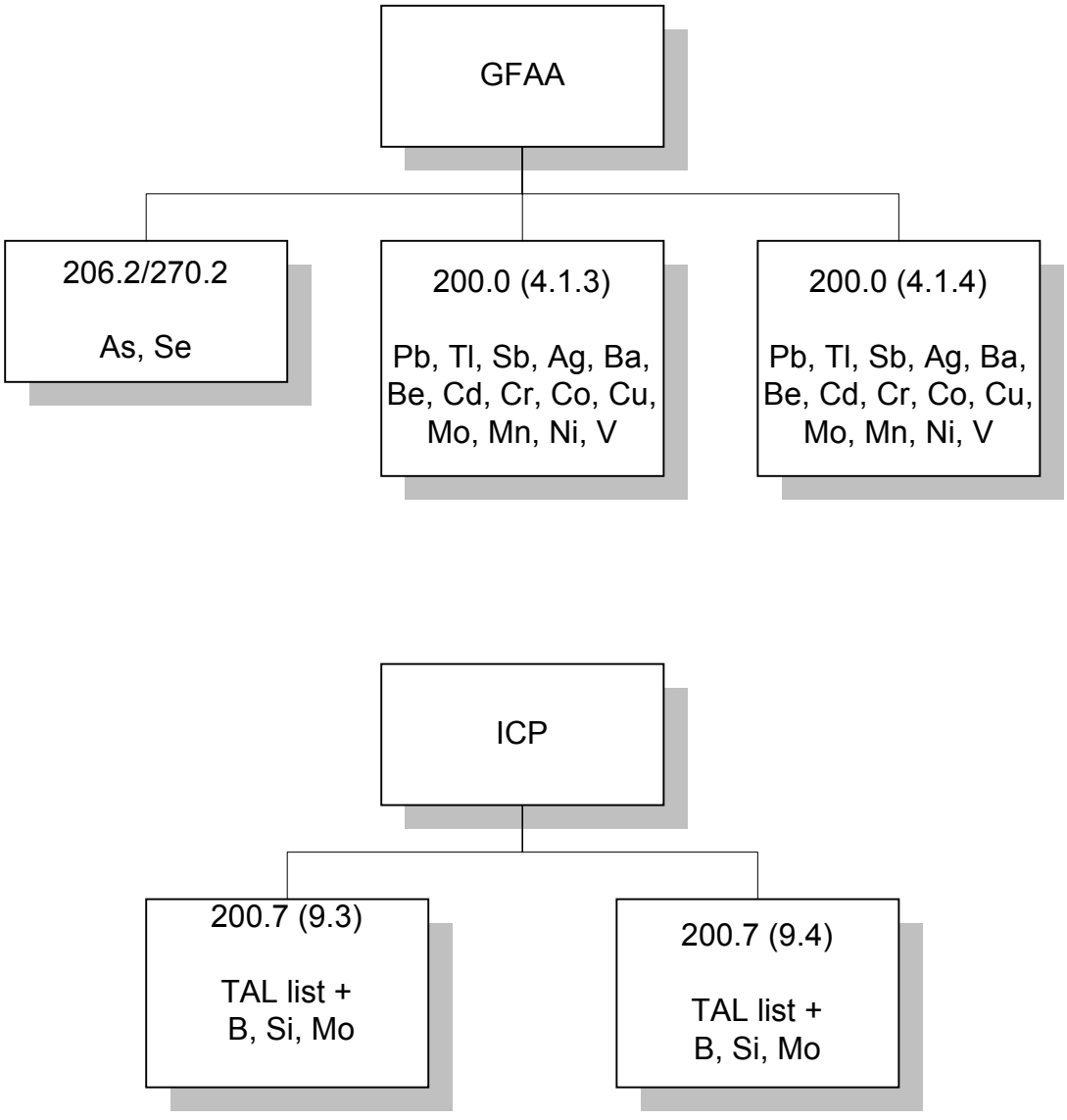


Figure 6. Overview of SW846 Aqueous Preparation Methods by Determinative Method



TAL list : Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

Figure 7. Overview of MCAWW Aqueous Preparation Methods By Determinative Technique



TAL list : Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

APPENDIX A

TABLES

TABLE I. Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010 A	3020 A	7060 A 7740
Aluminum	Al	7429-90-5	X	X		
Antimony	Sb	7440-36-0	X			
Arsenic	As	7440-38-2	X	X		X
Barium	Ba	7440-39-3	X	X		
Beryllium	Be	7440-41-7	X	X	X	
Cadmium	Cd	7440-43-9	X	X	X	
Calcium	Ca	7440-70-2	X	X		
Chromium	Cr	7440-47-3	X	X	X	
Cobalt	Co	7440-48-4	X	X	X	
Copper	Cu	7440-50-8	X	X		
Iron	Fe	7439-89-6	X	X		
Lead	Pb	7439-92-1	X	X	X	
Magnesium	Mg	7439-95-4	X	X		
Manganese	Mn	7439-96-5	X	X		
Molybdenum	Mo	7439-98-7	X	X	X	
Nickel	Ni	7440-02-0	X	X		
Potassium	K	7440-09-7	X	X		
Selenium	Se	7782-49-2	X	X		X
Silver	Ag	7440-22-4	X	X		
Sodium	Na	7440-23-5	X	X		
Thallium	Tl	7440-28-0	X	X	X	
Vanadium	V	7440-62-2	X	X	X	
Zinc	Zn	7440-66-6	X	X		

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE II. Approved Preparation Method Analytes - NPDES

ELEMENT	Symbol	CAS Number	200.7 (9.4)	200.7 (9.3)	200.0 (4.1.4)	200.0 (4.1.3)	206.2 270.2
Aluminum	Al	7429-90-5	X	X			
Antimony	Sb	7440-36-0	X	X	X	X	
Arsenic	As	7440-38-2	X	X			X
Boron	B	7440-42-8	X	X			
Barium	Ba	7440-39-3	X	X	X	X	
Beryllium	Be	7440-41-7	X	X	X	X	
Cadmium	Cd	7440-43-9	X	X	X	X	
Calcium	Ca	7440-70-2	X	X			
Chromium	Cr	7440-47-3	X	X	X	X	
Cobalt	Co	7440-48-4	X	X	X	X	
Copper	Cu	7440-50-8	X	X	X	X	
Iron	Fe	7439-89-6	X	X	X	X	
Lead	Pb	7439-92-1	X	X	X	X	
Magnesium	Mg	7439-95-4	X	X			
Manganese	Mn	7439-96-5	X	X	X	X	
Molybdenum	Mo	7439-98-7	X	X	X	X	
Nickel	Ni	7440-02-0	X	X	X	X	
Potassium	K	7440-09-7	X	X			
Selenium	Se	7782-49-2	X	X			X
Silicon	Si	7631-86-9	X	X			
Silver	Ag	7440-22-4	X	X	X	X	
Sodium	Na	7440-23-5	X	X			
Thallium	Tl	7440-28-0	X	X	X	X	
Vanadium	V	7440-62-2	X	X	X	X	
Zinc	Zn	7440-66-6	X	X			

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE III. ICP and FLAA Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/ MS Level * (ug/l)
Aluminum	200	2000
Antimony	50	500
Arsenic	200	2000
Barium	200	2000
Beryllium	5	50
Cadmium	5	50
Calcium	5000	50000
Chromium	20	200
Cobalt	50	500
Copper	25	250
Iron	100	1000
Lead	50	500
Lithium	100	1000
Magnesium	5000	50000
Manganese	50	500
Molybdenum	100	1000
Nickel	50	500
Phosphorous	1000	10000
Potassium	5000	50000
Selenium	200	2000
Silver	5	50
Sodium	5000	50000
Strontium	100	1000
Thallium	200	2000
Vanadium	50	500
Zinc	50	500
Boron	100	1000
Silica	1000	10000
Tin	200	2000
Titanium	100	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.3) to 50 mL of sample.

TABLE IV. GFAA Matrix Spike and Aqueous LCS Spike Levels

ELEMENT	Stock LCS/MS Standard (mg/L)	Working LCS/MS Standard (ug/L)	Aqueous LCS/ MS Level * (ug/l)
Arsenic	400	4000	40
Selenium	400	4000	40
Lead	400	4000	40
Thallium	400	4000	40
Antimony	400	4000	40
Cadmium	40	400	4
Chromium	100	1000	10
Silver	50	500	5

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.4) to 50 mL of sample.

TABLE V. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE VI. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze samples associated with the method blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	See Corrective Action for Matrix Spike.

APPENDIX B

STL METALS PREP BENCHSHEET

Quanterra Metals Preparation Log

Prep Date :
Analyst : __

Matrix : _____
Prep Type (circle): ICP GFAA

QC Batch:
Method #:

SOP (circle)
CORP-IP-0001 Rev 0
CORP-IP-0002 Rev 0
CORP-IP-0003 Rev 0
Other _____

SPIKE	ID	LOT #	Prep Date	Vol. Added	Custom Spike/Comments
LCS					
MS/MSD					

#	Sample ID	Initial Wt (g)/Vol(mL)	Final Wt (g)/Vol(mL)	Comments
BLK				
LCS				
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
MS				
MSD				

Analyst Signature: _____ Date: _____ Reviewed by: _____ Date:

CHAIN-OF-CUSTODY INFORMATION FOR DIGESTATES:
Relinquished By: Date: Received By: Date:

APPENDIX C

CONTAMINATION CONTROL GUIDELINES

APPENDIX C. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

Control Copy No._____
Implementation Date: 04/01/02

LABORATORY-SPECIFIC

STL STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND MCAWW 245.1

(SUPERSEDES: CORP-MT-0005, REVISION 1)

Prepared by: _____

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

TABLE OF CONTENTS

LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1. Both the water bath digestion and the autoclave digestion are available at the STL Pittsburgh facility, however the default practice is the autoclave digestion. Both are described in this SOP.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A (see CORP-MT-0007) is usually the method of choice. All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. The STL reporting limit for mercury in aqueous matrices is 0.0002 mg/L except for TCLP, SPLP or EPTOX leachates for which the reporting limit is 0.002 mg/L.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. CRA: A standard which is run a part of the initial calibration, also known as "The Reporting Level Verification Standard"

3.2. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.3. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.4. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample head space before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for

leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining a temperature of 90-95 °C) or autoclave that is able to obtain conditions of 15 lbs., 120 °C for 15 minutes.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide

accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (i.e., Gortex filter).

NOTE: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Thermometer (capable of accurate readings at 95 °C).

6.8. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3. This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.11. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.12. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.13. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS) are not included in the sample count for determining the size of a preparation batch. MS/MSD are not included in the sample count unless there are multiple sets of MS/MSD per batch. In other words, the first MS/MSD are not counted; all additional MS and MSDs are counted as samples.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit, or above 10% of either the measured concentration of that analyte in associated samples or the regulatory limit. See QA-003 for more detail on criteria and corrective actions. In addition, blank contamination should always be evaluated against project specific requirements.

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The CCV results can be reported as LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to

MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 20% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.11 and Section 11.2.12 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.11 and 11.2.12 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples.

Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.13 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up . The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥ 0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples. *An exception to this is for Method 245.1 samples. The calibration curve samples are **not** heated.*

11.1.2. Transfer 100 mL of well mixed sample or standard to a clean sample digestion bottle.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

11.1.3. Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 mixing after each addition.

Note: All spiking should be done after the initial addition of acids.

11.1.4. Add 15 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 25 mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

Note: When performing analyses using automated vs. manual techniques the sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for by the addition of the same volume of permanganate to all associated samples, standards, *and QC samples (e.g. LCS and blank)* in the run. In instances, where this is not feasible, the addition of excess reagent can be addressed through mathematical correction of the results to account for the resultant dilution effect.

be addressed through mathematical correction of the results to account for the resultant dilution effect.

11.1.5. Add 8 mL of potassium persulfate solution and heat for two hours in a water bath at 90 - 95 °C.

NOTE: Alternatively, for RCRA analyses using 7470A, samples may be digested using an autoclave for 15 minutes at 120 °C and 15 lbs.

11.1.6. Cool samples.

11.2. Sample Analysis:

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6 mL increments until the permanganate is completely reduced.

11.2.4. Manual determination:

11.2.4.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.4.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.4.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.4.4. Place the aeration device into 100 mL of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.5. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.6. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.7. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.8. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.9. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.10. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.11. The following analytical sequence must be used with 7470A and 245.1:

Instrument Calibration
ICV
ICB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7470A and 245.1.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.12. The following run sequence is consistent with 7470A, CLP and 245.1 and may be used as an alternate to the sequence in 11.2.11. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA* (Reporting Level Verification Standard)
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOPs (CORP-MT-0006) for quality control requirements for QC samples.

* Refer to the CLP SOPs for information on the CRA.

11.2.13. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.6. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R\ = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = \text{C x D}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.6. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.7. Appropriate factors must be applied to sample values if dilutions are performed.

12.8. Sample results should be reported with up to three significant figures in accordance with the STL significant figure policy.

13. METHOD PERFORMANCE

13.1. The CCV will be varied perodically to demonstrate verification of linearity of the curve.

13.2. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.3. Method performance is determined by the analysis of method blanks, laboratory control samples, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.3. The laboratory control sample should recover within 20% of the true value until in house limits are established.

13.4. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

16.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.1.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.4. QA-003, STL QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7470A and 245.1.

17.1.1.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.1.1.3. The alternate run sequence presented in Section 11.2.12 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7470A

17.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Olliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 °C and 15 lbs.).

17.1.2.3. Method 7470A does not state control criteria within the text of the method. The QC section of 7470A refers the analyst to Section 8.0 of Method 7000A, the generic atomic absorption method, which discusses flame and furnace methods. The ICV criteria stated in Method 7000A is ± 10%. This SOP requires ICV control limits of ± 20% based on the fact that the mercury ICV, unlike the ICV for the flame and furnace analytes, is digested and therefore is equivalent to a LCS. The CLP protocol 245.1 CLP-M recognizes this factor and requires control limits of ± 20%.

17.1.3. Modifications from 245.1

17.1.3.1. Method 245.1 Section 9.3 states concentrations should be reported as follows: Between 1 and 10 ug/L, one decimal; above 10 ug/L, to the nearest whole number. STL reports all Hg results under this SOP to two significant figures.

17.2. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Aqueous Sample Preparation - Mercury

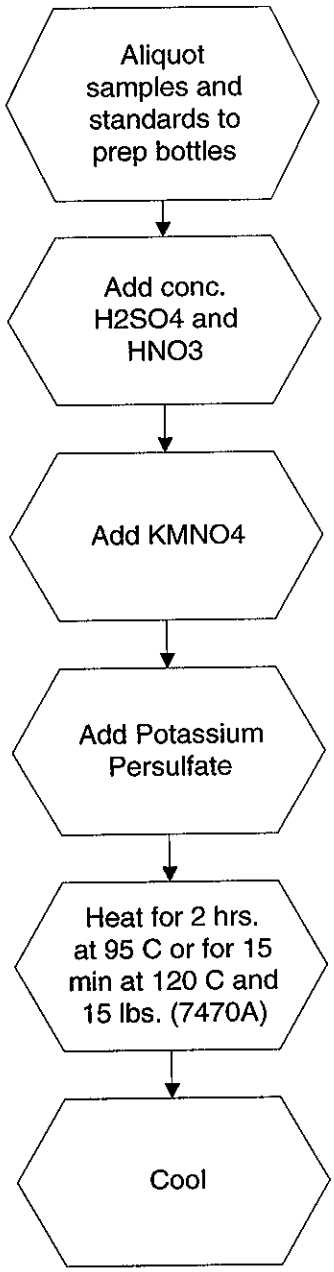
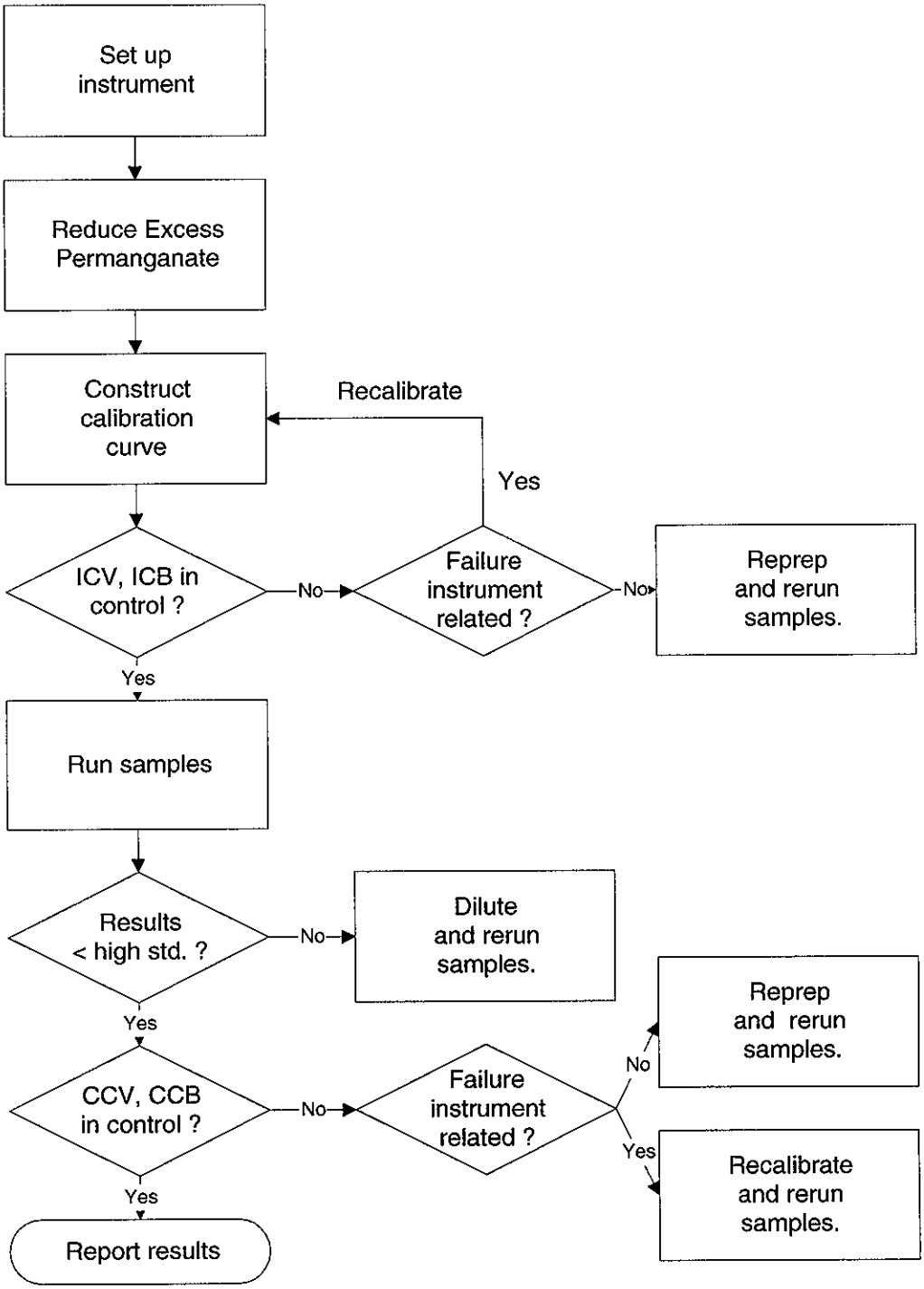


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I. MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Standard Aqueous RL	0.0002
TCLP RL	0.002
Std 0	0
Std 1	0.0002
Std 2	0.0005
Std 3	0.001
Std 4	0.002
Std 5	0.005
Std 6 **	0.010
ICV	0.001 or 0.0025 ***
LCS/CCV	0.0025 or 0.005 ***
Aqueous MS	0.001
TCLP MS	0.005

* **SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

** **Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2 ppb standard may be eliminated in favor of the 10 ppb standard.**

*** **Concentration level dependent on high calibration standard used. CCV must be 50% of high standard concentration and ICV must be 20-25% of high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

*See Sections 11.2.11 and 11.2.12 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.2.13
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B
STL Hg DATA REVIEW CHECKLIST

STL Hg Data Review Checklist

Run/Project Information

Run Date: _____ **Analyst:**_____ **Instrument:**_____
Prep Batches Run:_____

Circle Methods used: **7470A / 245.1** : CORP-MT-0005 Rev 1 **7471 / 245.5** : CORP-MT-0007 Rev 1
CLP - AQ : CORP-MT-0006 Rev 0 **CLP - SOL** : CORP-MT-0008 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ **Date:**_____
Comments:

_____

_____

2nd Level Reviewer : _____ **Date:**_____

_____

_____

APPENDIX C

MSA GUIDANCE

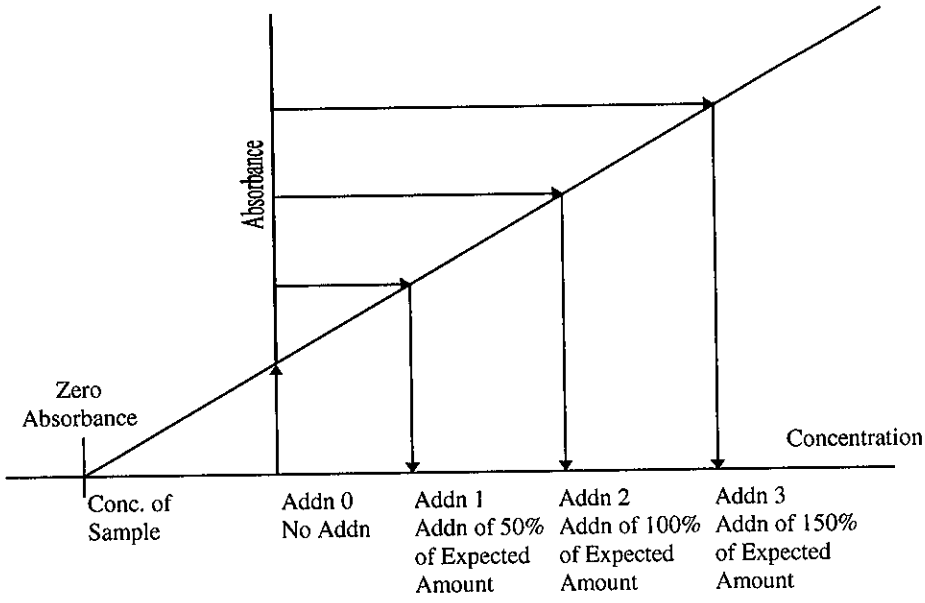
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D. TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on "Continuous"
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200) [1]

Daily	Semi-annually	Annually
Clean lens.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing.		
Check drain.		
Replace drying tube.		

Cold Vapor Atomic Absorption (PE 5000) [1]

Daily	Monthly
Clean aspirator by flushing with DI water.	Clean cell in aqua regia.
Check tubing and replace if needed.	Clean aspirator in aqua regia.
Clean windows with methanol.	
Change silica gel in drying tube.	
Check argon gas supply.	
Adjust lamp.	

APPENDIX 27

Controlled Copy
Copy No._____

SOP No.CORP-WC-0004
Revision No. 0
Revision Date: 1/1/97

STANDARD OPERATING PROCEDURE

TITLE: IGNITABILITY OF SOLIDS FOR WASTE CHARACTERIZATION EPA SW-846 CHAPTER 7, SECTION 7.1

(SUPERSEDES: NONE)

Prepared by: _____ 1/3/97
David Dawes and Richard Burrows

Reviewed by: _____ 1/3/97
Director, Technology

Approved by: _____
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Approved by: _____
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Management

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of ignitability of solids as it pertains to waste characterization outlined in Chapter 7 of EPA SW846. It is used to identify wastes that are fire hazards under routine storage conditions or which are capable of "severely exacerbating" a fire that is already burning.

1.2. There is no instrument or method detection limit applicable to this test. Results are reported qualitatively as either "Yes" or "No" depending on the ignitability of the sample.

1.3. Applicable Matrices: Solids, including domestic and industrial wastes, sludges, and petroleum wastes.

1.4. The analytical time depends on the matrix and method of analysis. For solids, the analytical time is approximately 5 minutes.

2. SUMMARY OF METHOD

2.1. Solids are analyzed by exposure to open flame for a set length of time after which the flame is removed and the sample observed to determine its ignitability characteristic. If the material will burn, a subsequent set of tests determine ignitability according to the definitions in Chapter 7 of SW-846.

3. DEFINITIONS

3.1. Ignitability: The capability of a solid sample, under standard conditions of temperature and pressure, to cause fire through friction, moisture absorption, or spontaneous chemical changes and, when ignited, to burn so vigorously and persistently as to create a hazard.

4. INTERFERENCES

4.1. Improper storage of samples may cause loss of volatiles and lead to erroneous results.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. Because of the unknown reactivity of the materials being tested, the operator will wear a face shield in addition to safety glasses. As an alternative, the sash of the hood will be pulled down to shield the operators face.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. In order to stabilize conditions during the actual test, the fume hood when the test is being conducted may be turned off.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor and/or the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Ceramic crucibles, nominal 50 mL capacity.

6.2. Source of open flame: "barbecue" butane lighter, or equivalent. NOTE: a butane cigarette lighter, short wooden matches, or a high temperature propane torch are not acceptable alternatives.

7. REAGENTS AND STANDARDS

7.1. There are no reagents and standards required for this method.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are to be collected in glass bottles or jars with a minimum of headspace and refrigerated to 4 ± 2°C.

8.2. There is no specified holding time for ignitability .

9. QUALITY CONTROL

9.1. The Quanterra QA Management Plan document provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

9.2. Sample/Sample Duplicate (SA/DU) - One Sample/Sample Duplicate pair must be processed for each QC batch per matrix, or every 20 client samples, whichever is more frequent.

9.2.1. The results of the SA/DU pair are used to determine analytical variability.

9.2.2. The SA/DU pair is evaluated qualitatively. If both the sample and its duplicate are found to be either both ignitable (YES/YES) or both not ignitable (NO/NO), the QC is considered in control.

9.2.3. The SA/DU QC is out of control if the two results are different (YES/NO). In this case, the data must be qualified appropriately (e.g. sample heterogeneity) and an explanation provided in the report narrative.

9.2.4. There are no other QC analyses applicable to this test.

10. CALIBRATION AND STANDARDIZATION

10.1. This method has no calibration or standardization requirements.

11. PROCEDURE

11.1. Any significant variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. In a fume hood, place a small quantity of sample (approx 1 gram) into the ceramic crucible. It is not necessary to weigh the sample, but a small quantity should be used to minimize any potential hazards.

11.3. Wear a face shield in addition to safety glasses, or pull the hood sash down to act as a shield. Turn off the hood (if necessary to maintain a stable flame), touch the ignition source (see section 6.2) to the sample. Keep the flame in contact with the sample for 5 ± 2 seconds.

11.4. Remove the ignition source and observe the sample.

11.5. Turn the fume hood back on. (if previously turned off).

11.6. Observations can be reduced to three broad categories:

Reaction of Sample	Classification
Sample does **not** ignite	Not ignitable, no further testing necessary
Sample ignites but burns only in contact with flame	Not ignitable, no further testing necessary
Sample ignites and burns continuously	Proceed to section 11.6.1

11.6.1. Wear a face shield in addition to safety glasses, or pull the hood sash down to act as a shield for the following steps. Place approximately 5g of solid into a crucible and stir for 10 seconds. If the sample ignites and burns continuously, then it is classified as ignitable. If not, proceed to section 11.6.2

11.6.2. Add 5 mL of water to the sample in the crucible. If the sample ignites and burns continuously, then it is classified as ignitable. If not, proceed to section 11.6.3.

11.6.3. Add approximately 5g of solid to a crucible. Heat the crucible from underneath with a burner for 30 seconds. If the sample ignites and burns continuously, then it is classified as ignitable. If not, the sample is classified as not ignitable.

12. DATA ANALYSIS AND REPORTING

12.1. If the result is "Ignitable", report as "Yes".

12.2. Samples which do not meet the "Ignitability" criteria should be reported as "No."

13. METHOD PERFORMANCE

13.1. Training Qualifications: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. Sample volumes have been reduced (maintaining proper ratios) in order to minimize laboratory waste.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The facility Environmental Health and Safety Coordinator should be contacted if additional information is required.

15.2. Dispose of samples in accordance with Quanterra waste disposal policies.

16. REFERENCES

16.1. Source Methods

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA SW846, 3rd edition, Chapter 7, "Ignitability", revision 2, September 1994.

APPENDIX 28

Section 4: 1613 Data Analysis & Reporting

Paradigm Analytical Labs - Standard Operating Procedure

Last Revised By:	Asst. Lab Director:	QA Officer:
W.M. Larkins	C.K. Cornwell	Greg Dickinson

Purpose

To describe the processes used in operating the HRGC/HRMS system, as well as the procedures followed in the generation, interpretation and review of laboratory data for Method 1613.

Summary

This SOP details how to analyze and report samples by EPA Method 1613. HRGC/HRMS is used to detect and quantitate PCDD/Fs. Samples arrive at the MS lab having been extracted and fractionated using procedures in Section 3. Analyses are grouped into 12-hour sequences that include analyses of samples and standards mixtures. Upon completion of the sequence, the analyst reviews the data associated with both standards and samples in order to confirm the validity of the sequence and to determine any potential need for re-analysis or re-extraction. The analyst generates quantitation reports and chromatograms using sophisticated software. These reports are used to generate forms that summarize the results of the analysis.

4.1 Operation of HRGC/HRMS

4.1.1 Equipment

- HP6890 GC, Micromass Autospec Ultima high resolution mass spectrometer, vortex mixer, 10-100 uL pipette

4.1.2 Procedure

- Recall the GC temperature/pressure/flow program.
- Recall the MS experiment (see Table 1).
- Perform any necessary maintenance.
- Tune the MS resolution to 100 ppm at 5% height.
- Acquire location data to calibrate the MS and print a copy of function one MS resolution.
- Inject the window defining/GC resolution/continuing calibration mix (RETCON). Evaluate descriptor-switching times for accuracy. If any window defining peaks have shifted outside the descriptor windows, adjust the switching times before injecting any samples. This injection is also used to verify that there is less than or equal to 25% peak to valley for the two close eluters of 2,3,7,8-TCDD. Print a copy of the GC resolution check. If the valleys are within specifications, proceed to calibrate or verify a previous calibration. If not, further investigation and/or maintenance may be required. Re-inject this solution after maintenance to check for improvement.
- Now that the GC/MS resolution and descriptor switching times have been verified, a series of five initial calibration standards may be injected and reviewed for method requirements. If an initial calibration already exists, a RETCON may be analyzed to verify continuing calibration. If the curve or the RETCON passes method requirements, sample analysis may begin.
- Reconstitution of a sample is accomplished by adding nonane containing the injection standards, capping the vial, and mixing well with a vortex mixer.
- Samples are injected under conditions identical to those used to establish calibration.
- A “back-end” print out of the MS resolution must be performed.
- The calibration data from a sequence is filed in a folder cabinet under the day it was analyzed and includes the all GC/MS resolution checks, window verification, valley verification, front end Retcons, run logs and window defining mix (WDM) retention time sheets.
- Each sample hardcopy should include the quant report, totals pages, deviations, chromatograms, and report forms.
- Columns: DB-225, 30 m, id 0.25 mm, 0.25 μm; DB-5MS, 60 m, id 0.25 mm, 0.25 μm.

Table 1: Mass Descriptors used for Selected Ion Recording HRMS

Function (#)	Channel (#)	Mass (amu)	Dwell Time (ms)	I.C. Delay (ms)
1	1	303.9016	100	20
1	2	305.8987	100	10
1	3	315.9419	40	10
1	4	316.9824	20	10
1	5	316.9824	(Lock)	50
1	6	317.9389	40	10
1	7	319.8965	100	10
1	8	321.8936	100	10
1	9	327.8847	40	10
1	10	331.9368	40	10
1	11	333.9339	40	10
1	12	375.8364	30	20
2	1	339.8597	100	20
2	2	341.8568	100	10
2	3	351.9000	40	10
2	4	353.8970	40	10
2	5	355.8546	100	10
2	6	357.8517	100	10
2	7	366.9792	20	10
2	8	366.9792	(Lock)	50
2	9	367.8949	40	10
2	10	369.8919	40	10
2	11	409.7974	30	20
3	1	373.8207	100	20
3	2	375.8178	100	10
3	3	380.9760	20	10
3	4	380.9760	(Lock)	50
3	5	383.8639	40	10
3	6	385.8610	40	10
3	7	389.8156	100	10
3	8	391.8127	100	10
3	9	401.8559	40	10
3	10	403.8530	40	10
3	11	445.7555	30	20
4	1	407.7818	100	20
4	2	409.7788	100	10
4	3	417.8253	40	10
4	4	419.8220	40	10
4	5	423.7767	100	10
4	6	425.7737	100	10
4	7	430.9728	20	10
4	8	430.9728	(Lock)	50
4	9	435.8169	40	10
4	10	437.8140	40	10
4	11	479.7165	30	20
5	1	441.7427	100	20
5	2	443.7398	100	10
5	3	454.9728	20	10
5	4	454.9728	(Lock)	50
5	5	457.7377	100	10
5	6	459.7348	100	10
5	7	469.7780	40	10
5	8	471.7750	40	10
5	9	513.6775	30	20

4.2 Data Generation, Interpretation and Review

Paradigm Analytical Labs defines a batch of samples as no more than 20 samples processed within a 12-hour shift. One LMB and one OPR are processed per analytical batch, following the same procedures as the field samples. Generally, soil is replaced by salt (Na_2SO_4), effluent by deionized water and biological tissues by vegetable oil. An invalid LMB or OPR requires a re-extraction of the affected samples.

4.2.1 Quality Assurance/Quality control

On an annual schedule, the laboratory shall perform Method Detection Limit studies (MDLs) for each matrix analyzed. Additionally, the laboratory shall perform and MDL study for each extraction method utilized per matrix. All MDL studies will be conducted following the guidelines set forth in 40 CFR, Part 136, appendix B and must be lower than one-third the regulatory compliance level or one third the Minimum Levels (ML) set forth in Table 2 of the reference method.

4.2.2 Initial Calibrations

The percent relative standard deviations for the mean response factors from the seventeen unlabeled standards must not exceed +/- 20%. The percent relative standard deviations from the labeled standards (i. e. extraction standards, cleanup standards and sampling standards) must not exceed +/- 35%. The signal to noise ratio for all signals present must be ≥ 10. The ion abundance ratios must be within specified control limits (see Table 2). Paradigm uses the concentrations in Table 3 to construct the initial calibration.

Table 2. Theoretical Ion Abundance Ratios and Their Control Limits

Level of Chlorination	Theoretical Ratio	Control Limits	
		Lower	Upper
4	0.77	0.65	0.89
5	1.55	1.32	1.78
6	1.24	1.05	1.43
6[a]	0.51	0.43	0.59
7	1.04	0.88	1.20
7[b]	0.44	0.37	0.51
8	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF
[b] Used only for ^{13}C-HpCDF

A new initial calibration is required when the continuing calibration criteria below are not met. Routine maintenance may be performed to correct any failures. Any major maintenance to the analytical system such as slit cleaning, analyzer lens cleaning, magnet shifts, and detector disk changes warrant a new ICAL. At a minimum, a new initial calibration must be performed annually.

Table 3. Initial Calibration Concentrations

Analyte	CS-1	CS-2	CS-3	CS-4	CS-5
	Concentration (pg/µL)				
Unlabeled					
2378-TCDD	0.25	2	10	40	200
2378-TCDF	0.25	2	10	40	200
12378-PeCDD	1.25	10	50	200	1000
12378-PeCDF	1.25	10	50	200	1000
23478-PeCDF	1.25	10	50	200	1000
123478-HxCDD	1.25	10	50	200	1000
123678-HxCDD	1.25	10	50	200	1000
123789-HxCDD	1.25	10	50	200	1000
123478-HxCDF	1.25	10	50	200	1000
123678-HxCDF	1.25	10	50	200	1000
123789-HxCDF	1.25	10	50	200	1000
234678-HxCDF	1.25	10	50	200	1000
1234678-HpCDD	1.25	10	50	200	1000
1234678-HpCDF	1.25	10	50	200	1000
1234789-HpCDF	1.25	10	50	200	1000
OCDD	2.5	20	100	400	2000
OCDF	2.5	20	100	400	2000
Extraction Standards					
^{13}C-2378-TCDD	100	100	100	100	100
^{13}C-2378-TCDF	100	100	100	100	100
^{13}C-12378-PeCDD	100	100	100	100	100
^{13}C-12378-PeCDF	100	100	100	100	100
^{13}C-23478-PeCDF	100	100	100	100	100
^{13}C-123678-HxCDD	100	100	100	100	100
^{13}C-123478-HxCDD	100	100	100	100	100
^{13}C-123478-HxCDF	100	100	100	100	100
^{13}C-123478-HxCDF	100	100	100	100	100
^{13}C-1234678-HpCDD	100	100	100	100	100
^{13}C-1234678-HpCDF	100	100	100	100	100
^{13}C-1234789-HpCDF	100	100	100	100	100
^{13}C-OCDD	200	200	200	200	200
Cleanup Standards					
^{37}Cl-2378-TCDD	0.25	2	10	40	200
Injection Standards					
^{13}C-1234-TCDD	100	100	100	100	100
^{13}C-123789-HxCDD	100	100	100	100	100

4.2.3 Continuing Calibrations

Check that all paperwork is present. A CCal package should contain the documentation listed below.

- Pass: Run log. HRMS Resolution Checks. WDM retention time sheet. WDM chromatograms. GC performance for 2,3,7,8-TCDD. CCal quantitation page. CCal chromatograms. Injection preparation log.
- Fail: The analyst listed on the run log can provide any missing paperwork.

Review the Run log.

- Pass: Check that the 12 hour windows have not been exceeded between the front end Ccal and the last sample of the sequence.
- Fail: Re-analysis of affected samples.

Review the HRMS Resolution checks.

- Pass: Verify 100ppm width at 5% height for PFK mass 318 or higher. Compare the resolution check times to those on the run log to be sure they bracket each sequence.
- Fail: Back end resolution checks do not have to meet the front end requirements. Should one fail, an assessment should be made to determine any data quality impact.

Review the Window Defining Mix and GC Performance Documentation.

- Pass: Check that the sample numbers on the WDM sheets match those on the run log. Check that the retention times are correct for the WDM chromatograms.
- Check that the valley between 2,3,7,8-TCDD and its close eluters does not exceed 25%.
- Fail: Any missing peaks in the window-defining sample should be re-identified with a survey scan. Determine proper switching times. These must be entered into the HRMS ion function descriptors before analysis may resume. If the GC performance valley is greater than 25% instrument maintenance may be required. When a valley fails all samples must be reinjected.

Review the CCal Quantitation and Chromatograms.

- Pass: Check that all ion ratios are in specification. Verify that all compounds are within the concentration limits set by the method (see Table 4) for all front end CCals
- Fail: Routine instrument maintenance such as installing new injection port hardware, inner source cleaning, retuning, column clipping etc. will usually correct a calibration failure. If these measures do not work, a new ICal is needed.

Compound Name	CCAL (pg/µL)	Limits (pg/µL)	Compound Name	CCAL (pg/µL)	Limits (pg/µL)
2,3,7,8-TCDD	10	7.8 - 12.9	$^{13}C_{12}$-2,3,7,8-TCDD	100	82 - 121
1,2,3,7,8-PeCDD	50	39 - 65	$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62 - 160
1,2,3,4,7,8-HxCDD	50	39 - 64	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	85 - 117
1,2,3,6,7,8-HxCDD	50	39 - 64	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85 - 118
1,2,3,7,8,9-HxCDD	50	41 - 61	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72 - 138
1,2,3,4,6,7,8-HpCDD	50	43 - 58	$^{13}C_{12}$-OCDD	200	96 - 415
OCDD	100	79 - 126	$^{13}C_{12}$-2,3,7,8-TCDF	100	71 - 140
2,3,7,8-TCDF	10	8.4 - 12	$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76 - 130
1,2,3,7,8-PeCDF	50	41 - 60	$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77 - 130
2,3,4,7,8-PeCDF	50	41 - 61	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76 - 131
1,2,3,4,7,8-HxCDF	50	45 - 56	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70 - 143
1,2,3,6,7,8-HxCDF	50	44 - 57	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	74 - 135
2,3,4,6,7,8-HxCDF	50	45 - 56	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	73 - 137
1,2,3,7,8,9-HxCDF	50	44 - 57	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78 - 129
1,2,3,4,6,7,8-HpCDF	50	45 - 55	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77 - 129
1,2,3,4,7,8,9-HpCDF	50	43 - 58	$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9 - 12.7
OCDF	100	63 - 159			

Table 4. Continuing Calibration Limits

Review the Injection Prep log sheet.

- Pass: Check that all samples have been spiked with 2 ng injection standard. Verify that final volume is 20 uL. Be sure that any dilutions or other comments are noted.
- Fail: Calculations of sample concentrations should reflect any deviations from normal injection prep parameters.

4.2.4 Quality Control Work Groups

The following elements should be present in a complete work group file:

- LMB topsheets
- LMB totals sheets
- LMB chromatograms (11 pages)

- OPR topsheets
- OPR chromatograms
- Extraction log sheet
- Cleanup log sheet
- ASE/Cleanup observation forms
- Dry weight sheet (where applicable)
- Any additional information (ex. re-extract request sheet)

The following procedure should be used for reviewing a work group:

- Review the header information on the LMB topsheets. Verify that the method and client sample ID (LMB or OPR) are correct.
- Review the footer information on the LMB and OPR topsheets. Verify that the following information is correct: Paradigm sample ID or OPR project number, extraction date, analysis date, method, matrix, sample weight/volume, percent solids/lipids, pH, work group number, sample datafile, retcheck datafile, beginning cal datafile and ICal datafile.
- Verify that no target analytes or EMPCs are present in the LMB above Method 23's Minimum Levels. If target analytes or EDL's are above this limit, the associated samples must have concentrations that exceed 10 times the LMB concentration for the specified analyte. Otherwise, samples must be re-extracted.
- Review the totals data for the LMB. Be sure that any ghosting peaks are removed from the totals concentrations and the associated detection limits are elevated to reflect the subtracted peaks.
- Verify that extraction and cleanup standard recoveries are within method specifications (see Table 5) for the LMB and OPR. These recoveries are found on the topsheets. Validate any failures based upon signal to noise and acceptable detection limits. If the lab validation fails a corrective action is required. Corrective actions may include re-extraction, re-cleanup, lower sample volume, extract dilution, etc.
- Verify that the recoveries in the OPR meet Paradigm's recovery limits, found in Table 6.

Compound Name	Amount Spiked (pg/µL)	Limits %
$^{13}C_{12}$-2,3,7,8-TCDD	100	25 - 164
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25 - 181
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32 - 141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28 - 130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23 - 140
$^{13}C_{12}$-OCDD	200	17 - 157
$^{13}C_{12}$-2,3,7,8-TCDF	100	24 - 169
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24 - 185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21 - 178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26 - 152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26 - 123
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	29 - 147
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	28 - 136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28 - 143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26 - 138
$^{37}Cl_4$-2,3,7,8-TCDD	10	35 - 197

Table 5. Labeled Standard Recovery Limits

Analyte	Amount Spiked (pg/µL)	Limit (pg/µL)
2378-TCDD	10	6.7-15.8
12378-PeCDD	50	35-71
123478-HxCDD	50	35-82
123678-HxCDD	50	38-67
123789-HxCDD	50	32-81
1234678-HpCDD	50	35-70
OCDD	100	78-144
2378-TCDF	10	7.5-15.8
12378-PeCDF	50	40-67
23478-PeCDF	50	34-80
123478-HxCDF	50	36-67
123678-HxCDF	50	42-65
123789-HxCDF	50	39-65
234678-HxCDF	50	35-78
1234678-HpCDF	50	41-61
1234789-HpCDF	50	39-69
OCDF	100	63-170
^{13}C-2378-TCDD	100	20-175
^{13}C-12378-PeCDD	100	21-227
^{13}C-123478-HxCDD	100	21-193
^{13}C-123678-HxCDD	100	25-163
^{13}C-1234678-HpCDD	100	26-166
^{13}C-OCDD	200	26-397
^{13}C-2378-TCDF	100	22-152
^{13}C-12378-PeCDF	100	21-192
^{13}C-23478-PeCDF	100	13-328
^{13}C-123478-HxCDF	100	19-202
^{13}C-123678-HxCDF	100	21-159
^{13}C-123789-HxCDF	100	17-205
^{13}C-234678-HxCDF	100	22-176
^{13}C-1234678-HpCDF	100	21-158
^{13}C-1234789-HpCDF	100	20-186
^{37}Cl-2378-TCDD	10	3.1-19.1

Table 6. OPR Recovery Limits

4.3 Data Review

4.3.1 Procedure

- Complete Data Review Checklist (Section 4, Appendix A)

4.3.2 Calculations

4.3.2.1 Target compound calculation

- $$\text{PCDD/PCDF (ppt)} = \frac{\text{(Sum Ion Abun. of analyte)(ES Amount)}}{\text{(Sum Ion Abun. of Int. Std)(RRF from ICal)(Amt. of Sample)}}$$

- EMPC (ppt) = $\frac{\text{(Sum Ion Abun. of analyte)(ES Amount)}}{\text{(Sum Ion Abun. of Int. Std)(RRF from ICal)(Amt. of Sample)}}$

- EDL = $\frac{\text{2.5 (Height of Noise)(Std. Amount)}}{\text{(Height of Noise from Int. STD.)(RF from ICal)(Amt. of Sample)}}$

The instrumentation software calculates the noise level. However, manual noise determination may be employed at the reviewer's discretion in order to more accurately report peaks of interest.

4.3.2.2 Extraction Standard Recovery Calculation

- % Recovery = $\frac{\text{(Sum Ion Abun. of ES)(JS Amount)}}{\text{(Sum Ion Abun. of JS)(ES RRF from ICal)(ES Amount)}}$

The clean-up standard recoveries are calculated as above, substituting the ion abundances from the individual clean-up standard for the extraction standard

4.3.3 Requests for Re-extraction

Review all supporting data, including spike profiles, extraction logs, clean-up logs, injection prep logs, observation forms, and the sample tracking forms in the folder. The project or work group folder may contain exceptions or changes to routine spiking procedures.

Check the sample for problems relating to analysis. These problems include response factors that may introduce quantitative errors, interference that could be diluted out, or any interference that causes de-tuning or chromatographic conditions that could lead to quantitative errors.

The Laboratory Supervisor or Director should be consulted when re-extraction is considered.

If re-extraction is necessary, complete the Re-Extraction Form, which indicates the sample id, re-extraction due date, and reason for re-extraction (ref. form DC18).

When the GC/MS analyst receives the form, the samples are marked "REX" in the LIMS. The Sample ID will receive an "R" suffix. If a sample requires a second or third re-extraction, the sample id suffix will change to S, then T, and so on. The sample id with the suffix is used in all paperwork. (extraction, clean-up, injection prep, and run logs).

4.4 Reference Method

"Guidelines Establishing Test Procedures for the Analysis of Pollutants; EPA Method 1613," *Federal Register*, Vol. 62(178): 48393-48442, September 15, 1997; *Final Rule*.

APPENDIX 29

STL STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF SOILS, SW846 METHOD 3050B

(SUPERSEDES: REVISION 1)

Prepared by: Kurt Ill and Richard Burrows

Reviewed by: _____
Technical Specialist

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

Proprietary Information Statement:

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of soil samples for the analysis of certain metals by Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption (FLAA) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) as specified in SW846 Method 3050B.

1.2. Samples prepared by the protocols detailed in this SOP may be analyzed by ICP, ICP/MS, FLAA or GFAA for the elements listed in Table I (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This method is not a total digestion, but will dissolve almost all metals that could become "environmentally available". By design, metals bound in silicate structures are not dissolved by this procedure as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes and sediments.

2. SUMMARY OF METHOD

A representative 1 gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP, FLAA or antimony by GFAA analysis. The digestates are then filtered and diluted to 100 mL/100 g.

3. DEFINITIONS

Additional definitions of terms used in this SOP may be found in the glossary of the QAMP.

3.1. Total Metals: The concentration determined on an unfiltered sample following digestion. Note that this method is designed to determine the total *environmentally available* metals.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix D for additional contamination control guidelines.

4.3. Boron and silica from the glassware will grow into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals . If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric media.

4.7. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. All heating of samples must be carried out in a fume hood.

5.4. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.11. Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block , steam bath or other heating source capable of maintaining a temperature of 90-95°C.

6.2. Thermometer that covers a temperature range of 0-200°C.

6.3. Griffin beakers of assorted sizes or equivalent.

6.4. Vapor recovery device (Watch glasses, ribbed or other device).

6.5. Whatman No. 41 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 100 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repipetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipet tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic bottles.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs..

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: The ICP LCS/MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS/MS spike solution by diluting the custom stock solution (7.2) 100x. The working spike solution must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working GFAA LCS/MS solution must be made fresh every three months.

7.5. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.6. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables II and III (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA LCS and matrix spike preparations.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.8. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.11. 30% Hydrogen peroxide (H_2O_2), reagent grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Soil samples do not require preservation but must be stored at 4 °C ± 2 °C until the time of analysis.

9. QUALITY CONTROL

Table IV (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using Method 3050B the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDL's must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in STL QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study- This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001, CORP-MT-0003).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.4.1. Soil method blanks are prepared by taking 1 mL or 1 g of reagent water through the procedure described in Section 11.10.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Tables II and III provide the details regarding the stock, working standards and final spike concentrations for ICP and GFAA. Refer to Section 7.3 or 7.4 for instructions on preparation of the aqueous LCS.

9.5.1. The LCS is prepared by spiking a 1 mL or 1 g aliquot of reagent water with 1 mL of the working LCS/MS spike solution (7.3 or 7.4). The LCS is then processed as described in either Section 11.10.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for

the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred. Tables II and III provide the details regarding the stock, working standards and final matrix spike concentrations for ICP and GFAA. Refer to Sections 7.3 and 7.4 for instructions on preparation of the working matrix spike solutions.

9.6.1. The soil matrix spike sample is prepared by spiking a 1 g aliquot of a sample with 1 mL of the working LCS/MS spike solution (7.3 or 7.4). The matrix spike sample is then processed as described in either Section 11.10.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Hotplate or block temperature must be verified daily for each unit used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate. For block digestors, use a tube containing water.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. All preparation procedures must be carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with

the proper sample. The use of automatic label printing programs is recommended to reduce transcription errors (Quantims option).

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project administrator for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. In most cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be weighed out and processed at the same time.

11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.10. Preparation of Soils, Sediments and Sludges for Analysis by GFAA, ICP, ICP/MS and FLAA.

11.10.1. Mix sample thoroughly by stirring with a clean plastic or wooden spoon or spatula.

11.10.2. For each digestion procedure required (i.e., ICP or GFAA), weigh a 1.0 portion of solid and record the exact weight to the nearest 0.01 g. A 2 g sample size may also be used if needed to meet the reporting limits.

11.10.3. Measure additional aliquots of the designated samples for the MS and MSD analyses.

11.10.4. Spike each of the MS and MSD aliquots with 1 mL of the working LCS/MS spiking solution (7.3 or 7.4).

11.10.5. Measure 1 mL of reagent water into a beaker for the method blank.

11.10.6. Measure 1 mL of reagent water into a beaker for the LCS. Spike the LCS aliquot with 1 mL of the working LCS/MS spiking solution (7.3 or 7.4).

11.10.7. Add 10 mL of 1:1 HNO_3 and mix the sample.

11.10.8. Heat sample to 95°C and reflux for 10 minutes without boiling, using a vapor recovery device.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be reprepared.

11.10.9. Allow sample to cool.

11.10.10. Add 5 mL of concentrated HNO_3 and replace vapor recovery device.

11.10.11. Reflux at 95°C for 30 minutes.(Add reagent water as needed to ensure that the volume of solution is not reduced to less than 5 mL.)

11.10.12. If brown fumes are observed, repeat step 11.10.10 until no more fumes are evolved.

11.10.13. Using a vapor recovery device, allow the sample to evaporate to 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry. Alternatively heat at 95^{o}C for 2 hours.

11.10.14. Allow the samples to cool.

11.10.15. Add 2 mL of reagent water and 3 mL of 30 % H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.10.16. Replace the vapor recovery device and heat sample until effervescence subsides.

11.10.17. Allow the sample to cool.

11.10.18. Continue adding 30% H_2O_2 in 1 mL aliquots with warming until effervescence is minimal or sample appearance is unchanged.

Note: Do not add more than a total of 10 mL of 30 % H_2O_2.

11.10.19. Continue heating at 95^{o}C until the volume is reduced to approximately 5 mL. Alternatively the sample may be heated for 2 hours.

11.10.20. If the sample is being prepared for ICP or FLAA analyses add 10 mL of concentrated HCl and reflux for an additional 15 minutes without boiling. This step is omitted for analysis by ICP-MS and GFAA

Note: Antimony and silver have poor solubility in dilute nitric acid solution. Therefore it is strongly recommended that these elements are determined by the ICP procedure that includes HCl as the final digestion acid.

11.10.21. Allow the sample to cool.

11.10.22. Wash down beaker walls and vapor recovery device with reagent water.

11.10.23. Filter sample through Whatman 41 filter paper or equivalent into a graduated cylinder or pre-weighed bottle. Other measuring bottles (for example, Corning Snap Seals™) may be used if their accuracy is documented and is better than $\pm$ 2%. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material

11.10.24. Dilute sample to 100 mL or 100g with reagent water. The sample is now ready for analysis.

Note: This SOP allows for samples to be weighed instead of measured volumetrically. This assumes the density of the diluted sample is close to 1.0 g/mL (See Section 17.1.2).

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in the determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial

demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

15.2. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996. Method 3050B.

16.2. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010B and Method 200.7.

16.3. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.4. QA-003, STL QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants, as defined in the determinative SOPs, are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.2. This SOP allows for aqueous samples to be weighed instead of measured volumetrically. This assumes the density of the sample is close to 1.0 g/mL. Samples with large amounts of sediment or suspended solids, sludges, non-aqueous liquids must be processed volumetrically. Weighing samples directly into the digestion vessel minimizes the potential for cross contamination, offers improved accuracy over the use of graduated cylinders (comparable to volumetric flask accuracy), uses less glassware and is more efficient.

17.2. Modifications from previous SOP

17.2.1. ICP/MS has been added as an appropriate determinative technique.

17.2.2. The table listing appropriate elements has been removed. Any elements meeting the requirements in section 13 may be determined.

17.2.3. Directions for digestion for set time periods rather than reduction to set volumes have been added.

17.2.4. The order of two steps in the digestion has been changed. (See section 11.10.20)

17.2.5. Definition of the method as determining total environmentally available metals has been added.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be

attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst name, matrix, prep type (ICP or GFAA), SOP reference.
- Sample ID, initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.
- Reviewer's Signature and date.

Figure 1. **Soil Sample Preparation (Section 11.10)**

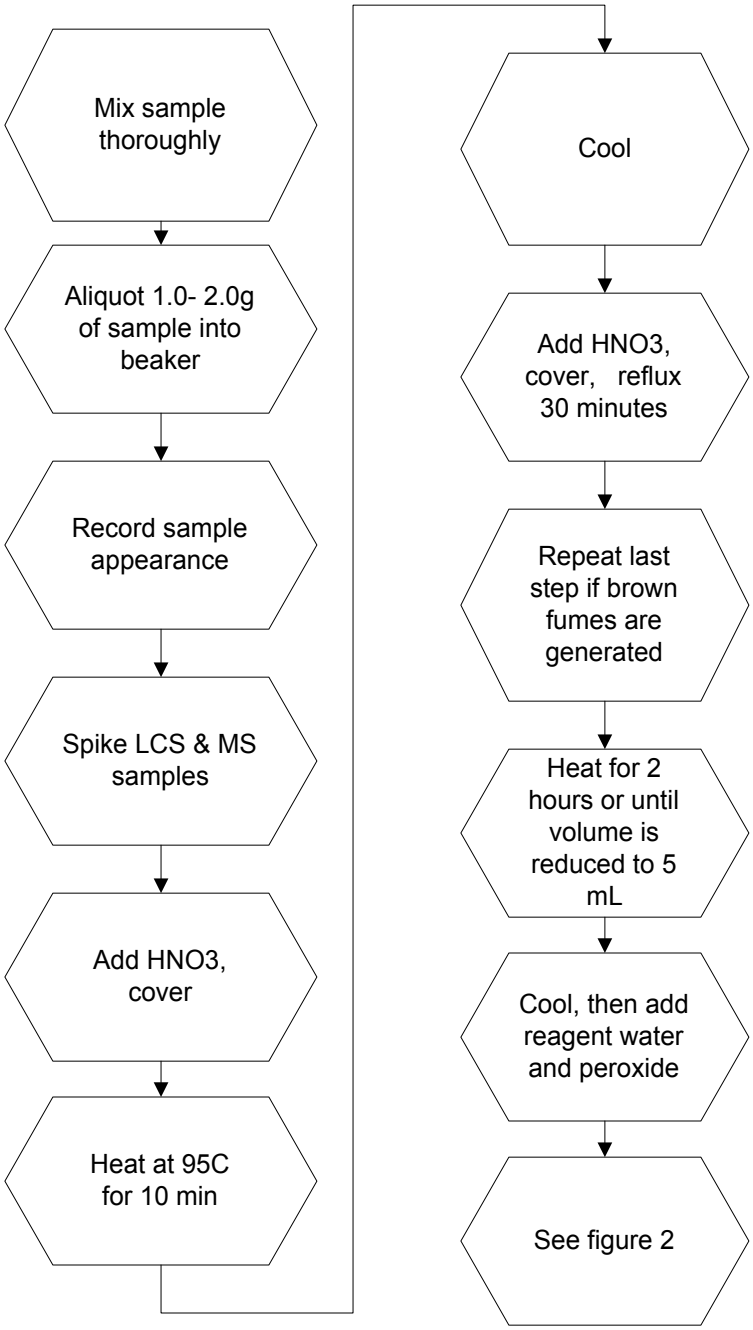
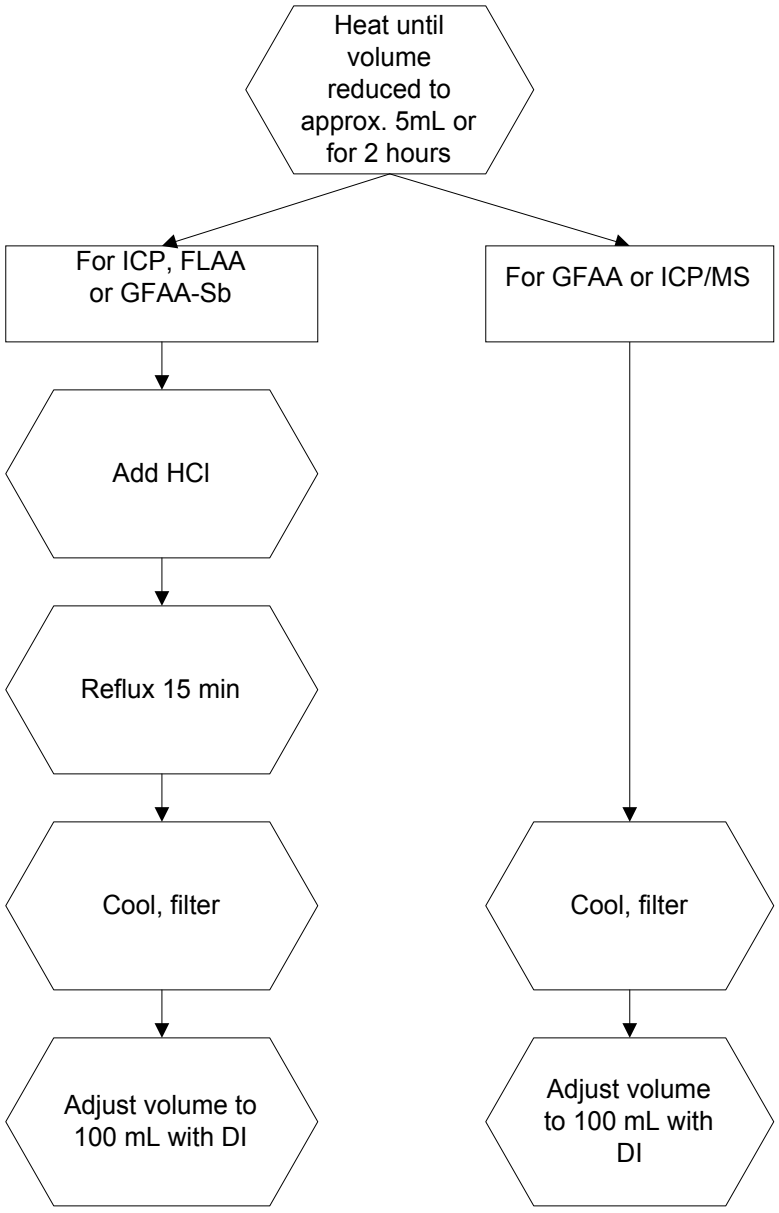


Figure 2. **Soil Sample Preparation (continued)**



APPENDIX A

TABLES

TABLE I. Method 3050A Approved Analyte List

ELEMENT	Symbol	CAS Number
Aluminum	Al	7429-90-5
Antimony *	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Osmium	Os	7440-04-2
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

TABLE II. ICP and FLAA Soil Matrix Spike and Aqueous LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)	Soil MS Level ** (mg/Kg)
Aluminum	200	2000	200
Antimony	50	500	50
Arsenic	200	2000	200
Barium	200	2000	200
Beryllium	5	50	5
Cadmium	5	50	5
Calcium	5000	50000	5000
Chromium	20	200	20
Cobalt	50	500	50
Copper	25	250	25
Iron	100	1000	100
Lead	50	500	50
Lithium	100	1000	100
Magnesium	5000	50000	5000
Manganese	50	500	50
Molybdenum	100	1000	100
Nickel	50	500	50
Phosphorous	1000	10000	1000
Potassium	5000	50000	5000
Selenium	200	2000	200
Silver	5	50	5
Sodium	5000	50000	5000
Strontium	100	1000	100
Thallium	200	2000	200
Vanadium	50	500	50
Zinc	50	500	50
Boron	100	1000	100
Silica	1000	10000	1000
Tin	200	2000	200
Titanium	100	1000	100

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.3) to 100 mL of sample.

** Final soil spike concentration based on the addition of 1.0 mL working spike (7.3) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE III. GFAA Soil Matrix Spike and Aqueous LCS Spike Levels

ELEMENT	Stock LCS/MS Standard (mg/L)	Working LCS/MS Standard (ug/L)	Aqueous LCS/ MS Level * (ug/L)	Soil MS Level** (mg/Kg)
Arsenic	400	4000	40	4
Selenium	400	4000	40	4
Lead	400	4000	40	4
Thallium	400	4000	40	4
Antimony	400	4000	40	4
Cadmium	40	400	4	0.4
Chromium	100	1000	10	1
Silver	50	500	5	0.5

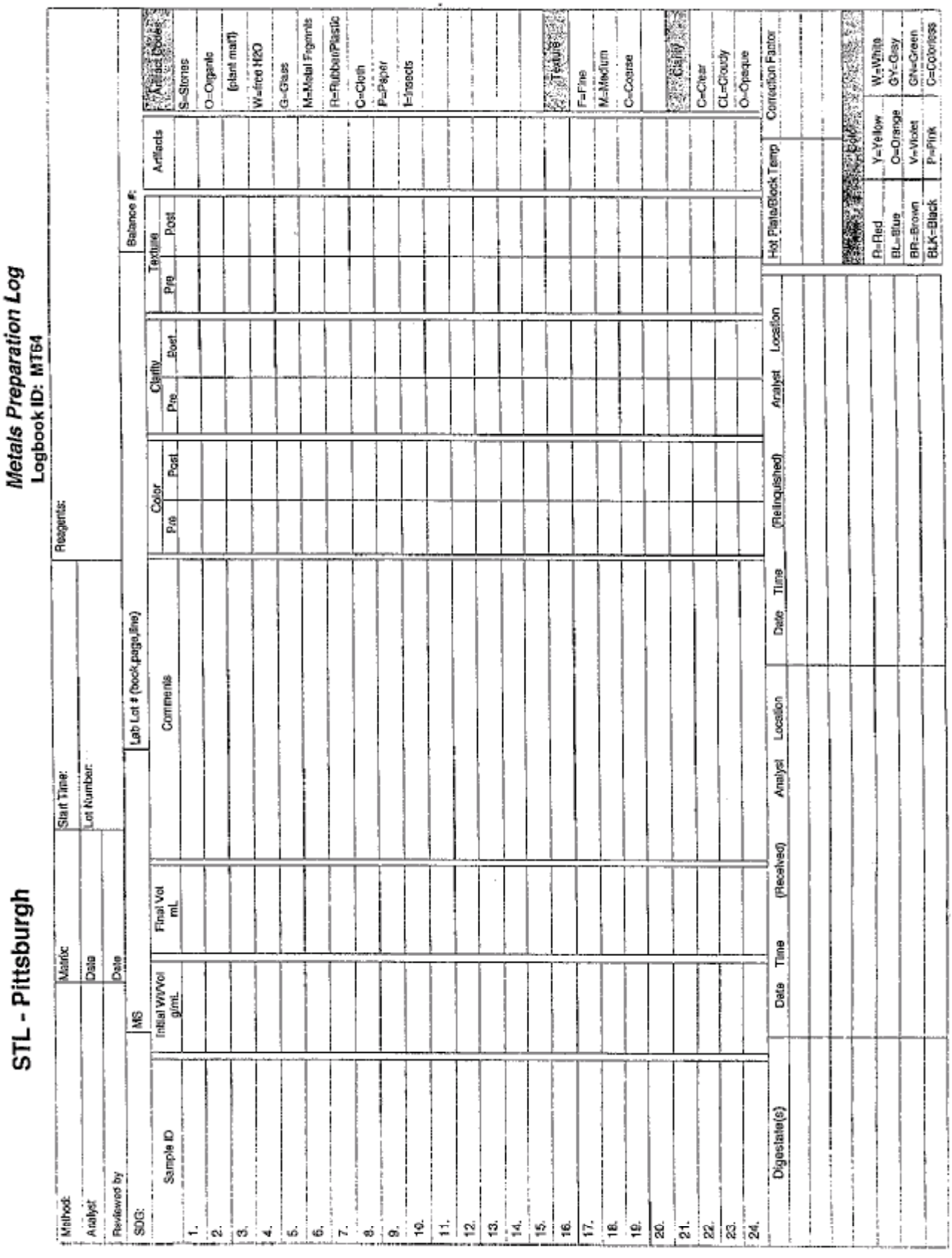
* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.4) to 100 mL of sample.

** Final soil spike concentration based on the addition of 1.0 mL working spike (7.4) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE IV. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze samples.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	See Corrective Action for Matrix Spike.

APPENDIX B - STL METALS PREPARATION BENCHSHEET



APPENDIX C

CONTAMINATION CONTROL GUIDELINES

APPENDIX C. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

STL STANDARD OPERATING PROCEDURE

TITLE: INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSES, SW-846 METHOD 6010B AND EPA METHOD 200.7

(SUPERSEDES: REVISION 2)

Prepared by: Kurt Ill and Richard Burrows

Reviewed by: _____
Technical Specialist

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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TABLE OF CONTENTS

LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010B and EPA Method 200.7 . Table I of Appendix A lists the elements appropriate for analysis by Methods 6010B and 200.7. Additional elements may be analyzed under Methods 6010B and 200.7 provided that the method performance criteria presented in Section 13.0 are met.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used. For instance, in comparison to conventional ICP technique, ICP-Trace can achieve detection levels comparable to those determined using the graphite furnace atomic absorption spectroscopy (GFAAS) technique.

1.3. Method 6010B is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of **dissolved samples** and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples and 50 mg/kg in solid matrix samples.

1.5. State-specific requirements may take precedence over this SOP for drinking water sample analyses

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line

emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.2. Refer to the appropriate SOPs for details on sample preparation methods.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

4.1.4. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. The following materials are known to be **corrosive**:

sulfuric acid, hydrochloric acid, nitric acid and hydrofluoric acid. (NOTE: sulfuric and hydrofluoric acids are used in cleaning the ICP torch and hydrofluoric acid is also commonly used in air toxics preparations.)

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. The plasma emits strong UV light and is harmful to vision. **NOTE**: **AVOID looking directly at the plasma**.

5.3.4. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Metals digestates can be processed outside of a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood or well ventilated area.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. The use of hydrofluoric acid requires special safety precautions. Consult the facility EH&S Manager and laboratory supervisor for guidance.

6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator.

6.3. Argon gas supply, welding grade or equivalent.

6.4. Coolflow or appropriate water cooling device.

6.5. Peristaltic Pump.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom STL multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2. Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids. An exception to this is in the event the Trace ICP is utilized without the internal standard. In this case, the standard acid matrix must be matched to the final preparation matrix as listed in Section 11.10.

7.3. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.4. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis. For samples that will be analyzed by Method 200.7 for compliance with Safe Drinking Water regulations, the samples must be held for a minimum of 16 hours prior to verifying the pH.

8.3. Soil samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation .

9. QUALITY CONTROL

Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using either Method 200.7 or Method 6010B, the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL must be determined annually. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the standard deviation obtained from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x - 5x the previously determined IDL, with seven consecutive measurements. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The result of the IDL determination must be below the STL reporting limit. The CLP IDL procedure can be used for this method.

9.1.2. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in STL QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be considered valid. The result of the MDL determination must be below the STL reporting limit (RL). MDL studies for the determination of metals in soil need not be performed; an appropriate soil MDL may be computed from the experimentally determined MDL for metals in aqueous solution.

9.1.3. Linear Range Verification (LR) - The linear range must be determined on an

annual basis for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to define the linear range limit must be analyzed during a routine analytical run. For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard should be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% less than the expected level extrapolated from lower standards. If the instrument is adjusted in any way that may affect the LRs, new dynamic ranges must be determined. The LR data must be documented and kept on file.

9.1.4. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the facility-specific instrument operation SOP and ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.5. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the facility specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than $\pm$ the RL as defined in Tables I, IA or II. To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element."

Note: Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace as reflected by the ICSA response.

9.1.6. Rinse Time Determination - Rinse times must be determined annually. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see 9.1.3) should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

9.2. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level).

- If the analyte is a common laboratory contaminant (copper, iron, lead (Trace only) or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such**

action must be taken in consultation with the client and must be addressed in the project narrative.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

- For dissolved metals samples which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.3. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table III (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, for method 6010B, a control limit of 80 - 120% (85-115% for 200.7) recovery must be applied.

- In the event that an MS/MSD analysis is not possible a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- In the instance where the LCS recovery is greater than 120% (115% for 200.7) and the sample results are < RL, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the report narrative.**

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

- For dissolved metals samples which have not been digested, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared

and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables III and VI (Appendix A).

- If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. For both methods 200.7 and 6010B, control limits of 75 - 125% recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- For dissolved metals samples which have not been digested, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample at the levels specified in Table III (Appendix A).

9.5. Dilution test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5x (1:4) dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample, after correction for dilution, should agree within 10% of the original sample determination when the original sample concentration is greater than 50x the IDL. If the results are not within 10%, the possibility of chemical or physical interference exists.

9.6. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). For analyses conducted under Method 200.7, the ICV result must fall within 5% of the true value for that solution with relative standard deviation <3% from replicate (minimum of two) exposures. For

Method 6010B, the ICV must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the RL from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the calibration reverified. (See Section 11.11 or 11.12 for required run sequence).

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV is be a mid-range standard made from a dilution of the calibration standard. The CCV for both methods must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. A CCB is analyzed immediately following each CCV. (See Section 11.11 or 11.12 for required run sequence.) The CCB result must fall within +/- RL from zero. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, reanalysis and recalibration are not required before continuation of the run. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 11.13 for an illustration of the appropriate rerun sequence).

9.8. Interference Check Analysis (ICSA/ICSAB) - The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table V (Appendix A) for the details of ICSA and ICSAB composition. Custom STL multielement ICS solutions must be used. All analytes should be spiked into the ICSAB solution, therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display overcorrection as a negative number then the non-routine elements can be controlled from the ICSA as described in section 9.8.3. Elements known to be interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

9.8.1. The ICSA and ICSAB solutions must be run at the beginning of the run. (See Section 11.11 or 11.12 for required run sequence.)

9.8.2. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples rerun.

9.8.3. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the STL guidelines of ± 2x RL from zero. ICSA results for the non-interfering elements with RLs> 10 µg/L must fall within the STL guidelines of ± 1x RL from zero. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL (RL ≤10) or ± 1xRL (RL>10) from zero the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.
- If the affected element was not required then the sample data can be accepted.
- If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than +/- 2x RL from zero then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.
- If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are recalculated manually the calculations must be clearly documented on the raw data.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.17 for additional information on when MSA is required as well as Appendix D for specific MSA requirements.

9.10. Quality Assurance/Project Summaries - Certain clients may require project- or program-specific QC which may supersede this SOP requirements. Quality Assurance Summaries (QASs) or equivalent documents providing project-specific requirements should be developed so that project staff clearly understand the special project requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.2. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and a standard. Refer to the facility-specific instrument SOP or ICP instrument manual for a detailed set up and operation protocols.

10.3. Calibration must be performed daily and each time the instrument is set up. Instrument runs may be continued over periods exceeding 24 hours as long as all calibration verification (CCV) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corresponding corrective actions.

11. PROCEDURE

11.1. For 200.7 analyses, dissolved (preserved) samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. Visibly transparent with a turbidity measurement of 1 NTU or less.

B. Is of one liquid phase and free of particulate or suspended matter following acidification.

C. Is NOT being analyzed for silver.

11.2. A minimum of <u>two</u> <u>exposures</u> for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

11.3. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 9.1.6 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

11.4. The use of an autosampler for all runs is strongly recommended.

11.5. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV,CCV), blanks

(ICB,CCB,PB), interference checks (ICSA,ICSAB) and field samples (linear range) to improve the data review process.

11.6. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.7. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.

11.8. For unattended overnight auto-runs it is strongly recommended that the frequency of ICSA/ICSAB analysis be increased to every 4 hours.

11.9. The use of an internal standard is recommended on the conventional, non-Trace ICPs as an alternative to using the method of standard additions. This technique is useful in overcoming matrix interferences especially in high solids matrices. However, for conventional ICP techniques, internal standards may not be necessary provided that one of the following is performed to minimize physical interferences: (1) peristaltic pump is used, (2) high solids nebulizer is used, or (3) high solids samples are diluted and reanalyzed.

11.10. The use of an internal standard is **required** on the Trace ICP unless the calibration and QC standards are matrix matched to each digestion procedure used as follows:

Preparation Method	% HNO_3	% HCl
CLP Aqueous	1	5
CLP Soil	5	2.5
SW846 3050	5	10
SW846 3005	2	5
SW846 3010	3	5

The following procedural guidelines must be followed when using an internal standard:

11.10.1. Typically used internal standards are: yttrium or scandium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.10.2. The internal standard (IS) must be added to every sample and standard at the

same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.10.3. The concentration of the internal standard should be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

11.10.4. The internal standard raw intensity counts must be printed on the raw data.

11.10.5. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte).

11.10.5.1. If the internal standard counts fall within ±30% of the counts observed in the ICB then the data is acceptable.

11.10.5.2. If the internal standard counts in the field samples are more than ±30% higher than the expected level, the field samples must then be:

(1) Diluted and reanalyzed;

(2) The IS concentrations must be raised; or

(3) A different internal standard must be used.

.

11.11. The following analytical sequence must be used for Methods 6010B and 200.7:

Instrument Calibration
ICV
ICB
ICSA
ICSAB
8 samples
CCV
CCB
10 samples
CCV
CCB

Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Method 6010B and 200.7 quality control criteria.

11.12. Additional quality control analyses are necessary for analysis under the Contract Laboratory Program (CLP). If these are included then CLP, 6010 and 200.7 samples can be included in the same sequence. Refer to CORP-MT-002 for details.

11.13. Full method required QC must be available for each wavelength used in determining reported analyte results.

11.14. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.15. All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an interelement correction exists for an analyte which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

11.16. For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table VI (Appendix A). Appendix E provides guidance on performing MSA analyses.

11.17. Any variation in procedure shall be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report and is approved by a Supervisor/Group Leader and QA Manager. If contractually required, the client shall be notified by the Project Manager.

11.18. Nonconformance documentation shall be filed in the project file.

11.19. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

12.5. The final concentration for a digested aqueous sample is calculated as follows:

$$mg / L = \frac{C \times V1 \times D}{V2}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg / Kg, dry\ weight = \frac{C \times V \times D}{W \times S}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:
I = Sample result (Instrument reading)
S = Dilution test result (Instrument reading × 5)

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

12.10. Sample results should be reported with up to three significant figures in accordance with the STL significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Refer to Tables I, IA & II in Appendix A for the list of Method 6010B and 200.7 analytes as well as additional analytes that may be analyzed using this SOP.

13.3. Method performance is determined by the analysis of MS and MSD samples as well as method blanks and laboratory control samples. The MS or MSD recovery should fall within +/- 25 % and the MS/MSD should compare within 20% RPD or within the laboratory's historical acceptance limits. These criteria apply to analyte concentrations greater than or equal to 10xIDL. Method blanks must meet the criteria specified in Section 9.2. The laboratory control samples should recover within 20% (15% for 200.7) of the true value or within the laboratory's historical acceptance limits.

13.4. Training Qualification:

The group/team leader or the supervisor has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed of according to the facility hazardous waste procedures and per the local, state, and federal regulations. The Environmental Health and Safety Director should be contacted, if additional information is required.

15.2. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

16.2. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B.

16.3. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

16.4. CORP-MT-0002, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method 200.7 & CLP-M, SOW ILMO3.0.

16.5. QA-003, STL QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method

17.1.1. Modifications/interpretations from <u>both</u> Methods 6010B and 200.7.

17.1.1.1. STL laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.

17.1.1.2. The alternate run sequence presented in Section 11.12 is consistent with method requirements. Additional QC (i.e., ICSA) analyses were added to accommodate the CLP protocol requirements.

17.1.1.3. Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. In determining IECs, because of lack of definition clarification for "concentration range around the calibration blank," STL has adopted the procedure in EPA CLP ILMO4.0.

17.1.1.4. Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because STL laboratories receive no prior information from clients regarding when to expect a new or

unusual matrix, STL may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At STL labs, matrix interference is determined by evaluating data for the LCS and MS/MSD. STL requires documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.1.2. Modifications from Method 200.7.

17.1.2.1. Method 200.7 defines the IDL as the concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength. STL labs utilize the CLP IDL definition as defined in Section 9.1.1 of this SOP.

17.1.2.2. The calibration blank is prepared in an acid matrix of 5% HNO_3/5% HCl instead of the specified 2% HNO_3/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

17.1.2.3. Method section 9.3.4 specifies that "Analysis of the IPC (ICSA/AB) solution immediately following calibration must verify that the instrument is within ± 5% of calibration with a relative standard deviation <3% from replicate integrations ≥ 4." STL uses a minimum of two exposures.

17.1.2.4. Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

17.1.2.5. The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.

17.1.2.6. Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. SOP section 9.7 provides the detailed corrective action criteria that must be followed.

17.1.3. Modifications from Method 6010B.

17.1.3.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.3.2. Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3x the IDLIf not, repeat the analysis two or more times and average the results. If the average is not within three standard deviation of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. See SOP Section 9.7 for a detailed description of the required corrective action procedures.

17.2. Modifications from previous SOP

Refer to revision 1 of this SOP.

17.3. Facility-Specific SOPs

Each facility shall review and revise as appropriate this SOP to reflect any facility-specific requirementsIf no facility-specific amendments are required, the SOP can be adopted as is.

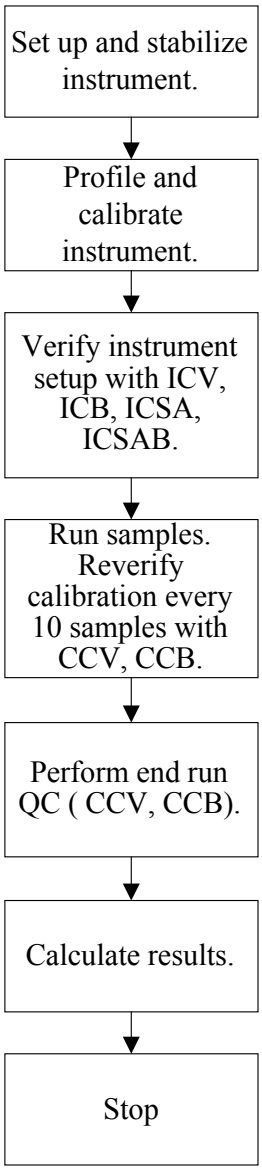
17.4. Documentation and Record Management

The following documentation comprises a complete ICP raw data package:

- Raw data (direct instrument printout).
- Relevant sample preparation benchsheets.

- Run log printout from instrument software where this option is available (TJA) or manually generated run log (i.e., Ward WSL printout).
- Data review checklist - See Appendix B.
- Standards documentation (including prep and expiration dates, source, and lot #).
- Nonconformance/anomaly documentation (if applicable).

17.5. Flow Diagram



APPENDIX A

TABLES

TABLE I. Method 200.7 and 6010B Target Analyte List

ELEMENT	Symbol	CAS #	6010B analyte	200.7 analyte	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	X	200	20
Antimony	Sb	7440-36-0	X	X	60	6
Arsenic	As	7440-38-2	X	X	300	30
Barium	Ba	7440-39-3	X	X	200	20
Beryllium	Be	7440-41-7	X	X	5.0	0.5
Boron	B	7440-42-8		X	200	20
Cadmium	Cd	7440-43-9	X	X	5.0	0.5
Calcium	Ca	7440-70-2	X	X	5000	500
Chromium	Cr	7440-47-3	X	X	10	1
Cobalt	Co	7440-48-4	X	X	50	5
Copper	Cu	7440-50-8	X	X	25	2.5
Iron	Fe	7439-89-6	X	X	100	10
Lead	Pb	7439-92-1	X	X	100	10
Lithium	Li	7439-93-2	X	X	50	5
Magnesium	Mg	7439-95-4	X	X	5000	500
Manganese	Mn	7439-96-5	X	X	15	1.5
Molybdenum	Mo	7439-98-7	X	X	40	4
Nickel	Ni	7440-02-0	X	X	40	4
Phosphorus	P	7723-14-0	X	X	300	30
Potassium	K	7440-09-7	X	X	5000	500
Selenium	Se	7782-49-2	X	X	250	25
Silicon	Si	7631-86-9		X	500	N/A
Silver	Ag	7440-22-4	X	X	10	1
Sodium	Na	7440-23-5	X	X	5000	500
Strontium	Sr	7440-24-6	X		50	5
Thallium	Tl	7440-28-0	X	X	2000	200
Vanadium	V	7440-62-2	X	X	50	5
Zinc	Zn	7440-66-6	X	X	20	2

TABLE IA. Method 200.7 and 6010B Trace ICP Target Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Arsenic	As	7440-38-2	10	1.0
Lead	Pb	7439-92-1	3.0	0.3
Selenium	Se	7782-49-2	5.0	0.5
Thallium	Tl	7440-28-0	10	1.0
Antimony	Sb	7440-36-0	10	1.0
Cadmium	Cd	7440-43-9	2.0	0.2
Silver	Ag	7440-22-4	5.0	0.5
Chromium	Cr	7440-47-3	5.0	0.5

TABLE II. Non-Routine Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Tin	Sn	7440-31-5	100	10
Titanium	Ti	7440-32-6	50	5
Bismuth	Bi	7440-06-99	200	20
Zirconium	Zr	7440-06-77	100	10
Tungsten	W	7440-03-37	500	50
Tellurium	Te	1349-48-09	500	50
Thorium	Th	7440-02-91	500	50
Uranium	U	7440-06-11	500	50
Palladium	Pd	7440-00-53	100	10

NOTE: Analysis of all elements listed may not be available at all STL facilities.

TABLE III. Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (ug/L)	Matrix Spike Level (ug/L)
Aluminum	2000	2000
Antimony	500	500
Arsenic	2000	2000
Barium	2000	2000
Beryllium	50	50
Cadmium	50	50
Calcium	50000	50000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1000	1000
Lead	500	500
Lithium	1000	1000
Magnesium	50000	50000
Manganese	500	500
Molybdenum	1000	1000
Nickel	500	500
Phosphorous	10000	10000
Potassium	50000	50000
Selenium	2000	2000
Silver	50	50
Sodium	50000	50000
Strontium	1000	1000
Thallium	2000	2000
Vanadium	500	500
Zinc	500	500
Boron	1000	1000
Silicon	10000	10000
Tin	2000	2000
Titanium	1000	1000
Bismuth	1000	1000
Zirconium	1000	1000
Tellurium	1000	1000
Thorium	1000	1000
Uranium	1000	1000
Tungsten	1000	1000
Palladium	1000	1000

TABLE IV. ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	100000	200	25000	50000
Antimony	10000	60	1000	5000
Arsenic	10000	300	1000	5000
Barium	10000	200	1000	5000
Beryllium	10000	5	1000	5000
Cadmium	10000	5	1000	5000
Calcium	100000	5000	25000	50000
Chromium	10000	10	1000	5000
Cobalt	10000	50	1000	5000
Copper	10000	25	1000	5000
Iron	100000	100	25000	50000
Lead	10000	100	1000	5000
Lithium	10000	50	1000	5000
Magnesium	100000	5000	25000	50000
Manganese	10000	15	1000	5000
Molybdenum	10000	40	1000	5000
Nickel	10000	40	1000	5000
Phosphorous	10000	300	1000	5000
Potassium	100000	5000	25000	50000
Selenium	10000	250	1000	5000
Silver	2000	10	500	1000
Sodium	100000	5000	25000	50000
Strontium	10000	50	1000	5000
Thallium	20000	2000	5000	10000
Vanadium	10000	50	1000	5000
Zinc	10000	20	1000	5000
Boron	10000	200	1000	5000
Silicon	10000	500	1000	5000
Tin	10000	100	1000	5000
Titanium	10000	50	1000	5000
Bismuth	10000	200	1000	5000
Zirconium	10000	100	1000	5000
Tellurium	10000	500	1000	5000
Thorium	10000	500	1000	5000
Uranium	10000	500	1000	5000
Tungsten	10000	500	1000	5000
Palladium	10000	100	1000	5000

TABLE IVA. Trace ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	50000	200	12500	25000
Antimony	1000	10	250	500
Arsenic	1000	10	250	500
Barium	4000	10	1000	2000
Beryllium	4000	5	1000	2000
Cadmium	1000	2	250	500
Calcium	100000	5000	25000	50000
Chromium	4000	5	1000	2000
Cobalt	4000	50	1000	2000
Copper	4000	25	1000	2000
Iron	50000	100	12500	25000
Lead	1000	3	250	500
Magnesium	100000	5000	25000	50000
Manganese	4000	15	1000	2000
Molybdenum	4000	40	1000	2000
Nickel	4000	40	1000	2000
Potassium	100000	5000	25000	50000
Selenium	1000	5	250	500
Silver	2000	5	500	1000
Sodium	100000	5000	25000	50000
Thallium	2000	10	500	1000
Vanadium	4000	50	1000	2000
Zinc	4000	20	1000	2000

TABLE V. Interference Check Sample Concentrations*

Element	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	500000	500000
Antimony	-	1000
Arsenic	-	1000
Barium	-	500
Beryllium	-	500
Cadmium	-	1000
Calcium	500000	500000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200000	200000
Lead	-	1000
Magnesium	500000	500000
Manganese	-	500
Molybdenum	-	1000
Nickel	-	1000
Potassium	-	10000
Selenium	-	1000
Silver	-	1000
Sodium	-	10000
Thallium	-	10000**
Vanadium	-	500
Zinc	-	1000
Tin	-	1000

* Custom STL solutions contain analytes common to all STL facilities. Non-routine elements not listed above should be spiked into the ICSAB at 1000 ug/L.

** Thallium level for Trace ICP should be at 1000 ug/L.

TABLE VI. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE VII. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met	RSD between duplicate exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery. Method 6010B: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate.
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate.
CCV	Every 10 samples and at the end of the run.	Method 200.7 & 6010B: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
ICSA	Beginning of every run	See Section 9.8.3	See Section 9.8.3.
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.8.2.

* See Sections 11.11 and 11.12 for exact run sequence to be followed.

TABLE VII. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Dilution Test	One per prep batch.	For samples > 50x IDL, dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Common lab contaminants may be accepted up to 2x the RL after consultation with the client (See 9.2). Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.2).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits. (85-115% for 200.7) Samples for which the contaminant is < RL and the LCS results are > 120% (115% for 200.7) may not require redigestion or reanalysis (see Section 9.3)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.

TABLE VII. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. I For TCLP See Section 11.17.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. For TCLP see Section 11.17.
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery; RPD ≤ 20% .	See Corrective Action for Matrix Spike.

APPENDIX B

STL ICP DATA REVIEW CHECKLIST

STL ICP Data Review Checklist

Run/Project Information:

Run Date: _____ **Analyst:**_____ **Instrument:**_____
Prep Batches Run:_____

Circle Methods used: 6010B / 200.7: CORP-MT-0001 Rev 2
CLP ILMO3.0/4.0 : CORP-MT-0002 Rev 1

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits ? (6010B, CLP = 90 - 110%, 200.7 = 95 -105%[ICV])				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP) ?				
4. CRI analyzed? (for CLP only)				
5. ICSA/ICSAB run at required frequency and within SOP limits ?				
B. Sample Results				
1. Were samples with concentrations > the linear range for any parameter diluted and reanalyzed ?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time ?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits ?				
5. Dilution Test done per prep batch (or per SDG for CLP) ?				
6. Post digest spike analyzed if required (CLP only) ?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/LR/IEC data on file ?				
3. Calculations checked for error ?				
4. Transcriptions checked for error ?				
5. All client/project specific requirements met ?				
6. Date/time of analysis verified as correct ?				

Analyst: _____ **Date:** _____
Comments:_____
_____
_____

2nd Level Reviewer : _____ **Date:** _____
Comments:_____
_____
_____

APPENDIX C

CROSS REFERENCE OF TERMS USED IN METHODS 6010B, 200.7, AND BY STL

CROSS REFERENCE OF TERMS COMMONLY USED IN METHODS EPA 200.7, SW6010B, AND STL INC. SOP

EPA 200.7	SW6010B	STL Inc. SOP
Calibration blank (CB)	Calibration blank	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test	Dilution Test
Instrument detection limit (IDL)	Instrument detection limit (IDL)	Instrument detection limit (IDL)
Instrument performance check (IPC)	Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard	Internal standard (IS)
Laboratory duplicates	n/a	n/a
Laboratory fortified blank (LFB)	n/a	Laboratory control sample (LCS)
Laboratory fortified sample matrix (LFM)	Matrix spike and matrix spike duplicate (MS/MSD)	Matrix spike and matrix spike duplicate (MS/MSD)
Laboratory reagent blank (LRB)	Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range (LDR)	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)	Method detection limit (MDL)
Quality control sample (QCS)	Check standard or Initial calibration verification (ICV)	Initial calibration verification (ICV)
Spectral interference check solution (SIC)	Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

APPENDIX D

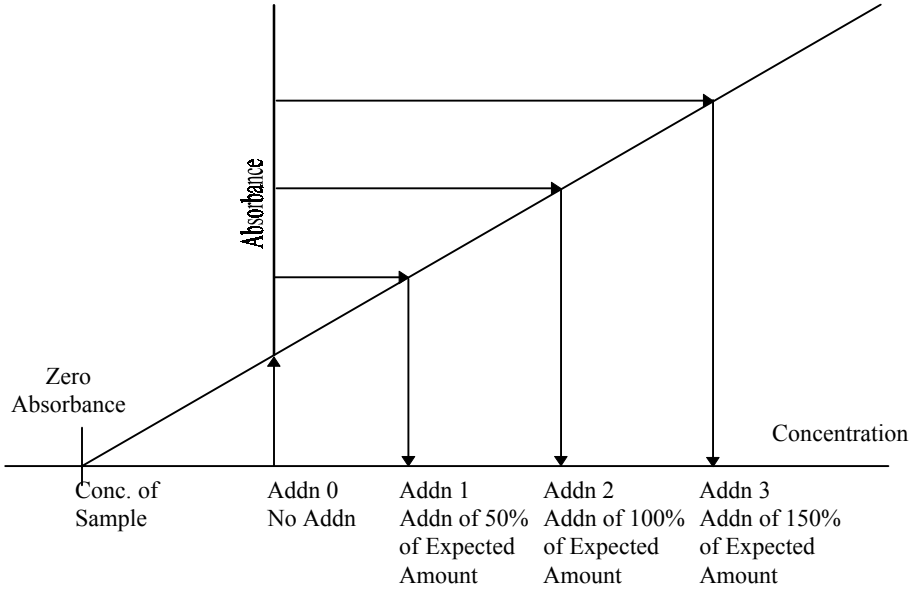
MSA GUIDANCE

Appendix D. MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX E

TROUBLESHOOTING GUIDE

APPENDIX E. TROUBLESHOOTING GUIDE

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber Lower Torch
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Reprofile Horizontal Mirror Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Cu/Mn Ratio Outside Limits or Low Sensitivity	Plasma conditions changed Clean nebulizer, torch or spray chamber Replace tubing (clogged) Realign torch Check IECs
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX F

CONTAMINATION CONTROL GUIDELINES

APPENDIX F. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipet tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX G

PREVENTIVE MAINTENANCE

APPENDIX G. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Daily	Change sample pump tubing and pump windings Check argon gas supply level Check rinse solution and fill if needed Check waste containers and empty if needed Check sample capillary tubing is clean and in good condition Check droplet size to verify nebulizer is not clogged. Check sample flow for cross flow nebulizer Check Cu/Mn ratio-should be 30% of value at date that IECs were performed Check pressure for vacuum systems
As Needed	Clean plasma torch assembly to remove accumulated deposits Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance Replace peristaltic pump tubing, sample capillary tubing and autosampler sipper probe
Weekly	Apply silicon spray on autosampler tracks Check water level in coolflow
Monthly	Clean air filters on back of power unit to remove dust Check D mirror for air instruments
Bi-yearly	Change oil for vacuum systems Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

STL STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY, SW846 7471A AND MCAWW 245.5

(SUPERSEDES: REVISION 1)

Prepared by: Kurt Ill

Reviewed by: _____
Technical Specialist

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7471A and MCAWW Method 245.5.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Methods 7471A and 245.5 are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits and sludge-type materials. All matrices require sample preparation prior to analysis.

1.4. The STL reporting limit for mercury in solid matrices is 0.033 mg/kg based a 0.6 g sample aliquot (wet weight).

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining temperature of 90- 95 °C) or autoclave capable of obtaining 15 lbs., 120 °C.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that acheive the same purpose are also acceptable (i.e., Gortex filter).

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Top-loading balance, capable of reading up to two decimal places.

6.8. Thermometer (capable of accurate readings at 95 °C).

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3 . This acid (2 mL of

concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.5. The calibration standards must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample prep bottles and proceeding as specified in Section 11.1

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.11. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.12. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.13. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.14. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.15. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of sample analysis.

8.2. Soil samples do not require preservation but must be stored at 4° C ± 2° C until the time of analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7471A or the 245.5, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined

using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136

Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level).

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such**

action must be taken in consultation with the client and must be addressed in the project narrative.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The CCV results can be reported as the LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative."

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential

variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 20% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.10 and Section 11.2.11 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.10 and 11.2.11 for required run sequence.) The CCB result must fall within +/- RL from zero. Each

CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the

affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.12 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥ 0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Standard and Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples.

11.1.2. Transfer 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working standard (7.5) into a series of sample digestion bottles.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

11.1.3. Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under 11.1.5 or 11.1.6 below.

11.1.4. Transfer triplicate 0.2 g portions of a well mixed sample into a clean sample digestion bottle. Continue preparation as described under 11.2.2 or 11.2.3 below.

11.1.5. Water Bath protocol:

11.1.5.1. To each **standard** bottle: Add 5 mL of aqua regia.
To each **sample** bottle: Add 5 mL of reagent water and 5 mL of aqua regia.

11.1.5.2. Heat for 2 minutes in a water bath at 90 - 95 ° C.

11.1.5.3. Cool.

11.1.5.4. Add 50 mL of distilled water.

11.1.5.5. Add 15 mL of potassium permanganate solution.

11.1.5.6. Add 8 mL of potassium persulfate solution, mix thoroughly.

11.1.5.7. Heat for 30 minutes in the water bath at 90 - 95 °C.

11.1.5.8. Cool.

11.1.5.9. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

11.1.5.10. To each **standard** bottle: Add 50 mL of reagent water.
To each **sample** bottle: Add 55 mL of reagent water.

11.1.5.11. Continue as described under Section 11.2.

11.1.6. Autoclave protocol:

11.1.6.1. Add 5 mL concentrated of H_2SO_4 and 2 mL of concentrated HNO_3.

11.1.6.2. Add 5 mL of saturated potassium permanganate solution.

11.1.6.3. Cover digestion bottle with aluminum foil or screw cap loosely applied.

11.1.6.4. Heat samples at 121 °C and 15 lbs. pressure for 15 minutes.

11.1.6.5. Cool.

11.1.6.6. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate.

Note: Alternate final volumes may be used as long as the standards and sample are treated the same way and reagents are adjusted proportionally.

11.1.6.7. Make up to volume of 100 mL with reagent water.

11.1.6.8. Continue as described under Section 11.2.

11.2. Sample Analysis:

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to

the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. Manual determination:

11.2.3.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.3.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.3.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.3.4. Place the aeration device into 100 mLs of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.4. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. ug of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.7. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.8. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.9. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.10. The following analytical sequence must be used with 7471A and 245.5:

Instrument Calibration
ICV
ICB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7471A and 245.5.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.11. The following run sequence is consistent with 7471A, CLP and 245.5 and may be used as an alternate to the sequence in 11.2.10. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0008) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

11.2.12. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sampe preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.6. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R\ =\ 100\left(\frac{SSR\ -\ SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = \quad (C \times V \times D)/(W \times S)$$

Where:
C = Concentration (ug/L) from instrument readout

V = Volume of digestate (L)
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.6. For manual (total) determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = (C)/(W \times S)$$

Where:
C = Concentration (ug) from instrument readout
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Sample results should be reported with up to three significant figures in accordance with the STL significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of method blank, laboratory control sample, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.3. The

laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

16.2. “Methods for the Chemical Analysis of Water and Wastes”, EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.5.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.4. QA-003, STL QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7471A and 245.5.

17.1.1.1. A potassium persulfate oxidation step has been included to facilitate the breakdown of organic mercurials which are not completely oxidized by potassium permanganate. Use of potassium persulfate in combination with the permanganate improves the recovery of mercury from organo-mercury compounds. The use of persulfate has been incorporated in several recent EPA mercury protocols.

17.1.1.2. The alternate run sequence presented in Section 11.2.11 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7471A

17.1.2.1. Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.2.2. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2.3. Method 7471A does not state control criteria within the text of the method. The QC section of 7471A refers the analyst to Section 8.0 of Method 7000A, the generic atomic absorption method, which discusses flame and furnace methods. The ICV criteria stated in Method 7000A is ± 10%. This SOP requires ICV control limits of ± 20% based on the fact that the mercury ICV, unlike the ICV for the flame and furnace analytes, is digested and therefore is equivalent to a LCS. The CLP protocol 245.5 CLP-M recognizes this factor and requires control limits of ± 20%.

17.1.3. Modifications from 245.5

17.1.3.1. Method 245.5 Section 9.3 states concentrations should be reported as follows: Between 0.1 and 1 ug/g, to the nearest 0.01 ug; between 1 and 10 ug/g, to the nearest 0.1ug; above 10 ug/g, to the nearest ug. STL reports all Hg results under this SOP to two significant figures.

17.2. Modifications from previous SOP

17.2.1. Section 1.4 reporting limit changed from 0.1 mg/kg based on a 0.2 g to 0.033 mg/kg based on a 0.6 g sample aliquot.

17.2.2. Section 9.3 added MS and MSDs as not counted in determination of preparation batches.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Solid Sample Preparation for Mercury - Autoclave Procedure

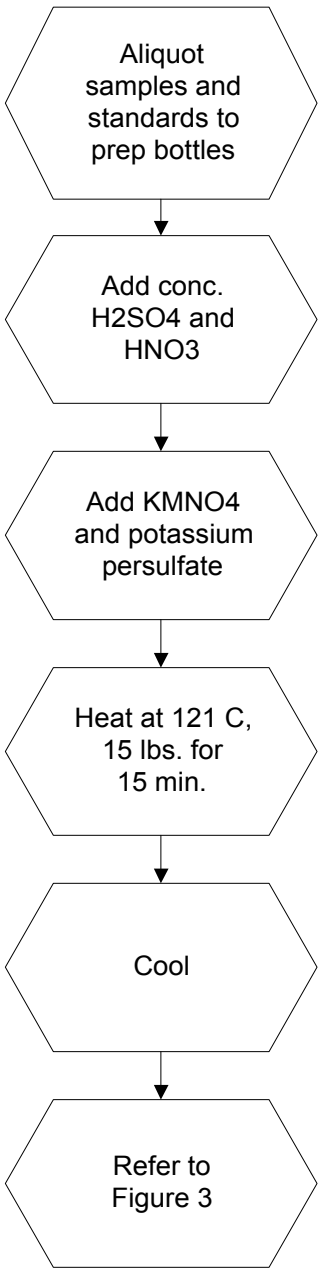


Figure 2. Solid Sample Preparation for Mercury - Water Bath Procedure

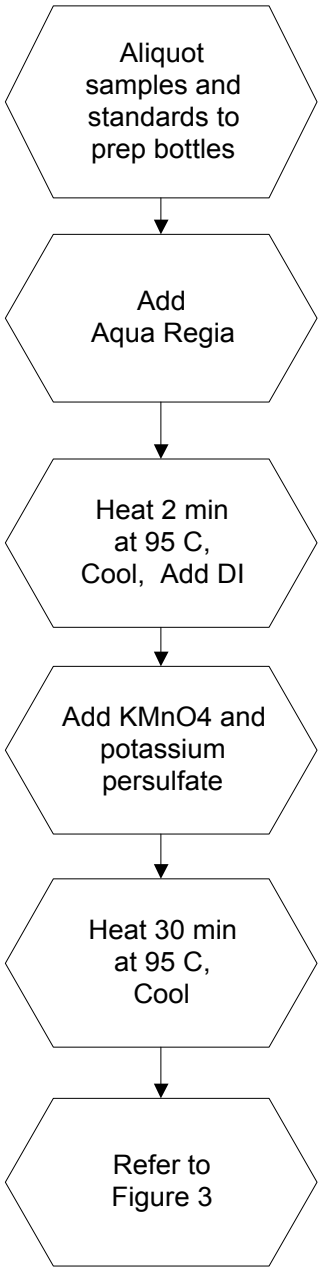
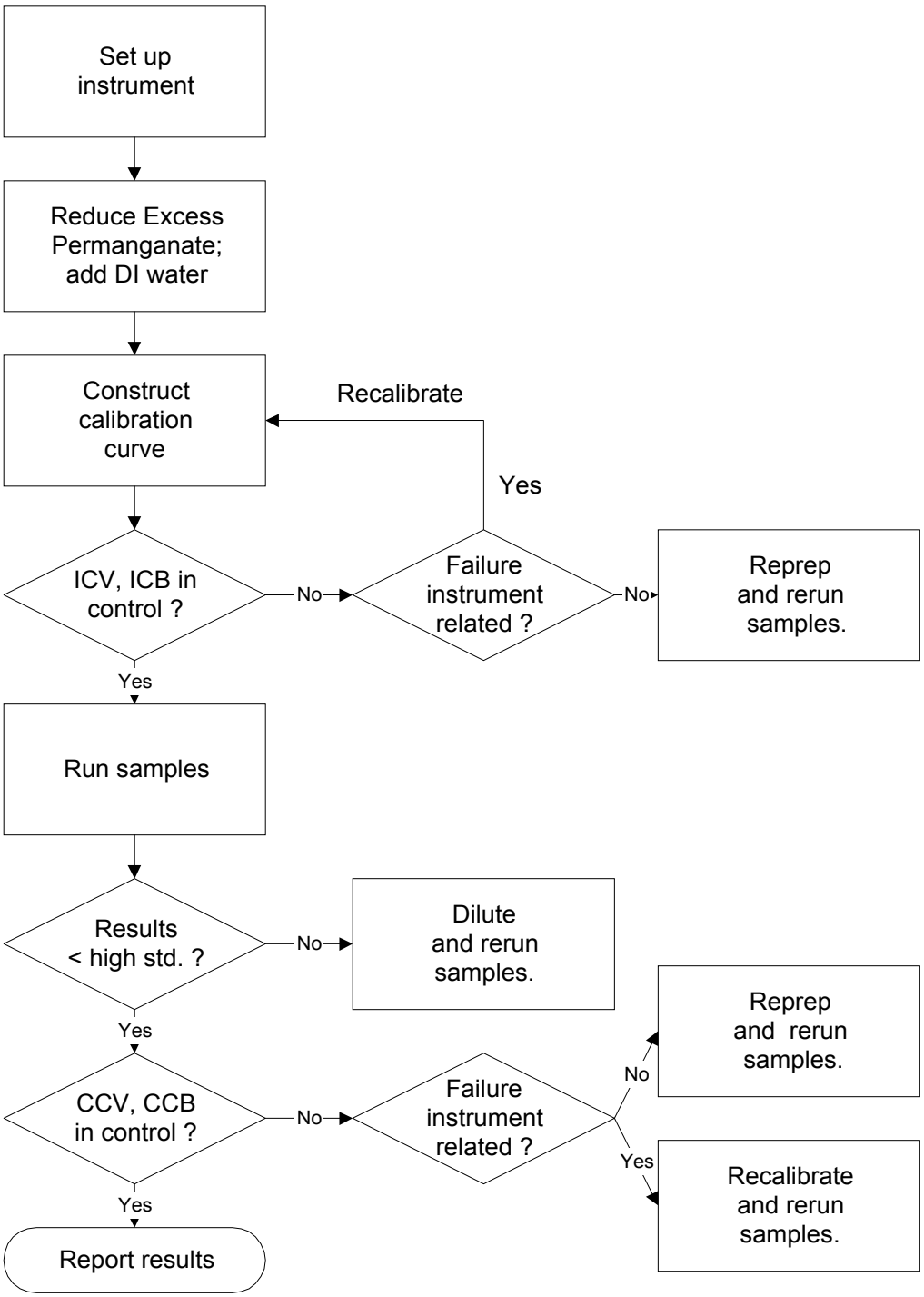


Figure 3. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg) SW-7471A	0.033
Soil RL (mg/kg) CLP	0.1
Std 0 (mg/L)	0
Std 1 (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.005
Std 5 (mg/L)	0.010
ICV (mg/L)	0.001 or 0.0025 **
CCV/LCS (mg/L)	0.0025 or 0.005 **
MS (mg/L)	0.001

*** SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

**** Concentration level dependent on high calibration standard used. CCV must be 50% of the high standard concentration and the ICV must be 20-25% of the high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4)	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

*See Sections 11.2.10 and 11.2.11 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.3.12
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B
STL Hg DATA REVIEW CHECKLIST

STL Hg Data Review Checklist

Run/Project Information

Run Date: _____ **Analyst:**_____ **Instrument:**_____
Prep Batches Run:_____

Circle Methods used: **7470A / 245.1 :** CORP-MT-0005 Rev 1 **7471 / 245.5 :** CORP-MT-0007 Rev 1
CLP - AQ : CORP-MT-0006 Rev 0 **CLP - SOL :** CORP-MT-0008 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ **Date:**_____
Comments:
_____
_____

2nd Level Reviewer : _____ **Date:**_____
_____
_____

APPENDIX C

MSA GUIDANCE

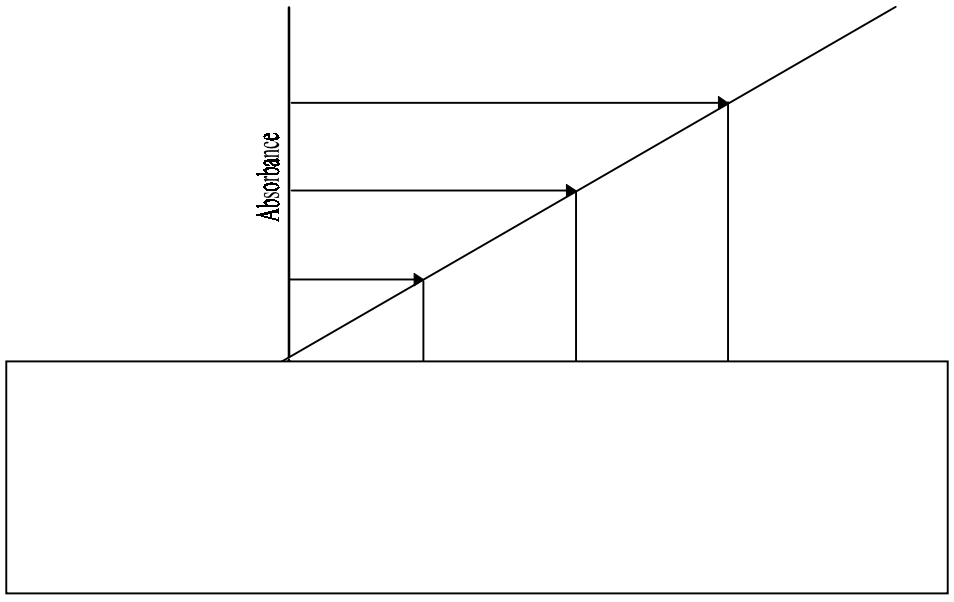
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D. TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won’t Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200) (1)

Daily	Semi-annually	Annually
Clean lens.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing.		
Check drain.		
Replace drying tube.		

Cold Vapor Atomic Absorption (PE 5000) (1)

Daily	Monthly
Clean aspirator by flushing with DI water.	Clean cell in aqua regia.
Check tubing and replace if needed.	Clean aspirator in aqua regia.
Clean windows with methanol.	
Change silica gel in drying tube.	
Check argon gas supply.	
Adjust lamp.	

APPENDIX 30

1.0 OBJECTIVES

This Standard Operating Procedure (SOP) describes the procedures that the auditor will use for performing field audits and the reporting of the audit findings. Field audits will be performed to provide GE with an indication of the quality of the field services that are being provided by the field contractor(s) as part of the Hudson River Design Support Sediment Sampling and Analysis Program and to ensure that the field contractor(s) are adhering to project requirements. This SOP applies to the contractor(s) involved in field data collection and the auditor.

2.0 EQUIPMENT

Not applicable.

3.0 SUPPORTING SOPs and DOCUMENTS

Applicable Field Sampling SOPs.

Quality Assurance Project Plan (QAPP).

Applicable Field Sampling Plan (FSP).

Health and Safety Plan

4.0 PROCEDURE

4.1 SCHEDULING

The frequency of field audits will be identified in the appropriate FSP and/or the QAPP. When it has been determined that the performance of a field audit is necessary, the auditor will coordinate a date and time for the audit with GE which consider both the field schedule and any deadline necessary to meet the needs of the FSP. The majority of the audits will be unannounced to the field contractors.

4.2 PRE-AUDIT PREPARATION

Once a field audit is scheduled, the auditor will review the applicable FSP and determine and review the applicable SOPs. The auditor will also prepare an audit checklist relevant to the specific task being performed. The individual sampling and field procedures SOPs applicable to the tasks being audited will provide the specific criteria against which the audit will be performed.

4.3 GENERAL AUDIT APPROACH

Upon arrival at the project site, the auditor will initiate a meeting with the appropriate field personnel (site manager) to give a brief introduction of what they can expect to occur during the field audit. This introduction focuses on several key points. The auditor(s) will identify that they will be performing the audit with the aid of a checklist that has been prepared by the auditor.

The checklist guides the auditor(s) through the field task in the basic order that events are expected to occur. Another key point that will be made is that the auditor(s) will focus their questions toward the field personnel who actually perform the work and **not** their supervisors. Field supervisors may be present during the audit but may not answer the questions for the field personnel unless specifically requested to provide an answer. In addition, the auditor will ask questions regarding appropriate general field service protocols during this initial meeting.

The field audit checklist must include the following 9 sections. The field audit will be performed in the basic order defined by the checklist, depending on the task being performed. Subdivisions of the following sections will be necessary and will be dependent on the type of work being performed. The approach of the audit on the

following topics is described in greater detail in the subsequent sections of this SOP. The narrative of the field audit report will also follow the subject order of the checklist but will give the audit findings and recommendations in sufficient detail that the checklist will not be included with the report.

1. Field Documentation/Records
2. Decontamination Procedures
3. Sampling/Field Procedures
4. Sample Containers
5. Sample Packaging and Shipment
6. Chain-of-Custody
7. Health and Safety/Personal Protective Equipment
8. Other
9. Summary

Finally, following the audit, the auditor(s) will convene another meeting with the field management personnel in order to debrief them on the audit findings. The debriefing meeting should accomplish several goals. First, the field personnel must be made aware of the major points of the audit findings. This way, any statements made in the field audit report will not be a surprise to the contractor, and the contractor is given a chance to respond to the findings before the report is written. Their responses can then be incorporated into the field audit report by the auditor. Secondly, the auditor(s) should emphasize that recommendations will be made even to the best of contractors. The major goals of a field audit is to determine the quality of services being provided by the contractor, document that appropriate procedures are being used, and to identify problems (or potential problems) so that appropriate corrective action can be initiated by

the contractor. The extent of the impact of the recommendation(s) will be indicated in the report. Additionally, the audit should stress when correct field procedures were in use.

4.4 FIELD DOCUMENTATION/RECORDS

The auditor(s) must evaluate the contractor's documentation procedures throughout the audit, and should verify that all pertinent information is being neatly recorded in a logbook for all field events. The minimum information to be entered in the logbook should include: on-site personnel and their arrival and departure times; weather conditions; calibration and background settings of monitoring equipment; location of collected samples; time of collection; the required sample analysis; relevant observations; photograph log; adherence to and/or deviations from the FSP; and other pertinent information.

4.5 DECONTAMINATION PROCEDURES

The auditor(s) will verify that the decontamination areas are established in a clean portion of the site and that correct decontamination procedures are being followed. The personnel performing the decontamination of the sampling equipment should be using the decontamination materials specified in the appropriate SOP and should be performed in the exact order listed in the SOP. Care should be taken to limit the amount of decontamination wastes generated during the cleaning process. The decontamination wastes should be properly managed and stored per SOP until appropriate disposal arrangements are made.

4.6 SAMPLE CONTAINERS

The auditor(s) will verify that the contractor is using laboratory supplied, pre-cleaned sample containers for analytical samples. The containers should be of the proper type (i.e. glass, plastic, metal), volume, and material (i.e. amber or clear glass). Any cracked or broken sample containers should not be used and should be discarded. The appropriate preservatives should already be placed in the sample containers by the laboratory, or they may be added to the sample containers in the field. Once the sample is collected and placed in the sample container, the container should be legibly labeled or preprinted with the following information; sample ID, date, time, sampler's initials, analysis, and project name and number.

4.7 SAMPLING/FIELD PROCEDURES

The auditor(s) must evaluate the procedures the contractor utilizes during the collection of samples and other field activities. Samples may be collected from various medias (i.e., surface and subsurface soil and ground water, sediment, and soil gas vapor) and for various purposes (i.e., chemical analysis, geotechnical testing, and geological characterization). The method of sample collection will also vary and will require assorted types of equipment to insure the proper collection of the sample. The auditor(s) must verify that a proper method of sample collection and proper equipment are being used for the media being sampled and the intended purpose of the sample collection. Deviations to the applicable FSP should be noted by the auditor(s).

4.8 SAMPLE PACKAGING AND SHIPMENT

After environmental samples have been collected, placed in sample containers, labeled and temporarily stored on-site, they should be packaged and shipped to the laboratory for chemical analysis per SOP. The auditor(s) will verify that the transport device (e.g., ice chest) to be used for shipment of the samples is cleaned of any obvious debris and old shipping labels are removed. The auditor(s) will check to see that the transport device is lined with an absorbent material and a plastic bag. The samples will be checked to see if they are individually wrapped or protected and properly aligned in the transport device so that they do not touch each other. The samples should then be packed using an approved packing material and iced down (with the exception of liquid samples for metal analysis) with sufficient "wet" ice or ice pack to keep the samples at 4 degrees Celsius. Packing tape and signed custody seals should be used to seal the transport device. Shipping air bills and content caution content labels (e.g., Fragile, This End Up, etc.) should be attached to the outside of the shipping container.

The packaging and shipment of samples collected for geotechnical testing will also be evaluated. Again, the procedures for the packaging and shipment will be dependent on the type of sample collected and the testing parameters. For example, the packaging of an undisturbed shelby tube sample should include a wax seal at each end of the tube using an approved wax and a label with the appropriate project and shipping information. It should be stored and transported in the vertical position as it was oriented in the subsurface.

4.9 CHAIN-OF-CUSTODY

The auditor(s) will verify that the chain-of-custody record and procedures are being properly completed per SOP. As soon as practicable after sample collection, the

following information must be recorded on the chain-of-custody form; project name and number, sampler(s), sample ID, date, time, type of sample (grab or composite), number of containers, sample analysis, remarks, and signature (when being relinquished). The field audit will include a determination that proper handling and transfer of chain-of-custody documentation is occurring.

4.10 HEALTH AND SAFETY/PERSONAL PROTECTIVE EQUIPMENT

The auditor(s) will observe the field personnel to verify that they are following the guidelines of the Health and Safety Plan. The auditor will make only general observations about the health and safety practices. The auditor(s) will check to see that the field personnel are wearing the specified protective clothing and equipment for the level of protection specified by the health and safety officer. The auditor(s) will also verify that the appropriate types of personal monitoring equipment is being used, and that personnel using the equipment are knowledgeable with the operation of the equipment.

4.11 OTHER

Due to the wide range of field services being performed on this project, the above discussed list of items may not always completely address the extent of the audit. At the auditor's discretion, other checklist items may be added to ensure that a complete audit is performed. The checklist used for a specific audit will not be provided to GE and the contractor at the start of the audit.

4.12 SUMMARY

The auditor(s) must summarize the major points of the field audit findings and the overall evaluation of the quality of service provided by the contractor. The summary should also reflect the overall attitude that the contractor has toward quality assurance and quality control.

4.13 REPORT FORMAT

The field audit report must contain the following sections in the following order. It must also contain a completed checklist as an attachment.

1. Introduction
2. Executive Summary
3. Audit Findings

The introduction should summarize who performed the audit, when the audit was performed, the name and address of the contractor, and the contractor's role in the FSP. The Executive Summary should address the major findings of the field audit along with the possible impact on the quality of the contractors service. The Audit Findings should follow the major headings of the checklist summarizing the findings presented on the checklist along with any recommendations for improvement or corrective action. The report will be signed by the auditor(s) who performed the audit.

5.0 TRAINING

The auditor's conducting the field audit must have demonstrated knowledge in field quality assurance/quality control practices. This knowledge will include experience in geological and hydrogeological investigations, sample collection of various medias, health and safety training, and technical report writing.

APPENDIX 31

1.0 OBJECTIVES

This Standard Operating Procedure (SOP) describes the procedures that the auditor will use for performing analytical laboratory audits and the reporting of the audit findings. Analytical laboratory audits will be performed to provide GE with an indication of the quality of the data that are being provided from the laboratories as part of the Hudson River Design Support Sediment Sampling and Analysis Program and to ensure that the laboratories are adhering to project requirements. This SOP applies to the laboratories and the auditor.

2.0 EQUIPMENT

Not applicable.

3.0 SUPPORTING SOPs and DOCUMENTS

Applicable Analytical SOPs.

Quality Assurance Project Plan (QAPP).

Applicable Field Sampling Plan (FSP).

Health and Safety Plan

Applicable Laboratory Quality Assurance Manual (LQAM)

4.0 PROCEDURE

4.1 SCHEDULING

The frequency of laboratory audits will be identified in the appropriate FSP and/or QAPP. When it has been determined that the performance of a laboratory audit is necessary, the auditor will initiate contact with the designated project laboratory. The auditor and the laboratory will mutually determine a date and time for the audit which is convenient for both parties and which

is within any deadline necessary to meet the needs of the FSP and/or QAPP. If necessary, unannounced audits may be performed.

4.2 PRE-AUDIT PREPARATION

At the time the laboratory audit is scheduled, the auditor will request any laboratory documents that would aid in the effectiveness of the audit if received prior to the audit. Such documents will include the LQAM, all analytical Standard Operating Procedures (SOPs) which are applicable to the analytical work being performed by the laboratory, and applicable recent Performance Evaluation (PE) sample analysis results.

Prior to the audit, the auditor will review all documents provided by the laboratory. In the laboratory audit report, a statement will be made as to the appropriateness and thoroughness of these documents in terms of the needs of the FSP and/or QAPP. In addition, the auditor will take notes upon this initial review that will aid in verifying that the laboratory is following the procedures described in the documents. Any deviations from the documents will also be noted in the laboratory audit report.

4.3 GENERAL AUDIT APPROACH

Upon arrival at the designated project laboratory, the auditor will initiate a meeting with the appropriate laboratory personnel (analytical laboratory supervisor(s) and quality assurance supervisor) to give a brief introduction of what they can expect to occur during the laboratory audit. This introduction focuses on several key points. The auditor(s) will identify that they will be performing the audit with the aid of a checklist that has been prepared by the auditor. The checklist will not be provided to the laboratory at any time.

This checklist guides the auditor(s) through the laboratory in the basic order that samples are processed through the laboratory starting with sample receipt and ending with data reporting. Another key point that will be made is that the auditor(s) will focus their questions toward the technicians and analysts who actually perform the work and **not** their supervisors. Laboratory supervisors may be present during the laboratory audit but may not answer the questions for the technicians/analysts unless the technicians/analysts cannot answer a given question. In addition, the auditor will ask questions regarding appropriate general laboratory information during this initial meeting.

The audit checklist is a proprietary document and has not been included with this SOP. It contains significant specific detail on the audit criteria and evaluation. The laboratory evaluation checklist includes the following eight sections. The laboratory audit will be performed in the basic order defined by the checklist, depending on the layout of the laboratory being audited. Subdivisions of the following sections will be necessary and will be dependent on the types of analytical work being performed for the FSP at the designated laboratory. The approach of the audit on the following topics is described in greater detail in the subsequent sections of this SOP. In addition to the following topics, the auditor(s) will also be evaluating the overall sample tracking throughout the audit and the communication between the various sections of the laboratory (with a special regard to how holding times are met). The narrative of the laboratory audit report will also follow the subject order of the checklist but will give the audit findings and recommendations in sufficient detail that the checklist will not be included with the report.

1. Organization and Personnel
2. Sample Receipt and Storage Area
3. Sample Preparation Area

4. Sample Analysis Instrumentation
5. Documentation
6. Quality Control Manual
7. Data Handling
8. Summary

Finally, following the audit, the auditor(s) will initiate another meeting with the appropriate laboratory personnel in order to debrief them on the audit findings. The debriefing meeting should accomplish several goals. First, the laboratory personnel must be made aware of the major points of the audit findings. This way, any statements made in the laboratory audit report will not be a surprise to the laboratory and the laboratory is given a chance to respond to the findings before the report is written. Their responses can then be incorporated into the laboratory audit report. Secondly, the auditor(s) should emphasize that recommendations will be made even to the best of laboratories. The major goal of a laboratory audit is to determine the quality of data which is currently being generated by the laboratory and to identify problems (or potential problems) so that appropriate corrective action can be initiated by the laboratory. However, laboratory audits are also attended to give all laboratories, no matter their level of quality, ideas on how to become a better laboratory. The extent of the impact of the recommendation(s) will be indicated in the report.

4.4 ORGANIZATION AND PERSONNEL

The auditor(s) must evaluate the size and experience of the organization and the number, working hours, experience, and education of the personnel in the context of the FSP analytical work which is being performed by the laboratory being audited. The general information about the organization and personnel should be addressed by the auditor(s) during the initial introduction meeting. The experience and education of the personnel are best evaluated at a later date by obtaining the staff's resumes during this introductory meeting. However, if the

resumes or some other similar summaries are not available, questions of this nature must be asked by the auditor(s) throughout the audit.

4.5 SAMPLE RECEIPT AND STORAGE AREA

The auditor(s) should interview the designated sample custodian in this area of the laboratory. If a sample custodian has not been designated by the laboratory, the auditor(s) must interview any personnel responsible for receiving and logging in samples upon receipt at the laboratory. The auditor(s) must determine whether the laboratory personnel do anything to compromise the integrity of the samples during the check-in process, such as subjecting samples to any procedures which might lead to contamination or allowing temperature-preserved samples to warm to room temperature. In addition, the auditor(s) must verify that the laboratory personnel check and record all appropriate information regarding the condition of the samples upon receipt (i.e., Chains-of-Custody, cooler temperature, preservation, etc.). Furthermore, the auditor(s) must determine whether the sample storage area(s) are kept at the proper well-documented temperatures without any possibility of cross-contamination of samples. Finally, the auditor(s) must verify that the laboratory properly documents the condition of the samples upon receipt and that the information is determined from the check-in procedure. It must also be determined whether the tracking system in which the samples have been logged is adequate to ensure that holding times are being met.

4.6 SAMPLE PREPARATION AREA

The auditor(s) must evaluate the overall appearance and appropriateness of the size of the sample preparation area and the condition of the facility and equipment in the sample preparation area. The auditor(s) must verify that the equipment, water, and standards used in sample preparation are appropriately calibrated, stored, and/or maintained and that all appropriate information regarding these issues is properly documented. While in this area, the auditor(s) must interview the sample preparation technicians responsible for the preparations for the analyses of concern for the FSP. During the interviews, the auditor(s) must determine whether the sample preparation technicians follow good laboratory practices as well as the required analytical preparation methods. The auditor(s) must evaluate whether the laboratory is introducing the appropriate type and number of quality control samples at this point and that the sample technicians' procedures or equipment do not introduce possible contamination (i.e., glassware is cleaned properly) or inaccuracies (i.e., proper glassware and standards are used correctly). The auditor(s) must also evaluate the laboratory's sample tracking system through this area to verify that holding times are properly tracked. Finally, the auditor(s) must verify whether all preparation procedures are appropriately documented.

4.7 SAMPLE ANALYSIS INSTRUMENTATION

In the various sample analysis instrumentation areas of the laboratory, the auditor(s) must interview the analyst(s) responsible for the analyses of concern for the FSP. When possible, analysts will also be observed performing assigned tasks. The auditor(s) must evaluate whether the instrumentation used for the analyses of concern for the FSP is appropriate and is properly maintained. Through the interviews with the analysts and observations of actual tasks, it must be determined if each instrument is calibrated (according to the associated analytical method) with well-documented calibration standards at the required frequency and that these instrument

calibrations are properly documented. The auditor(s) must determine if method detection limit studies have been performed on each instrument used for analysis. In addition, the auditor(s) must determine if standards and quality control samples are being analyzed at an appropriate frequency and whether appropriate quality control limits are being utilized for these analyses. The analysts' practices must be evaluated for their attention to the quality control results and to the possibility of instrument carryover. The auditor(s) must evaluate whether appropriate corrective actions are being taken when standard or quality control results are out of the method-required or laboratory-determined limits. Finally, the auditor(s) must determine whether all the analysis procedures and results are properly documented.

4.8 DOCUMENTATION

The auditor(s) must evaluate the laboratory's documentation procedures throughout the audit. It should be determined if well-labeled, neat, bound notebooks are being used to document and trace standards, calibrations, laboratory procedures, and any other routine quality control check. The auditor(s) must examine notebooks and observe whether they have been properly reviewed at the laboratory and that there are no obliterations.

The auditor(s) must also evaluate the data package preparation practices. Such practices include the system used for the collection of various hard copy data, validation of results prior to data package release, completeness checks, generation of cover letters or case narratives, and retention of data packages at the laboratory.

4.9 QUALITY CONTROL MANUAL

The appropriateness and thoroughness of the laboratory's quality control manual, as well as the LQAM and analytical SOPs, must be evaluated prior to the audit. However, throughout the audit, the auditor(s) must verify if the laboratory is actually following the practices defined in their documents. Any deviations from the documented procedures must be discussed in the laboratory audit report.

4.10 DATA HANDLING

The auditor(s) must determine whether the laboratory's data handling procedures are adequate. Proper data handling techniques include the checking of calculations by a second person, documenting calculations, recording all corrective actions taken on rejected data, and properly documenting detection limits and quality control results. In addition, data must be retained at the laboratory for an appropriate amount of time.

4.11 SUMMARY

The auditor(s) must summarize the major points of the laboratory audit findings and the overall impact on the quality of the data issued from the laboratory. The summary should also reflect the overall attitude that the laboratory has toward quality assurance and quality control.

4.12 REPORT FORMAT

The laboratory audit report must contain the following sections in the following order. It must also contain a completed checklist as an attachment.

1. Introduction
2. Executive Summary

3. Audit Findings

The introduction should summarize who performed the audit, when the audit was performed, the name and location of the laboratory, and the laboratory's role in the FSP. The Executive Summary should address the major findings of the laboratory audit along with the possible impact on the laboratory's data quality. The Audit Findings should follow the major headings of the checklist summarizing the findings presented on the checklist along with any recommendations for improvement or corrective action. The report will be signed by the auditor(s) who performed the audit.

5.0 TRAINING

The auditor's conducting the laboratory audit must have demonstrated knowledge in laboratory quality assurance/quality control practices. This knowledge will include experience in analytical data validation and having conducted at least two prior laboratory audits.

APPENDIX 32

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that Environmental Standards data reviewers will use to validate volatile organic data generated by SW-846 Method 8260B for the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to SW-846 Method 8260B and/or other reference documents (*e.g.*, analytical SOPs) as applicable to the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the volatile organic data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines applies strictly to data generated by Contract Laboratory Program (CLP) protocol and it is not directly applicable to validation of data generated by SW-846 Method 8260B; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELForms:

- Organic field duplicate comparison Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls

Chemistry Applications:

- FIT
- Mass Spec Database
- Methods Database
- Target Version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- SW-846 Method 8260B.

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8260B (Rev. 2, 12/96).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the volatile data based on an evaluation of information presented in the data package deliverables. Compliance with SW-846 Method 8260B and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by General Electric

Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subsection of the QAR and will be included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the volatile organic data based on an evaluation of the information presented in the data package deliverables. The findings of the volatile organic data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, common contaminants that were not qualified, unusable results (R/UR), tentative identifications of target compounds (N), estimated results (J/UJ), tentatively identified compounds (TICs), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the volatile organic data and the resultant qualifications will be as stated on the attached Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B. It should be noted that the Project Manager should be consulted when the use of "professional judgement" is indicated on the attached table.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Temperature and Conditions Upon Receipt (See Note #1 for additional information)	4±2°C. Aqueous samples should not have headspace.	If temperature is >6°C but ≤10°C, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If temperature is >10°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If aqueous samples are received with headspace >pea-size but ≤5 mL, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If aqueous samples are received with headspace >5mL, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note the time of sample collection relative to receipt at the laboratory; use professional judgement if < 8 hours has elapsed from collect to receipt to determine if the qualification for elevated temperature applies.
Technical Holding Time (See Note #2 for additional information)	Chemically preserved (pH≤2 with HCl) aqueous samples analyzed for aromatic compounds should be analyzed within 14 days of collection. Preserved solid/soil samples should be analyzed within 14 days of collection. Unpreserved (pH>2) aqueous samples analyzed for aromatic compounds should be analyzed within 7 days of collection.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded (*i.e.,* >twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
GC/MS Tuning (BFB) (See Note #3 for additional information)	Ion abundances should meet the method acceptance criteria.	If mass calibration was not performed, qualify all associated data as unusable ("R/UR"). If mass assignment is in error, qualify all associated data as unusable ("R/UR"). Use professional judgement if abundance criteria are not met. (See Note #3.) Use professional judgement if samples are analyzed more than 12 hours after a compliant tune and there is no evidence of a compliant tune following the samples.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Initial Calibration (See Note #4 for additional information.)	Average relative response factor (RRF) for each compound should be ≥0.050. %RSD should be ≤15% or a calibration curve should be generated. If a curve is generated, r (linear) or coefficient determination (COD; quadratic) should be ≥0.99.	If target compounds have an average RRF <0.050, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If target compounds have 15%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target compounds have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target compounds have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgement when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) is <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the initial calibration standards and the samples associated were not performed similarly (*e.g.,* the initial calibration standards were heated and the samples were not heated), qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Continuing Calibration Verification (CCV) (See Note #5 for additional information.)	CCV RRFs for target compounds should be ≥0.050. %drift or % difference (%D) should be ≤20%.	If target compounds have an RRF <0.050, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If target compounds have 20%< %D ≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target compounds have %D>20% with a response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If target compounds have %D>90%, with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Internal Standards	Area counts of the internal standard peaks should be 50-200% of the internal standard area observed in the associated CCV standard. Retention time (RT) for any internal standard should not vary by more than ±30 seconds from RT in the associated CCV standard.	If a sample area count is outside of criteria (50-200% of associated CCV), qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as estimated ("UJ"). If extremely low sample area counts (<25%) are reported, qualify positive results for compounds quantitated using the extremely low internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as unusable ("UR"). If an internal standard RT varies by more than 30 seconds and no peaks are observed in the sample chromatogram, qualification is not necessary. Use professional judgement if peaks are observed in the sample chromatogram.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Blanks (See Notes #6 and for additional information.)	Summarize all results greater than the method detection limit (MDL) in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target compound is detected in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× (10× for common contaminants) blank result, qualify the positive result as "not-detected" ("U*"). If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× (10×) the blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks by GC/MS), qualify the positive results as unusable ("R") due to interference. If a TIC is observed in blank and sample, or if the TIC is a known laboratory artifact, qualify the TIC result as unusable ("R").
Surrogate Recovery	Use laboratory acceptance limits. Use 70%-130% as the default limits if the laboratory limits are unreasonable.	If recoveries of one or more surrogates > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If recoveries of one or more surrogates < lower limit, but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If recoveries of one or more surrogates <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	For accuracy use recovery limits of 70-130%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of a compound is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >130%, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is <70% but ≥30%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <30%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the precision criteria (see field duplicate usability criteria) for non-spiked compounds are not met, qualify positive results in the native sample as estimated ("J") and qualify "not-detected" results in the native sample as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate should also be qualified if the MS/MSD %Rs or RPD are outside of the criteria (as stated above for the native sample).
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	For accuracy, use recovery limits of 70-130%. For precision, use RPD limit of 20% for aqueous samples and 40% for solid samples.	If the recovery is >130%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <70% but ≥30%, qualify positive results in the associated samples as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <30%, qualify positive results in the associated samples as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in the associated samples as estimated ("J") and do not qualify "not-detected" results.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Field Duplicate (See Note #7 for additional information.)	Use precision limits of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid samples when sample results are ≥5× RL. Use limit of ± RL (±2× RL for solids) when at least one sample value is <5× RL. (Use one-half the RL as a numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results for non-compliant compounds in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Target Compound Identification (See Note #8 for additional information.)	Relative Retention Time (RRTs) should be ±0.06 RRT units of the standard RRT. Mass spectra of sample and current laboratory-generated standard should match.	Use professional judgement when applying the qualitative criteria for GC/MS analysis of target compounds. If it is determined that incorrect identifications were made or positive results were not reported, professional judgment should be used to determine which of the following options should be used: (1) qualify affected results as unusable ("R"); (2) correct reported results based on the raw data; or (3) contact laboratory for clarification. If a positive result meets some qualitative criteria but an evaluation of all qualitative criteria is inconclusive (possibly due to mass spectral interferences), use professional judgment to determine if result should be qualified "N".
Percent Solids	Solid samples with less than 50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.

Table for the Validation of Volatile Organic Compounds Generated by SW-846 Method 8260B

Quality Control Item	Usability Criteria	Action(s)
Compound Quantitation (See Note #9 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution.	If target compound results exceeds the instrument calibration range, qualify positive results as estimated ("J"). If a target compound result is <RL but ≥MDL, qualify positive results as estimated ("J"). Use professional judgment to determine whether sample reanalyses and dilutions should be compared to the original analysis. If the precision criteria (see field duplicate usability) between the original sample results and the reanalysis sample result are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
System Performance (See Note #10 for additional information.)	Professional judgment should be used when assessing the degradation of the system performance during analyses.	Use professional judgement to qualify the data if it is determined that system performance degraded during sample analysis.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data that were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of the Volatile Organic Data Generated by SW-846 Method 8260B

1. If several sample vials are received at the laboratory for one aqueous sample and the laboratory indicates that only one vial was received with head space, the data should not be qualified. It may be necessary to contact the laboratory to determine if the laboratory utilized a sample vial without head space.

2. If the pH is not checked by the laboratory, contact the Project Manager to determine if pH logs should be requested from the laboratory. If pH logs are not obtained, check the chain-of-custody (COC) to determine if the sample was properly preserved. Assume the pH is within the specified criteria if the COC indicates the sample was preserved and include a comment in the QAR indicating this.

   If a sample is acid-preserved (HCl for aqueous or sodium bisulfate for solids), the priority pollutant level (PPL) compound 2-chloroethyl vinyl ether may not be recovered because it is an acid-labile compound. This lack of recovery can be confirmed by examining the MS/MSD %Rs of an acid-preserved sample. In acid-preserved samples, qualify positive results for 2-chloroethyl vinyl ether as estimated ("J") and qualify "not-detected" results for 2-chloroethyl vinyl ether as unusable ("R").

3. Mass Tuning Criteria (alternate tuning criteria may be used by laboratory [*e.g.*, CLP, Method 524.2, or manufacturer instructions] provided that method performance is not adversely affected.)

Notes for the Validation of the Volatile Organic Data Generated by SW-846 Method 8260B

Mass	Intensity Required
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

If using professional judgement to determine an impact when ion abundance criteria are not met, the most important factors to consider are the empirical results that are relatively insensitive to location on the chromatographic profile and the type of instrumentation. Therefore, the critical ion abundance criteria for BFB are the m/z 95/96, 174/175, 174/176, and 176/177 ratios. The relative abundances of m/z 50 and 75 are of less importance.

4. If the initial calibration %RSD is >50%, the linearity of the first three initial calibration standards for the compound should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r ≥0.99), do not qualify "not-detected" results. If the first three initial calibration standards for the compound are not linear, qualify "not-detected' results as estimated ("UJ").

Notes for the Validation of the Volatile Organic Data Generated by SW-846 Method 8260B

Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the samples should be evaluated for false negatives.

5. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration standard is %D>20% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this in the QAR support documentation.

6. The frequency of equipment/rinse/storage blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day; unless only one was collected for a several-day sampling event. In instances when more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

Notes for the Validation of the Volatile Organic Data Generated by SW-846 Method 8260B

The following compounds are considered common laboratory contaminants/artifacts. If these compounds are reported as target compounds, the 10× rule applies for the evaluation of blank contamination. If these compounds are reported as TICs, they should be considered laboratory artifacts.

a. Common laboratory contaminants on CLP target compound list (TCL): methylene chloride, acetone, 2-butanone, and cyclohexane.

b Other common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, freons, and phthalates.

c. Solvent preservatives such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexanone, cyclohexanol, chlorocyclohexene, and chlorocyclohexanol.

d. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

e. Silicon-containing compounds (*e.g.*, trimethyl silonol).

If a sample result qualified "U*" is < the RL and the laboratory did not report the RL on the data tables or Form the positive result (*e.g.*, 8 µg/L) should be replaced with the RL (*e.g.*, 10 µg/L).

7. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance

Notes for the Validation of the Volatile Organic Data Generated by SW-846 Method 8260B

than aqueous duplicate results.

8. Generally, all ions present in standard mass spectrum at relative intensity >10% should be present in the sample mass spectrum; however, the concentration of the compound should be considered when evaluating ions with a relative intensity of ≤30% in the standard mass spectrum. In addition, data for ions with a mz of ≤40 amu are often not collected and generally are not used for evaluation purposes.

   Characteristic ions from the reference mass spectrum (three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum) should maximize in the same scan or within one scan of each other. Relative intensities of these ions should agree within ±30% between the standard and the sample spectra.

   Ions that are not present in the standard mass spectrum may be present in the sample mass spectrum without impacting the qualitative identification of the target compound. The presence of such ions at relative intensity 10% may be indicative of a coeluting compound. If feasible, the coeluting compound should be tentatively identified in order to evaluate whether the coeluting compound's mass spectrum contains any of the characteristic ions of the target compound. If a coeluting compound that has a mass spectrum containing characteristic ions of the target compound is tentatively identified, use professional judgment to evaluate the impact on the sample result.

Notes for the Validation of the Volatile Organic Data Generated by SW-846 Method 8260B

9. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

10. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

- High background levels or shifts in absolute RT of internal standards
- Excessive baseline rise at elevated temperatures
- Extraneous peaks
- Loss of resolution
- Peak failing or peak splitting that may result in an inaccurate quantitation

11. The RL will be defined on a project-specific basis. If the project-required RL is lower than the low initial calibration standard concentration, the Project Manager should be consulted for instructions on how to apply qualification related to the RL.

APPENDIX 33

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that Environmental Standards data reviewers will use to validate semivolatile organic data generated by SW-846 Method 8270C for the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to SW-846 Method 8270C and/or other reference documents (*e.g.*, analytical SOPs), as applicable to the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the semivolatile organic data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and it is not directly applicable to validation of data generated by SW-846 Method 8270C; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparison Rev 1-01.xls
- Organic field quadruplicate comparison Rev 1-01.xls
- Organic field triplicate comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Mass Spec Database
- Methods Database
- Target Version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- SW-846 Method 8270C.

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, EPA – SOP for Data Validation for SW-846 Method 8270C.

- Region III – Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the semivolatile data based on evaluation of information presented in the data package deliverables. Compliance with SW-846 Method 8270C and/or other reference documents (*e.g.*, analytical SOPs or QAPjPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate

any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratory(ies) to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subsection of the QAR and will be included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the semivolatile organic data based on an evaluation of the information presented in the data package deliverables. The findings of the semivolatile organic data usability assessment will be presented in terms data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

order: blank qualification, common contaminants that were not qualified, unusable results (R/UR), tentative identifications of targets (N), estimated results (J/UJ), tentatively identified compounds (TICs), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the semivolatile organic data and the resulting qualifications will be as stated on the attached Table for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C. It should be noted that the Project Manager should be consulted when the use of "professional judgement" is indicated on the attached table.

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C.	If temperature is >6°C but ≤10°C, no action is required. If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If temperature is >20°C, qualify positive results as estimated ("J") and qualify "not-detected" results unusable ("UR"). Note time of sample collection relative to receipt at laboratory; use professional judgment if < 8 hours has elapsed from collection to receipt to determine if the qualification for elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days of sample collection. Solid/soil samples should be extracted within 14 days of sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, >twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
GC/MS Tuning (DFTPP) (See Note #1 for additional information.)	Ion abundances should meet the method acceptance criteria.	If mass calibration was not performed, qualify all associated data as unusable ("R"/"UR"). If mass assignment is in error, qualify all associated data as unusable ("R"/"UR"). Use professional judgement if abundance criteria are not met. (See Note #1.) Use professional judgement if samples are analyzed more than 12 hours after a compliant tune and there is no evidence of a compliant tune following the samples.

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #2 for additional information.)	Average RRF for each compound should be ≥0.050. %RSD should be ≤15% or a calibration curve should be generated. If a curve is generated, r (linear) or coefficient of determination (COD; quadratic) should be ≥0.99.	If a target compound has an average RRF <0.050, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Compounds with 15%<%RSD≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. Compounds with 50%< %RSD ≤ 90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. Compounds with %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) is <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Continuing Calibration Verification (CCV) (See Note #3 for additional information.)	CCV RRFs for target compounds should be ≥0.050. %drift or %difference should be ≤20%.	If target compounds have an RRF<0.050, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If target compounds have 20%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target compounds have %D>20% with a response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target compounds have %D>90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

Quality Control Item	Usability Criteria	Action
Internal Standards	Area counts of the internal standard peaks should be 50-200% of the internal standard area observed in the associated CCV. Retention time (RT) of the internal standard should not vary more than ±30 seconds from the RT of the internal standards observed in associated CCV standard.	If a sample area count is outside of the criteria (50-200% of associated CCV), qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as estimated ("UJ"). If extremely low sample area counts (<25%) are reported, qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as unusable ("UR"). If an internal standard RT varies by more than 30 seconds and no peaks are observed in the sample chromatogram, qualification of data is not necessary. Use professional judgment if peaks are observed in the sample chromatogram.
Blanks (See Notes #4 and #10 for additional information)	Summarize all results greater than the method detection limit (MDL) in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target compound is detected in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× (10× for common contaminants) blank result, qualify the positive result as "not-detected" ("U*"). If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× (or 10×) blank result, qualification is not required. If gross contamination exists (*i.e.,* saturated peaks by GC/MS), qualify the positive results as unusable ("R") due to interference. If a TIC is observed in blank and sample or if the TIC is a known laboratory artifact, qualify as unusable ("R") due to interference.

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

Quality Control Item	Usability Criteria	Action
Surrogate Recovery (See Note #5 for additional information.)	Use laboratory acceptance limits. Use default limits of 20-150% if laboratory limits are unreasonable.	If the recoveries of one or more surrogate in either fraction (acid or base) are > upper limit, qualify positive results for that fraction as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogate in either fraction (acid or base) are < lower limit but ≥10%, qualify positive results for that fraction as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogate in either fraction (acid or base) are < 10%, qualify positive results for that fraction as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Use 50-135% as recovery limits. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of a compound is > 4× spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is > 135%, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is <50% but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" result. If the precision criteria (see field duplicate usability criteria) for non-spiked compounds are not met, qualify positive results in the native sample as estimated ("J") and qualify "not-detected" results in the native sample as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate should also be qualified if the MS/MSD %Rs or RPD are outside of the criteria (as stated above for the native sample).

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

Quality Control Item	Usability Criteria	Action
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	Use 50-135% as recovery limits. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	If the recovery is >135%, qualify all positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <50% but ≥10%, qualify all positive results in all associated samples as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <10%, qualify all positive results in all associated samples as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results as estimated ("J") and do not qualify "not-detected" results.
Field Duplicate (See Note #6 for additional information.)	Use precision limits of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid samples when sample results are ≥5× RL. Use limit of ± RL (±2× RL for solids) when at least one sample value is <5× RL. (Use one-half the RL as a numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results for noncompliant compounds in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

Quality Control Item	Usability Criteria	Action
Target Compound Identification (See Note #7 for additional information.)	Relative Retention Time (RRT) should be ±0.06 RRT units of the standard RRT. Mass spectra of sample and current laboratory-generated standard should match.	Use professional judgement when applying the qualitative criteria for GC/MS analysis of target compounds. If it is determined that incorrect identifications were made or positive results were not reported, professional judgement should be used to determine which of the following options should be used: (1) qualify affected results as unusable ("R"); (2) correct reported results based on the raw data; or (3) contact laboratory for clarification. If a positive result meets some qualitative criteria but an evaluation of all qualitative criteria is inconclusive (possibly due to mass spectral interferences), use professional judgment to determine if result should be qualified "N".
Percent Solids	Solid samples with less than 50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.
Compound Quantitation (See Note #8 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution.	If a target compound result exceeds the instrument calibration range, qualify the positive result as estimated ("J"). If a target compound result is < RL but ≥ MDL, qualify positive results as estimated ("J"). Use professional judgement to determine whether sample reanalyses and dilutions should be compared to the original analyses. If the precision criteria (see field duplicate usability) between the original sample result and the reanalysis sample result are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target compound result is <RL but ≥MDL, qualify positive results as estimated ("J").
System Performance (See Note #9 for additional information.)	Professional judgement should be used when assessing the degradation of the system performance during analyses.	Use professional judgement to qualify the data if it is determined that system performance degraded during sample analysis.

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

Quality Control Item	Usability Criteria	Action
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgment to determine the need to qualify data not qualified based on the QC previously addressed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

1. GC/MS Tuning Criteria (Alternate tuning criteria may be used by the laboratory [*e.g.*, CLP, Methods 525, or manufacturer instructions], provided that method performance is not adversely affected.)

m/z	ion abundance criteria
51	30-60% of m/z 198
68	less than 2% of m/z 69
70	less than 2% of m/z 69
127	40-60% of m/z 198
197	less than 1% of mass 198
198	base peak, 100% relative abundance
199	5-9% of m/z 198
275	10-30% of m/z 198
365	greater than 1% of m/z 198
441	present, but less than m/z 443
442	greater than 40% of m/z 198
443	17-23% of m/z 442

If using professional judgement to determine impact when ion abundance criteria are not met, some of the most critical factors in the DFTPP criteria are the non-instrument specific requirements that are also unduly affected by the location of the spectrum on the chromatographic profile. The m/z ratios for 198/199 and 442/443 are critical. These ratios are based on the natural abundances of C^{12} and C^{13} and should always be met. Similarly, the relative abundances for m/z 68, 70, 197, and 441 indicate the condition of

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

the instrument and the suitability of the resolution adjustment and are very important. For the ions at m/z 51, 127, and 275, the actual relative abundance is not as critical. The relative abundance of m/z 365 is an indicator of suitable instrument zero adjustment. If relative abundance of m/z 365 is zero, MDLs may be affected.

2. If the initial calibration %RSD is >50%, the linearity of the first three initial calibration standards for the compound should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r ≥0.99), do not qualify "not-detected" results. If the first three initial calibration standards for the compound are not linear, qualify "not-detected" results as estimated ("UJ").

   Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the samples should be evaluated for false negatives.

3. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

If the continuing calibration standard is %D>15% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this in the QAR support documentation.

4. The frequency of equipment/rinse blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day; unless, if only one was collected for a several-day sampling event. In instances when more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

   The following compounds are considered common laboratory contaminants/artifacts. If these compounds are reported as target compounds, the 10× rule applies for the evaluation of blank contamination. If these compounds are reported as TICs, the compounds should be considered laboratory artifacts.

   - Common phthalate contaminants.
   - Other common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, and certain freons.
   - Solvent preservatives, such as cyclohexene, which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanone.

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

- Aldol reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.
- Silicon containing compounds (*e.g.*, trimethylsilanol)

If a sample result qualified "U*" is <RL and the laboratory did not report the RL on the data tables or Form I the positive result (*e.g.*, 8 µg/L) should be replaced with the RL (*e.g.*, 10 µg/L).

5. The surrogate recovery limits do not apply to samples analyzed at dilutions greater than five-fold. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, greater than a five-fold dilution will affect the ability to even detect the surrogate. If a sample was analyzed at a five-fold dilution or less and the surrogates were not detected in the sample, qualify positive results as estimated ("J") and "not-detected" results estimated ("UJ").

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than aqueous duplicate results.

7. Generally, all ions present in the standard mass spectrum at relative intensity >10% should be present in the sample mass spectrum; however, the concentration of the

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

compound should be considered when evaluating ions with a relative intensity of ≤30% in the standard mass spectrum. In addition, data for ions with a m/z of ≤40 are often not collected and generally are not used for evaluation purposes.

Characteristic ions from reference mass spectrum (three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum) should maximize in the same scan or within one scan of each other. Relative intensities of these characteristic ions should be within ±30% between the standard and sample spectra.

Ions that are not present in the standard mass spectrum may be present in the sample mass spectrum without impacting the qualitative identification of the target compound. The presence of such ions at relative intensity greater than 10% may be indicative of a coeluting compound. If feasible, the coeluting compound should be tentatively identified in order to evaluate whether the coeluting compound's mass spectrum contains any of the characteristic ions of the target compound. If a coeluting compound that has a mass spectrum containing the characteristic ions of the target compound, use professional judgment to evaluate the impact on the sample result is tentatively identified.

N-nitrosodiphenylamine (TCL, PPL, App IX) cannot be distinguished from diphenylamine (App IX) because *N*-nitrosodiphenylamine degrades to diphenylamine in the injection port. A note to this effect should be included in the qualifier section if these compounds are detected. In addition, benzo(b)fluoranthene and benzo(k)fluoranthene

Notes for the Validation of Semivolatile Organic Data Generated by SW-846 Method 8270C

sometimes coelute and have similar mass spectra; therefore, if either of these compounds is detected in samples, the chromatograms of the samples and standards should be evaluated for separation. If coelution is observed, qualify "J" and/or "N" using professional judgment.

8. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis to a diluted reanalysis.

9. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

- high background levels or shifts in absolute retention times of internal standards
- excessive baseline rise at elevated temperatures
- extraneous peaks
- loss of resolution
- peak tailing or peak splitting that may result in inaccurate quantitation

10. The RL will be defined on a project-specific basis. If the project-required RL is lower than the low initial calibration standard concentration, the Project Manager should be consulted for instructions on how to apply qualification related to the RL.

APPENDIX 34

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate organochloride pesticide data generated by SW-846 Method 8081A for General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to SW-846 Method 8081A and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the pesticide data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by SW-846 Method 8081A; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls

Chemistry Applications:

- FIT
- Methods Database
- Target Version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- SW-846 Method 8081A.

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8081A (Rev 2. 12/96).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the pesticide data based on an evaluation of information presented in the data package deliverables. Compliance to SW-846 Method 8081A and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of certain deficiencies prior to submittal of the QAR (if feasible and sanctioned by General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a

significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the pesticide data based on an evaluation of the information presented in the data package deliverables. The findings of the pesticide data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable (R/UR) results, tentative identifications of target compound results (N), estimated (J/UJ) results, field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the pesticide data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A. It should be noted

that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >6° but ≤10°C, no action is required. If temperature is > 10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If temperature is >20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory; use professional judgement if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days after sample collection. Solid/soil samples should be extracted within 14 days after sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
GC Instrument Performance (See Note #1 for additional information.)	% Breakdown for 4,4′-DDT and endrin should be ≤15% for both GC columns.	Use professional judgement to determine if the associated sample data should be qualified if the instrument performance standard was not analyzed at the proper frequency. See Note #1 for action if the instrument performance standard criteria are not met.

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #2 for additional information.)	%RSD should be ≤20% or a calibration curve should be generated. If a curve is generated, the curve should have r (linear) or coefficient of determination (COD; quadratic) must be ≥0.99.	If target compounds have 20%<%RSD≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target compounds have 50%<%RSD≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target compounds have %RSD>90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgement when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) is <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Continuing Calibration Verification (CCV) (See Note #3 for additional information.)	%drift or %difference (%D) should be ≤15%.	Qualification is for all samples on both sides of the out-of-criteria calibration standards. If target compounds have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target compounds have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target compounds have %D>90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Retention Time Windows (See Note #4 for additional information.)	All target compound retention times (RTs) should be within the established RT windows. RT windows should be estimated or defined by the laboratory as 3× the standard deviation of three non-sequential standards over a 72-hour period.	If the CCV RT windows are not within the specific RT windows, evaluate the chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCVs, the direction of the RT drift should be applied to the sample chromatograms.
Blanks (See Note #5 and Note #10 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target compound is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5x the blank result, qualify the positive result as "not detected" ("U*"). If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× the blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on both GC columns), qualify the positive results as unusable ("R") due to interference.
Internal Standards (if used)	Area counts of the internal standard peaks should be 50-200% of the internal standard area observed in the associated CCV standard. RT for any internal standard should not vary by more than ±30 seconds from RT in the associated CCV standard.	If a sample area count is outside of criteria (50-200%), qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as estimated ("UJ"). If extremely low sample area counts (<25%) are reported, qualify positive results for compounds quantitated using the extremely low internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as unusable ("UR"). If an internal standard RT varies by more than 30 seconds and no peaks are observed in the sample chromatogram, qualification is not necessary. Use professional judgement if peaks are observed in the sample chromatogram.

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Surrogates (See Note #6 for additional information.)	Use laboratory acceptance limits. Use 20-150% as a default limit if the laboratory limits are unreasonable.	If samples are analyzed on two columns, samples should only be qualified if the out-of-criteria surrogate result is reported from the same column as the sample results. If the recoveries of one or more surrogates are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	For accuracy, use recovery limits of 50-135%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of a compound is 4× the spiking level for that compound. RPDs calculated using MS/MSD result can be used to evaluate precision. If the recovery is > 135%, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" results. If the recovery is < 50% but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" result. If the precision criteria (see field duplicate usability criteria) are not met for non-spiked compounds, qualify the positive result as estimated ("J") and qualify the "not-detected" result as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	For accuracy, use recovery limits of 50-135%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	If the recovery > 135%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery < 50% but ≥10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Field Duplicate (See Note #7 for additional information.)	Use precision limits of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid samples when sample results are ≥5× RL. Use limit of ± RL (±2× RL for solids) when at least one sample value is <5× RL. (Use one-half the RL as a numerical value for any "not-detected" results in the RPD calculations)..	If the criteria are not met, qualify positive results for the non-compliant compound in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Solid samples with less than 50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Compound Quantitation (See Note #8 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution.	If a target compound result exceeds the instrument calibration range, qualify positive results as estimated ("J"). Use professional judgement when evaluating sample reanalyses and dilutions. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target compound result is <RL but ≥MDL, qualify positive results as estimated ("J").
System Performance (See Note #9 for additional information.)	Professional judgement should be used when assessing the degradation of system performance during analyses.	Use professional judgement to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

1. $$\%\ \text{breakdown for 4,4′ - DDT} = \frac{\text{Total DDT degradation peak area (DDE+ DDD)}}{\text{peak areas (DDT + DDE +DDD)}} \times 100$$

$$\%\ \text{breakdown for Endrin} = \frac{\text{Total Endrin degradation peak area (Endrin aldehyde + Endrin ketone)}}{\text{peak areas (Endrin + Endrin aldehyde + Endrin ketone)}} \times 100$$

Qualification Due to High 4,4′-DDT (or Endrin) Breakdown				
Column # / Met criteria?	If 4,4′-DDT (or Endrin):	And if 4,4′-DDD and/or 4,4′-DDE (or Endrin ketone and/or Endrin aldehyde):	Then flag 4,4′-DDT (or Endrin):	And flag **positives** for 4,4′-DDD and/or 4,4′-DDE (or Endrin ketone and/or Endrin aldehyde):
(1)/no (2)/yes	+ +	any +'s +'s or ND's	"J" column (1) OK column (2)	"JN" column (1) "N" column (2)
(1)/no (2)/yes	ND + > RL^+	any +'s +'s or ND's	ND "R"	"JN" column (1) "N" column (2)
(1)/no (2)/yes	ND + < RL^+	any +'s +'s or ND's	ND OK	"JN" column (1) "N" column (2)
(1)/no (2)/yes	+ +	all ND's +'s or ND's	*	NA
(1)/no (2)/yes	ND + or ND	all ND's +'s or ND's	ND OK	NA
(1)/no (2)/yes	+ or ND ND	+'s or ND's +'s or ND's	ND OK	OK
(1)/no (2)/no	ND + or ND	any +'s any +'s	ND "R"	"JN"
(1)/no (2)/no	+ +	any +'s any +'s	"J"	"JN"
(1)/no (2)/no	+ ND	all ND's any +'s	ND "R"**	NA
(1)/no (2)/no	+ +	all ND's all ND's	*	NA
(1)/no (2)/no	+ or ND ND	+'s or ND's all ND's	ND OK	NA

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Where:

+ A peak was observed in the RT window for this pesticide on the corresponding GC column indicating a tentative identification for this pesticide. The positive result may quantitate to be below, at, or above the RL.

ND Not Detected regardless of the RL (flat baseline was observed in the area of the chromatogram where this compound would elute if it were truly present in the sample).

RL Reporting limit (RL) – will be defined on a project basis. If the project-required RL is greater than the low initial calibration standard concentration, the Project Manager should be consulted about application of qualifications related to the RL. Positives from a non-quantitative (conformational) GC column analysis should be considered above the RL for evaluation purposes, whether or not the result was quantitated above the RL on this non-quantitative column.

NA Not Applicable. Pesticide was not detected and only positive results are impacted.

* Although high breakdown was indicated by the associated standard on at least one column used for analysis, this positive result for 4,4′-DDT (or Endrin) has <u>not</u> been qualified because the breakdown components were not detected in the sample analysis on the noncompliant column(s). It is questionable, however, whether the peak(s) used for identification on the noncompliant column(s) truly represents 4,4′-DDT (or Endrin)

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

because high breakdown was indicated by the associated standard. It is highly unusual not to detect the breakdown components in the presence of 4,4′-DDT (or Endrin).

** This "not-detected" result for 4,4′-DDT (or Endrin) has been qualified as unusable ("R") because the breakdown components were observed in the sample analysis on this column on which high breakdown was indicated by the associated standard. However, it should be noted that the breakdown components were <u>not</u> detected in the sample analysis on the other column on which high breakdown was also indicated by the associated standard. It is questionable whether the peak used for identification on this other column truly represents 4,4′-DDT (or Endrin) because high breakdown was indicated by the associated standard on this other column. It is highly unusual not to detect the breakdown components in the presence of 4,4′-DDT (or Endrin).

2. If the initial calibration curve %RSD>50%, the linearity of the first three initial calibration standards should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r > 0.99), do not qualify "not-detected" results. If the first three initial calibration standards for the compound are not linear, qualify "not-detected" results as estimated ("UJ").

Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the sample should be evaluated for false negatives.

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Positive results should only be qualified if the results were reported from the out-of-criteria column. If samples are analyzed on two columns and an out-of-criteria initial calibration is reported on either column, the sample should be evaluated for tentative positive results. If a tentative positive result is observed on the compliant column, qualify "not-detected" results (laboratory should only report positive results that have been confirmed on a second column) as estimated ("UJ"). If an out-of-criteria initial calibration is reported on both columns, qualify "not-detected" results as estimated ("UJ") whether or not tentative positive results were observed.

3. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration standard is %D>15% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this within the QAR support documentation.

   Positive results should only be qualified if the results were reported for the out-of-criteria column. If samples are analyzed on two columns and an out-of-criteria CCV is reported on either column, the samples should be evaluated for tentative positive results. If a tentative positive result is observed on the compliant column, qualify "not-detected"

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

results (laboratory should only report positive results that have been confirmed on a second column) as estimated ("UJ"). If an out of criteria CCV is reported on both columns, qualify "not-detected" results as estimated ("UJ") whether or not tentative positive results were observed.

4. Use professional judgement when evaluating sample chromatograms. If the chromatograms reveal peaks corresponding to target compounds of interest using expanded RT windows, reported positive sample results for the compound outside of the RT window are replaced with the RL and are qualified as "not-detected" ("U"). If the chromatograms reveal peaks that interfere with potential detection of a target compound, reported positive results for that compound are qualified as unusable ("R").

5. The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected on the same day, unless only one blank was collected for a several-day sampling event. In instances when more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

   If a sample result qualified "U*" is <RL and the laboratory did not report the RL on the data tables or Form I, the positive result (*e.g.*, 8 µg/L) should be replaced with the RL (*e.g.,* 10 µg/L).

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank. If a positive result for a target compound is detected on the first column and not on the second column, the positive results should be qualified as tentative in all associated samples ("N"). Use professional judgement to determine if the result should be qualified as "not-detected" ("U*").

6. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. If a sample was analyzed at a five-fold dilution or less and either surrogate was not detected in the sample, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

7. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Soil duplicate results will have greater variance than aqueous duplicate results.

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

8. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

   If the laboratory provides the dual-column results for samples and both columns are quantitative, evaluate the %D between the results reported for both columns. If the sample results are ≥5× RL and the %D is >40% but ≤90%, qualify positive results as estimated ("J"). If the sample results are ≥5× RL and the %D is >90%, qualify positive results as unusable ("R"). If sample results are <5× RL and the difference between columns is >±2×RL, qualify results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

9. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   - high background levels or shifts in absolute RTs of internal standards
   - excessive baseline rise at elevated temperature
   - extraneous peaks
   - loss of resolution
   - peak tailing or peak splitting that may result in inaccurate quantitation

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

10. The RL will be defined on a project-specific basis. If the project-required RL is less than the low calibration standard concentration, the Project Manager should be consulted for instructions about application of qualification related to the RL.

APPENDIX 35

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate herbicide data generated by SW-846 Method 8151A for the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to SW-846 Method 8151A and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the herbicide data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and it is not directly applicable to validation of data generated by SW-846 Method 8151A; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCEL forms:

- Organic field duplicate comparison Rev 1-01.xls
- Organic field quadruplicate comparison Rev 1-01.xls
- Organic field triplicate comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- SW-846 Method 8151A and related preparation and cleanup methods.

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses.

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the herbicide data based on an evaluation of information presented in the data package deliverables. Compliance to SW-846 Method 8151A and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratory(ies) to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by General Electric

Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subsection of the QAR and will be included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the herbicide data based on an evaluation of the information presented in the data package deliverables. The findings of the herbicide data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the Organic Data Evaluation Section of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), tentative identifications of target compounds (N), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the herbicide data and the resultant qualifications will be as stated on the attached Table for the Validation of

Herbicide Data Generated by SW-846 method 8151A. It should be noted that the Project Manager should be consulted when the use of "professional judgement" is indicated on the attached table.

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C, but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as "UJ". If temperature is >20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory; use professional judgement if < 8 hours has elapsed from collect to receipt to determine if the qualification for elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days of sample collection. Solid samples should be extracted within 14 days of sample collection. All matrices should be analyzed within 40 days after extraction.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results ("UJ"). If holding time is grossly exceeded (*i.e.,* >twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #1 for additional information.)	%RSD should be <20% or a calibration curve should be generated. If a curve is generated, r (linear) or coefficient of determination (COD; quadratic) should be ≥0.99.	If any target compound result is associated with a low concentration initial standard that is not visible on the chromatogram, qualify "not-detected" results for that compound as estimated ("UJ"). If the standards indicate a severe lack of sensitivity (*e.g.*, the higher calibration standards are barely visible) the reviewer may qualify the "not-detected" results for that compound as unusable ("UR"); professional judgement should be used to determine the magnitude of the bias. Compounds with 20%<%RSD≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. Compounds with 50%<%RSD≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. (See Note #1) Compounds with %RSD >90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgement when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the initial calibration standards and the samples associated were not performed similarly (*e.g.*, the initial calibration standards were analyzed under different chromatographic conditions), qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Continuing Calibration Verification (CCV) (See Note #2 for additional information.)	%drift or % difference (%D) should be ≤15%.	Qualification is for all samples on both sides of the out of criteria CCV. If target compounds have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target compounds have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. (See Note #2) If target compounds have %D>90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If any target compound is not visible in the chromatogram qualify "not-detected" results as unusable ("UR").
Internal Standards (If used)	Area counts of the internal standard peaks should be 50-200% of the area of the target analytes in the mid-point calibration analysis. RT for any internal standard changes should only be ±30 seconds from the last calibration check standard.	If an area count is outside of the criteria (50-200%), qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as estimated ("UJ"). If extremely low area counts (<25%) are reported, qualify positive results for compounds quantitated using the extremely low internal standard as estimated ("J") and qualify "not-detected" results for compounds using that internal standard as unusable ("UR"). If an internal standard RT varies by more than 30 seconds and no peaks are observed in the sample chromatogram, qualification of data is not necessary. Use professional judgement if peaks are observed in the sample chromatogram.

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Retention Time Windows (See Note #3 for additional information.)	All target compound retention times (RTs) should be within the established RT windows. RT windows should be estimated or defined by the laboratory or 3× the standard deviation of three non-sequential standards over a 72-hour period	If the CCV RT windows are not within the specific RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCV, apply the direction of the RT drift to the sample chromatograms.
Blanks (See Notes #4 and #9 for additional information.)	Summarize all results greater than the method detection limit (MDL) in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target compound is detected in a blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not-detected" ("U*"). If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× the blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.
Surrogates (See Note #5 for additional information.)	Use laboratory acceptance limits. Use 20-150% as default limits if the laboratory limits are unreasonable.	If the recoveries of one or more surrogate are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogate are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogate are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicates (MS/MSD)	For accuracy, use recovery limits of 50-135%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPD calculated on %Rs) that are outside of criteria if the original concentration of a compound is >4× spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery > 135%, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" results. If the recovery < 50% but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native samples estimated ("UJ"). If the recovery < 10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" results. If the precision criteria (see field duplicate usability criteria) are not met for non-spiked compounds, qualify positive results in the native sample as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if the MS/MSD recoveries or RPD are outside of the criteria (as stated above for the native sample).

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	For accuracy, use recovery limits of 50%-135%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	If the recovery > 135%, qualify positive results for that compound in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery < 50% but ≥ 10%, qualify positive results for that compound in all associated samples as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery <10%, qualify positive results for that compound in all associated samples as estimated and qualify "not-detected" results as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive results for that compound in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Field/Laboratory Duplicate (See Note #6 for additional information.)	Use a default limit of 20% RPD (%RSD for triplicate or quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate or quadruplicate analyses) for solid samples for sample results ≥5× RL. Use a default limit of ± RL for aqueous samples and ±2× RL for solid samples when at least one sample value is <5× RL	If the criteria are not met, qualify positive results for out of criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Solid samples with <50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Compound Quantitation (See Note #7 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution.	If a target compound result exceeds the instrument calibration range, qualify positive results as estimated ("J"). If a target compound result is <RL but ≥MDL, qualify positive results as estimated ("J"). Use professional judgement to determine whether sample reanalyses and dilutions should be compared to the original analysis. If the precision criteria (see field duplicate usability) between the original sample results and the reanalysis sample result is not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
System Performance (See Note #8 for additional information.)	Professional judgement should be used when assessing the degradation of the system performance during analyses.	Use professional judgement to qualify the data if it is determined that the system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Herbicide Data Generated by SW-8151A

1. If the initial calibration %RSD is >50%, the linearity of the first three initial calibration standards for the compound should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r ≥ 0.99), do not qualify "not-detected" results. If the first thee initial calibration standards for the compound are not linear, qualify "not-detected" results as estimated ("UJ").

   Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the samples should be evaluated for false negatives.

2. If instrument instability (*i.e.*, several CCVs with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential CCVs, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration standard is %D>15% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this in the QAR support documentation.

   Positive results should only be qualified if the results were reported from the out of criteria column. If samples are analyzed on two columns and an out of criteria CCV is reported on either column, then the samples should be evaluated for tentative positive

Notes for the Validation of Herbicide Data Generated by SW-8151A

results. If a tentative positive result is observed on the compliant column, qualify "not-detected" results (laboratory should only report positive results that have been confirmed on a second column) as estimated ("UJ"). If an out of criteria CCV is reported on both columns, qualify "not-detected" results as estimated ("UJ") whether or not tentative positive results were observed.

3. Use professional judgement when evaluating sample chromatograms. If the chromatograms reveal peaks corresponding to target compounds of interest using expanded RT windows, reported positive sample results for the compound outside the RT window are replaced with the RL and qualified as "not-detected" ("U"). If chromatograms reveal peaks that interfere with potential detection of a target compound, reported positive results for the compound are qualified as unusable ("R").

4. When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the method blank associated with those samples should be analyzed on at least one of those instruments. A solvent blank should be analyzed on all other instruments on which the set of samples was analyzed to demonstrate that the instrument is not contributing contaminants to the samples.

   The frequency of equipment/rinse blanks is determined during the sampling event. The results of equipment/rinse blanks should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day; however, if only one was collected for a several-day sampling event. In instances when more than one blank is

Notes for the Validation of Herbicide Data Generated by SW-8151A

associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

If a sample result qualified "U*" is less than the RL and the laboratory did not report the RL on the data tables or Form I's, then the positive result (*e.g.*, 8 µg/L) should be replaced with the RL (*e.g.*, 10 µg/L).

5. The surrogate recovery limits do not apply to samples analyzed at dilutions greater than five-fold. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, greater than a five-fold dilution will affect the ability to even detect the surrogate. If a sample was analyzed at five-fold dilution or less and the surrogate was not detected in the sample, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicates should only be applied to the original sample and its laboratory duplicate. It is also expected that soil duplicate results will have a greater variance than aqueous duplicate results.

Notes for the Validation of Herbicide Data Generated by SW-8151A

7. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

   If the laboratory provides dual column results for samples and both columns are quantitative then the %D between the results reported for both columns needs to be evaluated. If sample results are ≥5× RL and the %D is >40% but ≤90%, qualify positive results as estimated ("J"). If sample results are >5× RL and the %Ds is >90%, qualify positive results as unusable ("R"). If sample results are <5× RL and the differences between columns is >±2×RL, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

8. Poor chromatographic performance affects both qualitative (lower dilution analyses) and quantitative results. Indications of substandard performance include:

   - high background levels or shifts in absolute retention times of internal standards
   - excessive baseline rise at elevated temperature
   - extraneous peaks
   - loss of resolution
   - peak tailing or peak splitting that may result in inaccurate quantitation

9. The RL will be defined on a project-specific basis. If the project-required RL is less than the low initial calibration standard concentration, the Project Manager should be consulted for instructions on how to apply qualification related to the RL.

APPENDIX 36

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate PCB data generated by SW-846 Method 8082 for the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to SW-846 Method 8082 and/or other reference documents (*e.g.*, analytical SOPs) as applicable to the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the PCB data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by the Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by SW-846 Method 8082; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls
- Aroclor.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- SW-846 Method 8082.

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8082 (Rev 2. 12/96).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the PCB data based on an evaluation of information presented in the data package deliverables. Compliance to SW-846 Method 8082 and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by to General Electric Company). At a minimum, corrections required to allow for a full evaluation of

the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the PCB data based on an evaluation of the information presented in the data package deliverables. The findings of the PCB data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) to General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination (U*), unusable results (R/UR), estimated results (J/UJ), tentative identifications of target compound results (N), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the PCB data and the resultant qualifications will be as stipulated on the attached Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082. It should be noted that the project

manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature is > 20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgement should be used if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days of sample collection. Solid/soil samples should be extracted within 14 days of sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information.)	%RSD should be ≤20% and a calibration curve should be generated. For the calibration curve, r (linear) or coefficient of determination (COD; quadratic) must be ≥0.99.	If target Aroclors have 20%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target Aroclors have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target Aroclors have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgement when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) is <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Continuing Calibration Verification (CCV) (See Note #2 for additional information.)	%drift or %difference should be ≤15%.	Qualification is for all samples on both sides of the out-of-criteria calibration standards. If target Aroclors have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target Aroclors have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target Aroclors have %D>90% with the response indicating a sensitivity decrease qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Retention Time Windows (See Note #3 for additional information.)	All target Aroclor peak retention times (RTs) should be within the established RT windows. RT windows should be estimated or defined by the laboratory or 3× the standard deviation of three non-sequential standards over a 72-hour period.	If the CCV RT windows are not within the specified RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCV, the direction of the RT drift should be applied to the sample chromatograms.
Blanks (See Note #4 and Note #9 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target Aroclor is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("U*"). If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Surrogates (See Note #5 for additional information.)	Use 60-140% as limits.	If the recoveries of one or more surrogates are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (IF REQUESTED)	For accuracy, use recovery limits of 60-140%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of an Aroclor is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >140%, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is <60% but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the precision criteria (see field duplicate usability criteria) for non-spiked compounds are not met, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native samples as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Laboratory Control Samples (LCS)	For accuracy, use recovery limits of 60-140%.	If the recovery is >140%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <60% but ≥10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR").
Field/Laboratory Duplicate (See Note #6 and Note #9 for additional information)	Use precision limits of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid samples when sample results are ≥5× RL. Use limit of ± RL (±2× RL for solids) when at least one sample value is <5× RL. (Use one-half the RL as a numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results for the out-of-criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Solid samples with less than 50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Compound Quantitation and Qualititative Identification (See Notes #3, #7, and #8 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution. All sample chromatograms must be evaluated to determine whether the laboratory correctly identified the correct Aroclor based upon pattern recognition, peak retention times, and qualititative matching with the associated calibration standards.	If a target Aroclor result exceeds the instrument calibration range, qualify positive result as estimated ("J"). Use professional judgement to determine whether sample reanalyses and dilutions should be compared to the original analyses. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target Aroclor is <RL but ≥MDL, qualify positive results as estimated ("J"). Use professional judgement to determine whether qualititative identifications are accurate and whether data qualification is necessary.
System Performance (See Note #8 for additional information.)	Professional judgement should be used when assessing the degradation of system performance during analyses.	Use professional judgement to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

1. If the initial calibration curve %RSD>50%, the linearity of the first three initial calibration standards should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r ≥0.99), do not qualify "not-detected" results. If the first three initial calibration standards for the compound are not linear, qualify "not-detected" results as estimated ("UJ").

   Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the sample should be evaluated for false negatives.

   The initial calibration is performed using five-point initial calibration curves for Aroclor-1221, Aroclor-1242, and Aroclor-1254 because these Aroclors are the target compounds for the project. Single-point calibrations for each of the other Aroclors should be analyzed at or just above the quantitation limits for pattern recognition. Curves (linear not through the origin or a quadratic) should be generated and relative standard deviations (%RSDs) must be ≤20%. If positive results are detected, other than the three Aroclors in the multi-peak initial calibration curves, in the samples, then a five-point initial calibration curve should be analyzed for the Aroclor in question and the extracts must be re-injected. Surrogates will be added to the Aroclor-1254 initial calibration curve and all surrogates in the samples/blanks/QC samples/CCVs will be quantitated based on the Aroclor-1254 initial calibration.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

2. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration standard is %D>15% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this within the QAR support documentation.

   The continuing calibration verification standard analysis utilizes only Aroclor-1221, Aroclor-1242, and Aroclor-1254; therefore, if the %D>15% for these three Aroclors, the impact on the other Aroclors (-1016, -1232, -1248, and -1260) should be evaluated. The impact depends upon the retention times of the other Aroclors. The retention times should be evaluated to determine which Aroclor (-1221, -1242, or -1254) will affect the other Aroclors. Usually, Aroclors-1016, Aroclor-1221, Aroclor-1232, Aroclor-1242, and Aroclor-1248 fall within similar retention times and Aroclor-1248, Aroclor-1254, and Aroclor-1260 fall within similar retention times; therefore, if %D>15% for Aroclor-1242 or Aroclor-1221, then –1016, -1232, and -1248 should be qualified (as stated above), and if %D>15% for Aroclor-1254, then Aroclor-1248 and Aroclor-1260 should be qualified (as stated above).

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

3. Use professional judgement when evaluating sample chromatograms. The Aroclor patterns should be evaluated when an RT shift is observed. If the Aroclor pattern is present, qualification is not necessary. If the chromatograms reveal peaks corresponding to target compounds of interest using expanded RT windows and the surrogate compounds do not display a similar shift in RT, reported positive sample results for the compound outside of the RT window are replaced with the RL and qualified as "not-detected" ("U").

   If the chromatograms reveal peaks that interfere with potential detection of a target compound, qualify reported positive results for the compound as unusable ("R").

4. The frequency of equipment/rinse blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected in the same day, unless only one blank was collected for a several-day sampling event. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

   If a sample result qualified "U*" is <RL and the laboratory did not report the RL on the data tables or Form I, the positive result (*e.g.*, 8 µg/L) should be replaced with the RL (*e.g.*, 10 µg/L).

   Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

5. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. If a sample was analyzed at a five-fold dilution or less and either surrogate was not detected in the sample, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Soil duplicate results are expected to have greater variance than aqueous duplicate results.

7. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

8. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   - High background levels or shifts in absolute RTs of internal standards

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

- Excessive baseline rise at elevated temperature
- Extraneous peaks
- Loss of resolution
- Peak tailing or peak splitting that may result in inaccurate quantitation

9. The RL will be defined on a project-specific basis. If the project-required RL is less than the low calibration standard concentration, the Project Manager should be consulted for instructions about application of qualification related to the RL.

APPENDIX 37

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate PCB data generated by US EPA Method 680 for the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to US EPA Method 680 and/or other reference documents (*e.g.*, analytical SOPs) as applicable to the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the PCB data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by the Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by US EPA Method 680; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- US EPA Method 680 as presented in SOP GEHR680.

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8082 (Rev 2. 12/96).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the PCB data based on an evaluation of information presented in the data package deliverables. Compliance to US EPA Method 680 and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/ comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by to General Electric Company). At a minimum, corrections required to allow for a full evaluation of

the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the PCB data based on an evaluation of the information presented in the data package deliverables. The findings of the PCB data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) to General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination (U*), unusable results (R/UR), estimated results (J/UJ), tentative identifications of target compound results (N), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the PCB data and the resultant qualifications will be as stipulated on the attached Table for the Validation of PCB (Aroclor) Data Generated by US EPA Method 680 (SOP GEHR680). It should be noted

that the project manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of PCB Data Generated by US EPA Method 680

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature is > 20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgement should be used if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days of sample collection. Solid/soil samples should be extracted within 14 days of sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
GC/MS Tuning (DFTPP)	Ion abundances should meet the method acceptance criteria. (See Note #1 for criteria.)	If mass calibration was not performed, qualify all associated data as unusable ("R"). If mass assignment is in error, qualify all associated data as unusable ("R"). Use professional judgment if abundance criteria are not met. Use professional judgment if samples are analyzed more than 12 hours after a compliant tune and there is no evidence of a compliant tune following the samples.

Table for the Validation of PCB Data Generated by US EPA Method 680

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #2 for additional information.)	Nine selected PCB congeners are used as calibration standards to represent each homolog group, the mono- through octachlorobiphenyls and decachlorobiphenyl. Decachlorobiphenyl is used as the calibration congener for both nona- and decachlorobiphenyl homolog groups. Five response factors (RFs) for each PCB calibration congener and surrogate must be calculated relative to chrysene-d_{12}. If interference or problems exist with chrysene-d_{12} then RFs will be calculated using phenanthrene-d_{10}. Each %RSD should be ≤20%.	If a PCB congener has 20%< %RSD ≤50%, qualify positive results for the associated homolog group(s) and total PCBs as estimated ("J") and do not qualify "not-detected" results for the associated homolog group(s) and total PCBs. If a PCB congener has 50%< %RSD ≤90%, qualify positive results for the associated homolog group(s) and total PCBs as estimated ("J") and use professional judgement to qualify "not-detected" results for the associated homolog group(s) and total PCBs. If a PCB congener has %RSD > 90%, qualify positive results for the associated homolog group(s) and total PCBs as estimated ("J") and qualify "not-detected" results for the associated homolog group(s) and total PCBs as unusable ("UR").
Continuing Calibration Verification (CCV) (See Note #3 for additional information.)	A CCV is required at the beginning and end of each 12-h period during which analyses are performed. The % difference (%D) for each PCB calibration congener and surrogate in each CCV should be ≤20%.	Qualification is for all samples on both sides of the out-of-criteria calibration standards. If a PCB congener has 20%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results for the associated homolog group(s) and total PCBs as estimated ("J") and qualify "not-detected" results for the associated homolog group(s) and total PCBs as estimated ("UJ"). If a PCB congener has %D>20% with the response indicating a sensitivity increase, qualify positive results for the associated homolog group(s) and total PCBs as estimated ("J") and use professional judgement to qualify "not-detected" results for the associated homolog group(s) and total PCBs. If a PCB congener has %D>90% with the response indicating a sensitivity decrease qualify positive results for the associated homolog group(s) and total PCBs as estimated ("J") and qualify "not-detected" results for the associated homolog group(s) and total PCBs as unusable ("UR").

Table for the Validation of PCB Data Generated by US EPA Method 680

Quality Control Item	Usability Criteria	Action
SIM PCB Data Performance Criteria for Calibration Standards	GC separation -- Baseline separation of PCB congener #87 (Cl_5) from congeners #154 (Cl_6) and #77 (Cl_4), which may coelute.	If baseline separation is not observed and the unresolved congeners are observed in an associated sample, qualify positive results for the associated homolog groups and total PCBs as estimated ("J").
	MS sensitivity -- Signal/noise ratio of ≥ 5 for m/z 499 of PCB congener #209, Cl_{10} -PCB, and for m/z 241 of chrysene-d_{12}.	If the S/N ratio was <5, use professional judgment to determine potential qualitative impacts.
	MS calibration -- Abundance of ≥ 70% and ≤ 95% of m/z 500 relative to m/z 498 for congener #209, Cl_{10} -PCB.	If the relative ion abundance ratio was not with the stated range, use professional judgment to determine the accuracy of qualitative identifications (both positive and "not-detected" results), focusing on chlorine cluster ions. Carefully evaluate sample ion ratios.
Internal Standards	The area measured for m/z 240 for chrysene-d_{12} nor that for m/z 188 for phenanthrene-d_{10} should not have changed by more than 30% from the area measured in the most recent previous analysis of a CCV standard or decreased by more than 50% from the mean area measured during initial calibration. Retention time (RT) of the internal standard should not vary more than ±10 seconds from the RT of the internal standards observed in associated CCV standard.	If a sample area count is outside of the criteria (70-130% of associated CCV or ≥50% of the associated ICV), qualify positive results for the homolog groups quantitated using that internal standard and total PCBs as estimated ("J") and qualify "not-detected" results for the homolog groups quantitated using that internal standard and total PCBs as estimated ("UJ"). If extremely low sample area counts (<35% of the associated CCV or <25% of the associated ICV) are reported, qualify positive results for the homolog groups quantitated using that internal standard and total PCBs as estimated ("J") and qualify "not-detected" results for the homolog groups quantitated using that internal standard and total PCBs as unusable ("R"). If an internal standard RT varies by more than 10 seconds and no peaks are observed in the sample chromatogram, qualification of data is not necessary. Use professional judgment if peaks are observed in the sample chromatogram.

Table for the Validation of PCB Data Generated by US EPA Method 680

Quality Control Item	Usability Criteria	Action
Retention Time (RT) Windows (See Note #4 for additional information.)	The time (scan number) for initiation of data acquisition with each ion set must be carefully determined from the RTs (scan numbers) of the RT congeners in the PCB Window defining mixture. Approximate relative RTs of calibration congeners and approximate relative RT windows for PCB isomer groups are shown on Table 7 of SOP GEHR680. Absolute RTs of PCB congeners #77, #104, #202, and #189 should not vary by more than ±10 s from one analysis to the next of the PCB Window defining mixture. (RT reproducibility is not as critical for congeners #1 and #209 as for the other four congeners, which are used to determine when ion sets are changed.)	If the PCB Window defining mixture RTs are not within the specified RT windows, evaluate sample ion current profiles (ICPs) for false positives and false negatives. If a constant drift in RT is observed in the bracketing PCB Window defining mixtures, the direction of the RT drift should be applied to the sample ICPs.

Table for the Validation of PCB Data Generated by US EPA Method 680

Quality Control Item	Usability Criteria	Action
Blanks (See Note #5 and Note #10 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks (identified by PCB congener). The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a PCB congener is found in the blank but not in the associated sample(s), no action is required. If a PCB congener in a sample is ≤5× the blank result, subtract the PCB congener concentration from the associated homolog group and total PCB results (and note in the validation report). If all PCB congeners of a homolog group result are ≤5× the blank results, qualify the positive result for the homolog group as "not detected" ("U*") and subtract the homolog group result from the total PCB result. If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a PCB congener in a sample is >5× blank result, no action/qualification is required. If gross contamination exists (*i.e.*, saturated peaks on the GC/MS), qualify the positive results as unusable ("R") due to interference.
Surrogates (See Note #6 for additional information.)	Use 60-140% as limits.	If the recoveries of one or more surrogates are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB Data Generated by US EPA Method 680

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (**IF REQUESTED**)	**Calculated for Total PCBs only.** For accuracy, use recovery limits of 60-140%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of Total PCBs is >4× the spiking level for Total PCBs. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >140%, qualify the positive total PCB results in the native sample as estimated ("J") and do not qualify the "not-detected" total PCB results. If the recovery is <60% but ≥10%, qualify the positive total PCB results in the native sample as estimated ("J") and qualify the "not-detected" total PCB results in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive total PCB results in the native sample as estimated ("J") and qualify the "not-detected" total PCB results in the native sample as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive total PCB results in the native sample as estimated ("J") and do not qualify the "not-detected" total PCB results. If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).
Laboratory Control Samples (LCS)	**Calculated for Total PCBs only.** For accuracy, use recovery limits of 60-140%.	If the recovery is >140%, qualify positive total PCB results in all associated samples as estimated ("J") and do not qualify "not-detected" total PCB results. If the recovery is <60% but ≥10%, qualify positive total PCB results in all associated samples as estimated ("J") and qualify "not-detected" total PCB results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive total PCB results in all associated samples as estimated ("J") and qualify "not-detected" total PCB results in all associated samples as unusable ("UR").

Table for the Validation of PCB Data Generated by US EPA Method 680

Quality Control Item	Usability Criteria	Action
Field/Laboratory Duplicate (See Note #7 and Note #10 for additional information)	Use precision limits of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid samples when sample results are ≥5× RL. Use limit of ± RL (±2× RL for solids) when at least one sample value is <5× RL. (Use one-half the RL as a numerical value for any "not-detected" results in the RPD calculations). Compare both individual total homolog results and total PCB results separately.	If the criteria are not met, qualify positive results for the out-of-criteria total homolog group or total PCBs in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Solid samples with less than 50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.

Table for the Validation of PCB Data Generated by US EPA Method 680

Quality Control Item	Usability Criteria	Action
Quantitation and Qualititative Identification (See Notes #4, #8, and #9 for additional information.)	Calculations should be performed in accordance with Section 12 of SOP GEHR680. Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution. EICPs must be evaluated to determine whether the laboratory correctly identified the PCB congeners based upon the identification procedures and criteria defined in Sections 11.3 and 11.4 of SOP GEHR680.	If a PCB congener result exceeds the instrument calibration range, qualify the positive result fro the associated homolog group as estimated ("J"). Use professional judgement to determine whether sample reanalyses and dilutions should be compared to the original analyses. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement to determine whether qualititative identifications are accurate and whether data qualification is necessary.
System Performance (See Note #9 for additional information.)	Professional judgement should be used when assessing the degradation of system performance during analyses.	Use professional judgement to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of PCB Data Generated by US EPA Method 680

1. Criteria for DFTPP Spectrum

m/z	Relative Abundance
127	40-60%
197	<1%
198	100% (Base Peak)
199	5-9%
275	10-30%
365	>1%
441	Present and <m/z 443
442	>40%
443	17-23% of m/z 442

2. If the initial calibration curve %RSD>50%, the linearity of the first three initial calibration standards should be evaluated. If the first three initial calibration standards for the PCB congener are linear (*i.e.*, r ≥0.99), do not qualify "not-detected" results. If the first three initial calibration standards for the PCB congener are not linear, qualify "not-detected" results as estimated ("UJ").

3. If instrument instability (*i.e.*, several CCV standards with PCB congeners exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential CCV standards, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a CCV standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

Notes for the Validation of PCB Data Generated by US EPA Method 680

If the CCV standard is %D>20% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this within the QAR support documentation.

4. Use professional judgement when evaluating sample ion current profiles (ICPs) when an RT shift is observed. If the ICPs reveal peaks corresponding to PCB congeners of interest using expanded RT windows and the surrogate compounds do not display a similar shift in RT, the concentrations of the PCB congeners that are outside of the RT window are subtracted from the associated total homolog and total PCB results.

   If the ICPs reveal peaks that interfere with potential detection of a PCB congener, qualify reported positive results for the associated total homolog group as unusable ("R").

5. The frequency of equipment/rinse blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected in the same day, unless only one blank was collected for a several-day sampling event. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

   If a sample result qualified "U*" is <RL and the laboratory did not report the RL on the data tables or Form I, the positive result (*e.g.*, 8 µg/L) should be replaced with the RL (*e.g.*, 10 µg/L).

Notes for the Validation of PCB Data Generated by US EPA Method 680

Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank.

6. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. If a sample was analyzed at a five-fold dilution or less and either surrogate was not detected in the sample, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

7. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Soil duplicate results are expected to have greater variance than aqueous duplicate results.

8. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

Notes for the Validation of PCB Data Generated by US EPA Method 680

9. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

- High background levels or shifts in absolute RTs of internal standards
- Excessive baseline rise at elevated temperature
- Extraneous peaks
- Loss of resolution
- Peak tailing or peak splitting that may result in inaccurate quantitation

10. The RL will be defined on a project-specific basis. If the project-required RL is less than the low calibration standard concentration, the Project Manager should be consulted for instructions about application of qualification related to the RL.

APPENDIX 38

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards, Inc. data reviewer will use to validate polychlorinated dibenzodioxin (dioxin) and polychlorinated dibenzofurans (furan) organic data generated by US EPA Method 1613B for General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to US EPA Method 1613B and/or other reference documents (*e.g.*, analytical SOPs), as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the dioxin/furan organic data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dioxin/Furan Data Validation" (Draft 9/2000) (National Functional Guidelines). It should be noted that the National Functional Guidelines applies strictly to data generated by the Contract Laboratory Program (CLP) protocol. As such, it is not directly applicable to validation of data generated by US EPA Method 1613B; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared from one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and all data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

Organic field duplicate comparison Rev 1-01.xls
Organic field quadruplicate comparison Rev 1-01.xls
Organic field triplicate comparison Rev 1-01.xls

Chemistry Apps

FIT
Methods database

3.0 REFERENCE DOCUMENTS

US EPA Method 1613B (10/94)

US EPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dioxin/Furan Data Validation (Draft 9/2000)
Region III – SOP for Dioxin/Furan Data Validation (Draft 3/99)
Region IV – Data Validation SOP for Polychlorinated Dibenzodioxin and Polychlorinated Dibenzofurans Analysis by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (9/96)
Region II – Data Validation SOP for EPA Method 1613, Revision A (Revision 2 9/99)

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the dioxin/furan data based on an evaluation of information presented in the data package deliverables. Compliance to US EPA Method 1613B and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or any certain aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to the submittal of the QAR (if feasible and sanctioned by General Electric Company) at a minimum corrections necessary for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would take a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as

a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the dioxin/furan organic data based on an evaluation of the information presented in the data package deliverables. The findings of the dioxin/furan organic data usability assessment will be described in terms of certain qualifications of the data that the project team should consider in order to best utilize the data. These qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank qualification, common contaminants that were not qualified, unusable results ("R/UR"), estimated results ("J/UJ"), field duplicate comparison and a general qualifier for all results reported the quantitation limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the dioxin/furan organic data and the resulting qualifications will be as stated in the attached Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B. It should be noted that the Project Manager should be consulted when directed to use "professional judgement" in the attached table.

Table for the Validation of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	0-4°C for aqueous <-10°C for solid and tissue	Due to the stability of PCDDs and PCDFs, there is no direct impact on data usability due to receipt temperatures outside the specified range.
Holding Time (See Note #1 for additional information.)	All matrices should be extracted within 30 days of sample collection and analyzed within 45 days of extraction.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded (>twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Chromatographic Resolution (Isomer Specificity Test Standard, See Note #2 for additional information)	Should be analyzed at the beginning of each 12-hour period of sample and standard analysis. The % valley between unlabeled 2,3,7,8-TCDD and all other unlabeled TCDD should be <25%. The RT of the first and last eluting isomers are used to establish the RT windows for each congener class of PCDD/PCDF compounds.	Use professional judgement if the Isomer Specificity Test Standard was not analyzed at the required frequency. If the % valley between unlabeled 2,3,7,8-TCDD and all other unlabeled TCDD is >25%, qualify positive results for 2,3,7,8-TCDD as estimated ("J").
Window Defining Mix (WDM)	Should be analyzed at the beginning of each 12-hour period of sample and standard analysis.	If frequency is not met, qualify positive results for total homologues as estimated ("J").
Instrument Performance-Mass Spectrometer Performance (PFK)	Should be analyzed at the beginning of each 12-hour period during which samples are to be analyzed and prior to the analysis of the initial and continuing calibration standards. A static resolving power of at least 10,000 (10% valley definition) should be demonstrated at appropriate masses before any analysis is performed and at the end of each 12-hour period.	Use professional judgement if the mass calibration was not performed at the required frequency or if the resolving power was less than 10,000.

Table for the Validation of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #3 for additional information)	Should be established with a minimum of 5 different concentration levels. The %RSD should be ≤20% for the 17 unlabeled standards and ≤35% for the labeled reference compounds. The relative ion abundance ratios should be within the limits specified in Note #3. The retention times of all target compounds, internal standards, and recovery standard should be within the windows established. The two monitored ions for each homologue should be present and should maximize simultaneously within 3 seconds of the corresponding ^{13}C-labeled isomer ions. The signal-to-noise (S/N) ratio for the GC signals present in the selected ion current profiles (SICPs) should be ≥ 10.	If the %RSD >20% but ≤90% (for unlabeled), qualify positive result as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the %RSD >90% (for unlabeled), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the relative ion abundance ratios for the two quantitation ions of the target compounds, internal standard, and/or recovery standards were not with the stated range, qualify positive results as unusable ("R"). Qualify positive results associated with the out of criteria ion abundance ratio internal standards and/or recovery standards. If the retention time of any target compound, internal standard, and/or recovery standard is not within the established retention time windows (±10 seconds of retention times in the WDM), qualify all data as unusable ("R/UR"). If the two monitored ions for a native isomer are not present and/or did not maximize simultaneously within 3 seconds of the corresponding ^{13}C-labeled isomer ion, qualify positive results as "not-detected" ("U") (the reported concentration with be reported at the detection limit). If the S/N ratio was <10, qualify "not-detected" results as unusable ("UR").

Table for the Validation of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Continuing Calibration (See Notes #3 and #4 for additional information)	Should be analyzed at the beginning of each 12-hour shift. The relative ion abundance ratios should be within the limits specified in Note #3. The recoveries (%Rs) should be within the limits specified in Note #4. The retention times for all compounds should be within the windows established. The two monitored ions for each homologue should be present and should maximize simultaneously within 3 seconds of the corresponding ^{13}C-labeled isomer ions. The signal-to-noise (S/N) ratio for the GC signals present in the SICPs should be ≥ 10.	If the unlabeled target compound recovery < lower limit but ≥ 50% of the lower limit, qualify positive result as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the unlabeled target compound recovery is > the upper limit but ≤ 150% of the upper limit, qualify positive result as estimated ("J"). If the unlabeled target compound recovery is < 50% of the lower limit or > 150% of the upper limit, qualify positive and "not-detected" results as unusable ("R/UR"). If the relative ion abundance ratio for the two quantitation ions are not within the specified range, qualify positive results as unusable ("R"). If the retention time of any target compound is not within the specified retention time window, qualify positive results as unusable ("R"). If the two monitored ions for a native isomer are not present and/or did not maximize simultaneously within 3 seconds of the corresponding ^{13}C-labeled isomer ion, qualify positive results as "not-detected" ("U") (the reported concentration with be reported at the detection limit). If the S/N ratio was <10, qualify "not-detected" results as unusable ("UR").
Internal Standards and Recovery Standards	Added to all samples and standards. %Rs should be within the limits specified in Note #4. The relative ion abundance ratios should be within the limits specified in Note #3. The retention times should be within the windows established.	Use professional judgement to determine if qualification is necessary due to relative ion abundance ratio being outside the specified range and if the retention times are not within the windows established. If the %R is > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the %R is < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the %R is <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Blanks (See Note #5 for additional information)	Summarize all results greater than the estimated detection limit (EDL). The highest positive results associated with a sample should be utilized for evaluation of contamination.	If a target compound is found in blank but not in the associated sample(s), no action is taken. If a sample result is ≤5× the blank result, qualify the results as "not-detected" ("U*"). The value of the positive result should be used as the revised EDL. If a sample result >5× (or 10× for OCDD only) blank result, no qualification is necessary. If gross contamination exists (*i.e.*, saturated peaks by GC/MS), qualify samples as unusable ("R") due to interference.

Table for the Validation of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicates (MS/MSD)	For accuracy, use laboratory acceptance limits. For precision, use RPD limit of 40% for all matrices.	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if original concentration of a compound is > 4× spiking level for that compound. RPDs calculated using MS/MSD results can still be used to evaluate precision. If the recovery is > upper limit, qualify positive results for that compound in the native sample as estimated ("J") and do not qualify "not-detected" results. If the recovery is < lower limit but ≥10%, qualify positive results for that compound in the native sample as estimated ("J") and qualify "not-detected" results for that compound in the native sample as estimated ("UJ"). If the recovery is <10%, qualify positive results in the native sample as estimated ("J") and qualify "not-detected" results for that compound in the native samples as unusable ("UR"). If the precision is >20%, qualify positive results for that compound in the native sample as estimated ("J") and do not qualify "not-detected" results. If the precision criteria (See field duplicate usability criteria) for non-spiked compounds are not met, qualify positive results in the native sample as estimated ("J") and qualify "not-detected" results in the native sample as estimated ("UJ"). If a field duplicate of the native (unspiked) sample was collected and analyzed, the field duplicate should also be qualified if the MS/MSD %Rs or RPD are outside of criteria as stated above for the native sample.
Ongoing Precision and Recovery (OPR) Standard	%Rs should be within the limits specified in Note #4. The relative ion abundance ratios should be within the limits specified in Note #3. The retention times should be within the windows established.	If the recovery for a target compound is outside of the acceptance criteria, qualify all positive results and "not-detected" results as unusable ("UR").

Table for the Validation of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Field Duplicate/Laboratory Duplicate (See Note #6 for additional information)	Use precision limits of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid samples when sample results are ≥5× RL. Use limit of ± RL (±2× RL for solids) when at least one sample value is <5× RL. (Use one-half the RL as a numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results in original sample, and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Qualification is for solid samples with less than 50% solid content.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.

Table for the Validation of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Target compound Identification (See Note #7 for additional information)	For 2,3,7,8-substitued isomers for which an isotopically labeled internal standard is present, the absolute RT at the maximum peak height should be within –1 to +3 seconds of the RT of the corresponding labeled standard. For non-2,3,7,8-substitued isomers, the RT should be within the established window. The two quantitation ions for the compounds, internal standards, and recovery standards should maximize simultaneously (within 2 seconds). The relative ion abundance ratios should be within the limits specified in Note #3. All integrated ion current for each characteristic ion of the target compound should have an S/N ratio ≥2.5. The identification of a peak as a PCDF can only be made if no signal having a S/N ≥2.5 is detected at the same time in the corresponding polychlorinated diphenyl ether (PCDPE) channel. Any results reported for 2,3,7,8-TCDF should be confirmed on a DB-225 column.	Use professional judgement to determine if the result should be changed to "not-detected" or flagged "EMPC" if one or more of the identification criteria specified was not met. Use professional judgement if a PCDPE peak was detected at the same retention time as a reported PCDF result.
Compound Quantitation and Detection Limits	The laboratory should reextract samples (utilizing a smaller sample aliquot) with compound concentrations above the instrument calibration range.	If a target compound result exceeds the instrument calibration range, qualify the positive result as estimated ("J"). If a target compound result is below the low calibration standard concentration, qualify the positive result as estimated ("J"). If the laboratory performed a dilution of a sample that had a target compound result that exceeded the instrument calibration range instead of reextracting a smaller sample aliquot, qualify positive results for the dilution analysis as estimated ("J").
System Performance (See Note #8 for additional information)	Professional judgement should be used when assessing the degradation of the system performance during analyses.	Professional judgement should be used to qualify the data if it is determined that the system performance has degraded during sample analysis.

Table for the Validation of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data that were not qualified based on the QC previously addressed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information on the intended use and required quality of the data is available, the reviewer should include the assessment of the usability of the data within the given context.

Notes for the Validation of PCDD and PCDF Data Generated by the US EPA Method 1613B

1. The holding time of extraction within 30 days of sample collection is a recommendation; however, since PCDDs and PCDFs are very stable in many matrices, the holding time may be as high as one year. Use professional judgement when evaluating samples that were extracted beyond the 30 day holding time.

2.

DB-5 Column GC Retention Time WDM

Congener	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

DB-5 Column TCDD Isomer Specificity Test Standard

1,2,3,4-TCDD	1,2,3,7-TCDD
1,2,3,9-TCDD	2,3,7,8-TCDD

DB-225 Column TCDF Isomer Specificity Test Standard

2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

3. If the initial calibration %RSD is >50% but ≤90%, the linearity of the first three initial calibration standards for the compound should be evaluated. If the first three initial calibration standards for the compound are linear then do not qualify "not-detected"

results. If the first three initial calibration standards for the compound are not linear, then qualify "not-detected" results as estimated ("UJ").

Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive then the samples should be evaluated for false positives. If the concentration intercept is negative then the samples should be evaluated for false negatives.

Relative Ion Abundance Criteria for PCDDs and PCDFs

PCDDs	Relative Intensity
Tetra	0.65-0.89
Penta	1.32-1.78
Hexa	1.05-1.43
Hepta	0.88-1.20
Octa	0.76-1.02
PCDFs	Relative Intensity
Tetra	0.65-0.89
Penta	1.32-1.78
Hexa	1.05-1.43
Hexa[1]	0.43-0.59
Hepta	0.88-1.20
Hepta[2]	0.37-0.51
Octa	0.76-1.02

1 - used only for ^{13}C-HxCDF (internal standard)
2 - used only for ^{13}C-HpCDF (internal standard)

4.

Acceptance Criteria for Performance Tests When All PCDD/PCDF Are Tested

PCDD/PCDF	Concentration (ng/ml)	OPR (ng/ml)	Verification (ng/ml)
2,3,7,8-TCDD	10	6.7-15.8	7.8-12.9
2,3,7,8-TCDF	10	7.5-15.8	8.4-12.0
1,2,3,7,8-PeCDD	50	35-71	39-65
1,2,3,7,8-PeCDF	50	40-67	41-60
2,3,4,7,8-PeCDF	50	34-80	41.61
1,2,3,4,7,8-HxCDD	50	35-82	39-64
1,2,3,6,7,8-HxCDD	50	38-67	39-64
1,2,3,7,8,9-HxCDD	50	32-80	41-61
1,2,3,4,7,8-HxCDF	50	36-67	45-56
1,2,3,6,7,8-HxCDF	50	42-65	44-57
1,2,3,7,8,9-HxCDF	50	39-65	45-56
2,3,4,6,7,8-HxCDF	50	35-78	44-57
1,2,3,4,6,7,8-HpCDD	50	35-70	43-58
1,2,3,4,6,7,8-HpCDF	50	41-61	45-55
1,2,3,4,7,8,9-HpCDF	50	39-69	43-58
OCDD	100	78-144	79-126
OCDF	100	63-170	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	20-175	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	22-152	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	21-227	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	21-192	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	13-328	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	21-193	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	25-163	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	19-202	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	21-159	70-143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	17-205	74-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	22-176	73-137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	26-166	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	21-158	78-129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	20-186	77-129
$^{13}C_{12}$-OCDD	200	26-397	96-415

Acceptance Criteria for Performance Tests When All PCDD/PCDF Are Tested

PCDD/PCDF	Concentration (ng/ml)	OPR (ng/ml)	Verification (ng/ml)
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.1-19.1	7.9-12.7

Acceptance Criteria for Performance Tests When Only Tetra Compounds Are Tested

PCDD/PCDF	Concentration (ng/ml)	OPR (ng/ml)	Verification (ng/ml)
2,3,7,8-TCDD	10	7.3-14.6	8.2-12.3
2,3,7,8-TCDF	10	8.0-14.7	8.6-11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-141	85-117
$^{13}C_{12}$-2,3,7,8-TCDF	100	26-126	76-131
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.7-15.8	8.3-12.1

Acceptance Criteria for Labeled Compound Recovery in Samples When All PCDD/PCDFs Are Tested

PCDD/PCDF	Concentration (ng/ml)	Recovery (ng/ml)	Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-164	25-164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24-169	24-169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25-181	25-181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24-185	24-185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21-178	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32-141	32-141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28-130	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26-152	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26-123	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29-147	29-147
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	28-136	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23-140	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28-143	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26-138	26-138
$^{13}C_{12}$-OCDD	200	34-313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5-19.7	35-197

Acceptance Criteria for Labeled Compound Recovery in Samples When Only Tetra Compounds Are Tested

PCDD/PCDF	Concentration (ng/ml)	Recovery (ng/ml)	Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	31-137	31.137
$^{13}C_{12}$-2,3,7,8-TCDF	100	29-140	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2-16.4	42-164

5. The frequency of equipment blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (unless only one was collected for a several-day sampling event; results would be applied to all samples in the SDG). In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

6. Duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than aqueous duplicate results.

7. US EPA Method 1613B (Section 16.6) requires that a result meet all identification criteria or the result should not be reported. The sample should undergo reextraction with additional cleanup to remove any interference. Therefore, the laboratory should not be reporting the estimated maximum possible contamination (EMPC) results. If the presence of a reported positive is questioned (mostly due to chlorinated ether interference or if ratio/retention times are out), quality the result as "EMPC".

8. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. high background levels or shifts in absolute retention times of internal standards
   b. excessive baseline rise at elevated temperatures
   c. extraneous peaks
   d. loss of resolution
   e. peak tailing or peak splitting that may result in inaccurate quantitation

APPENDIX 39

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate inorganic data generated by SW-846 Method 6010B for the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to SW-846 Method 6010B and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the inorganic data provided by the project laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Inorganic Data Review" (2/94; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by SW-846 Method 6010B; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELForms:

- Inorganic field duplicate comparison Rev 1-01.xls
- Inorganic triplicate comparison Rev 1-01.xls
- Total versus dissolved comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (2/94).

- SW-846 Method 6010B.

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

- Region III, Modifications to Natural Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the inorganic data based on evaluation of information presented in the data package deliverables. Compliance with SW-846 Method 6010B and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic Data Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of certain deficiencies prior to submittal of the QAR (if feasible and sanctioned by General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include

sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. In addition, the data reviewer should contact the project laboratories if feasible to request the correction of all correctable deficiencies that impact sample results or that the data reviewer was unable to correct prior to the submittal of the QAR, if time allows. Any laboratory resubmittals as a result of such requests will be discussed in the comments substation of the QAR and will be included as an attachment of the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the inorganic data based on an evaluation of the information presented in the data package deliverables. The findings of the inorganic data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic Data Qualifier subsection of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation/reporting limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the inorganic data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Metals Data Generated by SW-846 Method 6010B. It should be noted that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Metals Generated by SW-846 Method 6010B

Quality Control Item(s)	Usability Criteria	Action(s)
Temperature and Conditions Upon Receipt	Aqueous samples should be preserved with nitric acid to pH≤2. Solid/soil samples should be preserved to 4±2°C.	If pH is >2 and the laboratory did not adjust the pH and allow the sample to sit for 16 hours before digestion, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Solid/soil samples should not be qualified due to out-of-criteria temperature upon receipt.
Technical Holding Time	All matrices should be analyzed within 6 months of sample collection.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded (>1 year from date of sample collection), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration	Should be established with a minimum of one blank and one standard.	Use professional judgement if the minimum number of standards was not used or if instrument was not calibrated daily and/or not calibrated each time set up.
Instrument Performance (See Note #1 for additional information.)	%D or %RSD between replicate exposures should be ≤20%. Samples should not display negative results >2× the instrument detection limit (IDL).	If %RSD or %D>20%, qualify positive results greater than the reporting limit as estimated ("J") and do not qualify "not-detected" results. If a negative result >5× IDL, qualify the "not-detected" result as unusable ("UR"). If an analyte displays a negative result >2× IDL, qualify the "not-detected" result as estimated ("UJ").
Initial Calibration Verification (ICV)	For accuracy, use recovery limits of 90-110%.	**Qualify samples for an entire analytical sequence.** If an analyte recovery is >110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Metals Generated by SW-846 Method 6010B

Quality Control Item(s)	Usability Criteria	Action(s)
Continuing Calibration Verification (CCV)	For accuracy, use recovery limits of 90-110%.	**Qualify samples analyzed before and after a non-compliant CCV.** If an analyte recovery is >110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
CRDL/CRI Standard (not required, but frequently analyzed.) (See Note #2 and Note #8 for additional information.)	For accuracy, use recovery limits of 85-115%.	**Qualify samples analyzed before and after a non-compliant CRDL/CRI standard.** If an analyte recovery is >115%, qualify positive results ≤3× the spike level as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <85% but ≥50%, qualify positive results ≤ 3× the spike level as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is <50%, qualify positive results ≤3× the spike level as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If an analyte recovery is >150%, qualify positive results ≤ 3× the spike level as unusable ("R"), qualify positive results >3× the spike level but ≤5× as the spike level estimated ("J"), and do not qualify "not-detected" results.

Table for the Validation of Metals Generated by SW-846 Method 6010B

Quality Control Item(s)	Usability Criteria	Action(s)
Initial Calibration Blank (ICB)/Continuing Calibration Blank (CCB)/Preparation Blank (PB)/Field Blank/Equipment Blank (See Note #3 and Note #8 for additional information.)	The highest positive result (greater than the IDL) associated with a sample should be summarized and utilized for evaluation of contamination.	For ICBs and CCBs qualify samples per analytical sequence; for PBs, field blanks, and equipment blanks qualify per batch and for SDG. If an analyte is detected in the blank but not in the associated samples, no action is required. If a sample result is >MDL/DL but ≤5× blank result, qualify the positive result as "not-detected" ("U*"). If a sample result is >5× blank result, qualification is not required. If a blank has a negative result with an absolute value >2× IDL, qualify positive results ≤5× the absolute value of the blank result as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Metals Generated by SW-846 Method 6010B

Quality Control Item(s)	Usability Criteria	Action(s)
ICP Interference Check Sample Analysis (ICSA/ICSAB) (See Note #4 for additional information.)	For accuracy, use recovery limits of 80-120% for ICSA/ICSAB. The absolute value of analytes not present in ICSA solution should be <2× IDL.	Qualify samples analyzed before and after ICSA/ICSAB standard. Sample data are acceptable if the concentrations of interferents (*i.e.*, Al, Ca, Fe, and Mg) in the samples are ≤ 50% of the respective ICSA concentrations. For samples with concentrations of interferents (*i.e.*, Al, Ca, Fe, and Mg) >50% of the respective concentrations in the ICSA, qualify as follows: If an ICSAB recovery is > 120%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an ICSAB recovery is 50-79%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an ICSAB recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If positive results are observed in the ICSA for non-ICSA analytes that are >2× DL, qualify positive results up to 5× ICSA concentration in samples with high (>50% ICSA interferents) interferents as estimated ("J") and do not qualify "not-detected" results. If negative results with an absolute value >2× DL are observed in the ICSA for non-ICSA analytes, qualify positive results up to 5× the concentration observed in the ICSA in samples with high (>50% ICSA interferents) interferents as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Metals Generated by SW-846 Method 6010B

Quality Control Item(s)	Usability Criteria	Action(s)
Laboratory Control Sample (LCS) (See Note #5 for additional information.)	For accuracy, use recovery limits of 80-120% for aqueous samples and 70-130% for solid samples.	For aqueous samples, if a recovery is >120% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For aqueous samples, if a recovery is <80% but ≥50%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For aqueous samples, if a recovery is >150%, qualify all positive results as unusable ("R") and do not qualify "not-detected" results. For aqueous samples, if a recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). For solid samples, if a recovery is >130%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For solid samples, if a recovery is <70% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For solid samples, if recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Matrix Spike/Matrix Spike Duplicates (MS/MSD) (See Note #6 and Note #8 for additional information.)	For accuracy, use recovery limits of 75-125%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPDs calculated using %Rs) that are outside of criteria if the original concentration of an analyte is >4× the spiking level for that analyte. RPDs calculated using MS/MSD results can be used to evaluate precision. If a recovery is >125%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If a recovery is <75% but ≥30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If a recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
ICP Serial Dilution Analysis	%D<10% if original undiluted concentration is >50× IDL.	If %D is >10%, qualify positive results as estimated ("J") and do not qualify "not-detected" results.

Table for the Validation of Metals Generated by SW-846 Method 6010B

Quality Control Item(s)	Usability Criteria	Action(s)
Field Duplicate/Laboratory Duplicate (See Note #6, Note #7 and Note #8 for additional information.)	Use default limits of 20% RPD (%RSD for triplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate analyses) for solid samples when sample results are ≥5× RL. Use default limit of ± RL for aqueous samples and ±2× RL for solid samples when at least one sample result is <5× RL.	If the criteria are not met, qualify positive results for non-compliant analyte in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Total vs. Dissolved Comparison (See Note #8 for additional information.)	When the dissolved result is greater than the total result: use default limits of ± IDL if at least one result is <10× IDL. Use default limit of percent difference <10% if both results are ≥10× IDL.	If the criteria are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If at least one result is <10× IDL and the difference is >5× IDL, qualify positive results and "not-detected" results as unusable ("R/UR"). If both results are ≥10× IDL and the percent difference is >50%, qualify positive results as unusable ("R").
Percent Solids	Solid samples with < 50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information of the intended use and required quality of the data is available, the reviewer should include the assessment of the usability of the data within the given content.

Notes for the Validation of Metals Data Generated by SW-846 Method 7470A/7471A

1. Due to the nature of trace ICP data, IDL may be very low such that 5× the IDL may be below the laboratory reporting limit. If the IDL is very low, use professional judgement to determine if the reporting limits should be qualified due to negative sample results.

2. If the spike concentration of the CRDL/CRI standard is < the IDL/MDL, do no utilize the results for qualification. Use professional judgement if the spike concentration of the CRDL/CRI standard is ≥ IDL but < the reporting limit.

3. Generally, if more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. When evaluating blank contamination, sample weights, volumes, and initial dilution factors should be taken into account. Sample results should not be blank corrected.

   The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (if only one blank was collected for a several-day sampling event, results would be applied to all samples in the SDG).

4. When comparing ICSA results to sample results, the units of each should be the same (*i.e.*, if the sample results are in mg/kg and the ICSA results are in µg/L, convert the ICSA results to mg/kg before comparing the results.) If the negative interference in the ICSA solution is comparable (similar level) to the negative values observed in the CCBs,

Notes for the Validation of Metals Data Generated by SW-846 Method 7470A/7471A

the negative ICSA values should not be utilized for qualification. If the negative interference in the ICSA solution is not comparable to the negative values observed in the CCBs, the negative ICSA values should be utilized for qualification.

5. The spike level for the solid LCS should be comparable to the detection limit. Use professional judgement if the spike level is not comparable to the detection limit.

6. The laboratory may choose to analyze an MSD instead of a laboratory duplicate. The laboratory may include a post-digestion matrix spike (PDS) analysis. These results are not utilized for qualification; however, the results are utilized to evaluate the MS/MSD recoveries.

7. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicates should be applied to all samples in a batch. It is also expected that soil duplicate results will have a greater variance than aqueous duplicate results.

8. The use of RL/DL in evaluating laboratory quality is as follows:

   - when evaluating negative values, total verses dissolved results, and the ICSA (non-spiked) compounds, the DL should be used.

Notes for the Validation of Metals Data Generated by SW-846 Method 7470A/7471A

- when evaluating field duplicates and laboratory duplicates, the RL/QL should be used.

The DL is defined as the number that the positive results are reported down to; therefore, the DL may be the IDL, MDL, or RL.

The RL is defined as the quantitation limit or project reporting limit. If the laboratory did not provide the RL, the IDL or MDL should be used.

APPENDIX 40

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate mercury data generated by SW-846 Methods 7470A/7471A for General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to SW-846 Methods 7470A/7471A and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the mercury data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (2/94; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by SW-846 Methods 7470A/7471A; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel form available in R:/Templates/Chemistry/XCELForms:

- Inorganic field duplicate comparison Rev 1-01.xls
- Inorganic triplicate comparison Rev 1-01.xls
- Total versus dissolved comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (2/94).
- SW-846 Methods 7470A/7471A.

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Inorganic Data Acquired Using SW-846 Methods 7470A/7471A (Rev. 2, 12/94).

- Region III, Modifications to National Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the mercury data based on evaluation of information presented in the data package deliverables. Compliance with SW-846 Methods 7470A/7471A and/or other reference documents (*e.g.*, analytical SOPs) as applicable to the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic Data Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by the General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such request will be discussed in the comments subsection of the QAR and will be included as an attachment of the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the mercury data based on an evaluation of the information presented in the data package deliverables. The findings of the mercury data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic Data Qualifier Section of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation/reporting limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the mercury data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A. It should be noted that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Temperature and Conditions Upon Receipt	Aqueous samples should be preserved to pH ≤2 with HNO_3. Solid/soil samples should be preserved to 4±2°C.	If pH is >2 and the laboratory did not adjust the pH and allow the sample to sit for 16 hours before digestion, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Solid/soil samples should not be qualified due to out-of-criteria temperatures.
Technical Holding Time	All matrices should be analyzed within 28 days of sample collection.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded *i.e.*, twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information.)	Calibration should be daily and each time the instrument is set up, with at least one blank and three standards. r (linear) should be ≥ 0.995.	Use professional judgement if the appropriate number of standards is not used or if the instrument was not calibrated daily and/or not calibrated each time set up. If the r is <0.995 but ≥0.850, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r is <0.850, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Instrument Performance	Samples should not display negative results with an absolute value >2× the instrument detection limit (IDL).	If a negative result with an absolute value >2× IDL is observed, qualify the "not-detected" result as estimated ("UJ").

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Initial Calibration Verification (ICV)	For accuracy, use recovery limits of 80-120%.	Qualify samples for an entire analytical sequence. If the recovery is >120% but ≤135%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recovery is <80% but ≥65%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <65%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the recovery is >135%, qualify positive results as unusable ("R") and do not qualify "not-detected" results.
Continuing Calibration Verification (CCV)	For accuracy, use recovery limits of 80-120%.	Qualify samples analyzed before and after a non-compliant CCV. If the recovery is >120% but ≤135%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recovery is <80% but ≥65%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <65%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the recovery is >135%, qualify positive results as unusable ("R") and do not qualify "not-detected" results.

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
CRDL/CRA Detection Limit (DL) standard (not required but frequently analyzed.) (See Note #2 and Note #7 for additional information.)	For accuracy, use recovery limits 75-125%.	Qualify samples analyzed before and after a non-compliant CRDL/CRA standard. If the recovery is >125% but ≤150%, qualify positive results ≤ 2 × the spike level as estimated ("J") and do not qualify "not-detected" results. If the recovery is <75% but ≥ 50%, qualify positive results ≤ 2 × the spike level as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <50%, qualify positive results ≤ 2 × the spike level as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the recovery is >150%, qualify positive results ≤ 2 × the spike level as unusable ("R"), qualify positive results >2× the spike level but ≤5× the spike level as estimated ("J"), and do not qualify "not-detected" results.
Initial Calibration Blank (ICB)/ Continuing Calibration Blank (CCB)/ Preparation Blank (PB)/Field Blank/Equipment Blank (See Note #3 and Note #7 for additional information.)	The highest positive result (greater than the IDL) associated with a sample should be summarized and utilized for the evaluation of contamination.	For ICBs and CCBs, qualify samples per analytical sequence; for PBs, field blanks, and equipment blanks, qualify per batch and/or SDG. If mercury is detected in blank but not in sample, no action is required. If a sample result is >MDL/IDL but ≤5× blank result, qualify the positive result as "not-detected" ("U*"). If sample is >5× blank result, qualification is not required. If a blank has a negative result with an absolute value >2 × IDL, qualify positive results ≤ 5 × the absolute value of the blank result as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Laboratory Control Sample (LCS) (See Note #4 for additional information.)	For accuracy, use recovery limits of 80-120% for aqueous samples and 70-130% for solid samples.	For aqueous samples, if the recovery is >120% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For aqueous samples, if the recovery is <80%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For aqueous samples, if the recovery is >150%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. For aqueous samples, if the recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). For solid samples, if the recovery is >130%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For solid samples, if the recovery is <70% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For solid samples, if the recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Matrix Spike/Matrix Spike Duplicates (MS/MSD) (See Note #5 for additional information.)	For accuracy use recovery limits of 75-125%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPDs calculated using %Rs) that are outside of criteria if the original concentration of an analyte is >4× the spiking level for that analyte. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >125%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <75% but ≥30%, qualify all positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify all "not-detected" results in all associated samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Field Duplicate/Laboratory Duplicate (See Note #6 and Note #7 for additional information.)	Use default limits of 20% RPD (%RSD for triplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate analyses) for solids when sample results are ≥5× DL. Use default limit of ±DL for aqueous samples and ±2× DL for solid samples when at least one sample result is <5× DL.	If the criteria are not met, qualify positive results for the non-compliant analyte in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Mercury Data Generated by SW-846 Methods 7470A/7471A

Quality Control Item	Usability Criteria	Action(s)
Total vs. Dissolved Comparisons (See Note #7 for additional information.)	When the dissolved result is greater than the total result: use default limits of ± IDL when at least one result is <10× IDL. Use default limits of percent differences <10% when both results are ≥ 10× IDL.	If the criteria are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If at least one result is <10× IDL and the differences is >5× IDL, qualify positive and "not-detected" results as unusable ("R/UR"). If both results are ≥10× IDL and the percent difference is >50%, qualify positive results as unusable ("R").
Percent Solids	Solid samples with less than 50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the nature of the analytical problems.	Use professional judgement to determine the need to qualify data that were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Mercury Data Generated by SW-846 Method 7470A/7471A

1. Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, samples should be evaluated for false positives. If the concentration intercept is negative, samples should be evaluated for false negatives. Furthermore, samples should not display negative values >2× the detection limit (DL).

   The laboratory may utilize a non-linear regression curve fit. Due to different software programs, it may not be possible to reproduce the laboratory results.

2. The action limit of 2× the spike level assumes that the spike level is based on the RL; therefore, if the RL is < the action limit, the CRDL/CRA standard results should be utilized to qualify the sample data. If the RL is > the action level, the CRDL/CRA standard results should not be utilized to qualify sample data.

3. Generally, if more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. When evaluating blank contamination, sample weights, volumes, and initial dilution factors should be taken into account. Sample results should not be blank corrected.

   The frequency of equipment blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (if only one blank was

Notes for the Validation of Mercury Data Generated by SW-846 Method 7470A/7471A

collected for a several-day sampling event; results would be applied to all samples in the SDG).

4. The spike level for the solid LCS should be comparable to the detection limit. Use professional judgement if the spike level is not comparable to the detection limit.

5. The laboratory may choose to analyze an matrix spike duplicate instead of a laboratory duplicate.

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicate results should be applied to all samples in a batch. It is expected that soil duplicate results will have a greater variance than aqueous duplicate results.

7. The use of RL/DL in evaluating laboratory quality is as follows:

   - When evaluating negative values and total verses dissolved results, the DL should be used.
   - When evaluating field duplicates and laboratory duplicates, the RL/QL should be used.

Notes for the Validation of Mercury Data Generated by SW-846 Method 7470A/7471A

The DL is defined as the number that the positive results are reported down to; therefore, the DL may be the IDL, MDL, or RL.

The RL is defined as the quantitation limit or project-reporting limit. If the laboratory did not provide the RL then the IDL or MDL should be used.

APPENDIX 41

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that Environmental Standards' data reviewers will use to validate total organic carbon (TOC) data generated by the Lloyd Kahn Method for General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to the Lloyd Kahn Method and/or other reference documents (*e.g.*, analytical SOP) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the TOC data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (2/94) (National Functional Guidelines). It should be noted that the National Functional Guidelines applies strictly to data generated by the Contract Laboratory Program (CLP) protocol. As such, it is not directly applicable to validation of data generated by the Lloyd Kahn Method; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared from one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELForms:

Inorganic field duplicate comparison Rev1-01.xls
Organic field triplicate comparison Rev1-01.xls

Chemistry Applications:

FIT
Methods Database

3.0 REFERENCE DOCUMENTS

US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (2/94).

Northeast Analytical, Inc.- Standard Operating Procedure for the Determination of Total and Particulate Organic Carbon According to Tekmar Dohrmann Application Note TOC-011 (Rev. 3; 2/10/00).

Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

Region III, Modifications to Natural Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the TOC data based on an evaluation of information presented in the data package deliverables. Compliance to the Lloyd Kahn Method and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or any certain aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to the submittal of the QAR (if feasible and sanctioned by General

Electric Company). At a minimum, corrections necessary for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would take a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the TOC data based on an evaluation of the information presented in the data package deliverables. The findings of the TOC data usability assessment will be described in terms of certain qualifications of the data that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, common contaminants that were not qualified, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the TOC data and the resultant qualifications will be as stated in the attached Table for the Validation of Total Organic Carbon (TOC) Data Generated by the Lloyd Kahn Procedure. It should be noted that the Project Manager should be consulted when directed to use "professional judgement" in the attached table.

Notes for the Validation of TOC Data Generated by the Lloyd Kahn Procedure

Quality Control Item	Usability Criteria	Action
Temperature and Conditions Upon Receipt	4±2°C pH<2 for aqueous samples	If temperature >10°C, but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature >20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgement should be used if less than 8 hours had lapsed from collection to receipt to determine if the qualification above applies. If the aqueous samples have pH values >2, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Technical Holding Time	Soil samples should be analyzed within 14 days of sample collection. Aqueous samples should be analyzed within 28 days of sample collection.	If the aqueous analysis was performed >28 days but <56 days, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the soil analysis was performed >14 days but <28 days, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the aqueous analysis was performed >56 days, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the soil analysis was performed >28 days, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information)	r (linear) or coefficient of determination (COD) (quadratic) should be ≥0.99.	Use professional judgement when evaluating correlation coefficients and coefficients of determination (r or COD). If r or COD <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of TOC Data Generated by the Lloyd Kahn Procedure

Quality Control Item	Usability Criteria	Action
Independent Calibration Verification Standard (ICV) and Continuing Calibration Verification Standard (CCV)	ICV and CCV Recoveries (%R) should be 85-115%	If the ICV or CCV %R>115% qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the ICV or CCV 55%≤%R<85% qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the ICV or CCV %R <55%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Blanks (Preparation and/or Continuing Calibration Blanks) (See Note #2 for additional information)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target analyte is found in blank but not in the associated sample(s) no action is needed. If sample >RL, but <5× blank result, qualify the positive results as "not detected" ("U*"). If sample is positive, but <RL and <5× blank result, qualify the positive result as "not-detected" ("U*"). If sample result >5× blank result no qualification is necessary.
Laboratory Fortified Sample Matrix Sample (MS)	For accuracy, use default recovery limits of 75-125%. For precision, use RPD limits of 20% for aqueous and 40% for solid.	Data should not be qualified due to %Rs (or RPD calculated on %Rs) that are outside of criteria if the original concentration of a compound is > 4 × spiking level for that compound. RPDs calculated using MS/MSD results can still be used to evaluate precision. If the recovery is >125%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is 30%≤%R<75%, qualify positive results in the all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the precision exceeds the specified RPD, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.

Notes for the Validation of TOC Data Generated by the Lloyd Kahn Procedure

Quality Control Item	Usability Criteria	Action
Field/Laboratory Duplicate (See Note #3 for additional information)	Use limit of 20% RPD (%RSD for triplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate analyses) for solid samples for sample results ≥5× RL. Use default limit of ± RL for aqueous samples and ±2× RL for solid samples when at least one sample value is <5× RL. (Use one-half of the numerical value for comparison if the TOC was "not-detected")	If the criteria are not met, qualify positive results for the non-compliant analyte in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Solid samples with less than 50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data which were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, the reviewer should include his assessment of the usability of the data within the given context.

Notes for the Validation of TOC Data Generated by the Lloyd Kahn Procedure

1. Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive then the samples should be evaluated for false positives. If the concentration intercept is negative then the samples should be evaluated for false negatives.

2. The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (unless only one was collected for a several-day sampling event; results would be applied to all samples in the SDG). In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

3. Duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicate should be applied to all samples in a batch. It is also expected that soil duplicate results will have a greater variance than aqueous duplicate results.

APPENDIX 42

Environmental Standards, Inc.
General Electric Co. Hudson River PCBs Superfund Site
Electronic Data Deliverable Specifications

Introduction

The purpose of this document is to describe the processing of the analytical data received from the laboratory and includes the required specifications of the electronic data deliverable (EDD) along with the field sample and core data import format.

File Format

All data from the laboratory must be stored in an ASCII file using a tab-delimited standard format. Maximum length of text fields is indicated in the parentheses under Column Datatype. If the information is less than the maximum length, do not pad the record with spaces.

Each record must be terminated with a carriage return/line feed (i.e., standard DOS text file). The file can be produced using any software with the capability to create ASCII files. Date is reported as MM/DD/YY (month/day/year) and time as HH:MM (hour:minute). Time uses a 24 hour clock, thus 3:30 p.m. will be reported as 15:30.

Six files are required: one each for core data, field samples, laboratory samples, tests, results, and batches. The files must have valid DOS (8.3) filenames. The filename extensions are used to indicate the file type as follows:

*.COR for core data rows
*.FLD for field sample rows
*.SMP for laboratory sample rows
*.TST for test rows
*.RES for result rows
*.BCH for batch rows

The core data file (*.COR) and field sample file (*.FLD) are required files that will originate from the field contractor. The filenames for the .COR and .FLD deliverables are defined as the date of the file's creation.

The 8-character portion filenames for the lab generated files must be the same for each group of four files. Filename conventions are defined as the sample delivery group. Although Environmental Standards anticipates that all four files will be prepared and loaded into the database together in one group, this is not necessary. Each file can be loaded separately if desired.

Data Integrity Rules

If a field is to be considered part of the primary key of a table, it is indicated below by the presence of "PK" in the *PK* column. The combination of values in each primary key must be unique within the file. Also, referential integrity must be enforced between tables. That is, the values of `sys_sample_code` present in the Result and Test tables must also be present in the Sample table.

The key fields in the test table may appear complicated, so they are discussed further here. By default, only two fields are defined as part of a unique key: `sys_sample_code` and `lab_anl_method_name`. This means that each combination of sample ID and lab method can be used to uniquely define a lab test event. For this project, we are going to store retests or re-dilutions as separate test events. In order to achieve this, include `analysis_date and analysis_time` as part of the unique key of

test. This will allow multiple occurrences of a given combination of sample ID and lab method, provided that analysis date and time is different for each retest. Other common situations are discussed below. The fields that are included as part of the unique key on test are indicated below by the presence of "PK" in the *PK* column. These fields are part of the uniqueness constraint needed by the data management user, so they must be required in the EDD.

A. The data management users intend to import the full suite of test level information, including column-number and analysis-time. **Environmental Standards, Inc. requires the inclusion of both the column number and analysis time for this project.**

B. Some metal analyses can be done on unfiltered samples (to obtain total concentrations) or can be done on filtered samples (to get dissolved concentrations). The data management users need to use the same method name value for both of these tests, and therefore require another field to distinguish between these test types. **Environmental Standards, Inc. requires the total or dissolved field to be populated for this project.**

Null Format

Many fields are optional, and the list of valid values may be defined in a project or lab specific manner as determined by the laboratory and project manager. When a field is not listed as required, this means that a null or blank may be appropriate. However, the blank value must still be surrounded by tabs. In other words, the number of fields is always the same, whether or not the fields include data is optional.

OPL Naming Convention of Field Samples

Field Samples being submitted to the data management system follow the standard Organization, Project, Location (OPL) naming structure. As an example, a field sample ID of 'RS1-9594-WS001-' designates:

Organization = RS1
Project = 9594
Location = WS001

The field sample ID describes a core collected in River Section 1 (RS1) between river miles 195 and 194 (9594) at a screening location on the western half of the channel (WS) and is core number 1 (001). Additional depth information is added after the location (WS001) to complete the unique field sample ID.

There are to be no dashes used within in the OPL naming convention. For example river miles 195 and 194 should be characterized as 9594 and not 95-94. There is to be no deviation in this regard due to system requirements.

The contractor is responsible to let the lab know the proper Organization, Project, Location (OPL) structure to append to the field sample id on the chain of custody. If the field on the chain of custody is too small for the new sample naming convention, please place the proper OPL codes in the comments field so the lab can append the information to the field sample name. If this information is not present the EDD will fail EDD checks and will be returned to the data generator for corrections.

There are some samples, while having no real sampling location, should also follow the OPL naming convention. They are PE samples and Lab QC samples.

PE samples will use the same organization and project codes as the other samples with which they are sent. The location will be the concatenation of PE and the date in mmddyy format. The sample custodian ID and a sequential number will be used at the end to identify the sample. As an example, a PE sample sent on August 21, 2002 for the project above would look like RS1-9594-PE082102-A01. A second PE sample would have A02 at the end.

Lab QC samples will use the concatenation of LABQC and the SDG for the location code, while maintaining the same organization and project codes. Use the internal laboratory sample ID at the end to identify the sample. For example a method blank QC sample (A3910) for the project mentioned above would look like RS1-9594-LABQC[*SDG*]-A3910.

Examples

Below are examples of sample types to be used in the project, showing when fields need to be populated and when it is not necessary to populate fields.

QC fields in a normal field sample (i.e., Sample_type_code = FS, TB, etc.)

The following table shows a subset of the fields in the result file for a normal field sample. Notice that all QC fields are blank.

cas_rn	result value	qc original conc	qc spike added	qc spike measured	qc spike recovery	qc dup original conc	qc dup spike added	qc dup spike measured	qc dup spike recovery
93-76-5	1.56								
94-75-7	3.17								
94-82-6	2.31								

QC fields in a normal field sample with surrogates (i.e., Sample_type_code = FS, TB, etc.)

The following table shows a subset of the fields in the result file for a normal field sample. Notice that QC fields are blank except on surrogate rows.

Cas_rn	Result value	result unit	result type code	qc original conc	qc spike added	qc spike measured	qc spike recovery
93-76-5	1.56	mg/l	TRG				
94-75-7	3.17	mg/l	TRG				
PHEN2F		mg/l	SUR		12.5	12.9	103

QC fields in a matrix spike (i.e., Sample_type_code = MS)

The following table shows some of the fields in the result file for a matrix spike sample. Notice that all "dup" QC fields are blank, and that the result_value field is not needed. Also, the qc_rpd field would be blank for these rows.

Cas_rn	Result value	qc original conc	qc spike added	qc spike measured	qc spike recovery	qc dup original conc	qc dup spike added	qc dup spike measured	qc dup spike recovery
93-76-5		1.56	4.18	5.36	90.9				
94-75-7		3.17	4.18	7.15	95.2				
94-82-6		2.31	4.22	5.66	79.3				

QC fields in a matrix spike duplicate (i.e., Sample_type_code = SD)

The following table shows a subset of the fields in the result file for a matrix spike duplicate sample. Notice that all "dup" QC fields are completed, and that the result_value field is not needed. **Also, the qc_rpd field would be completed for these rows.**

cas_rn	result value	qc original conc	qc spike added	qc spike measured	qc spike recovery	qc dup original conc	qc dup spike added	qc dup spike measured	qc dup spike recovery
93-76-5						1.56	4.23	5.70	97.8
94-75-7						3.17	4.23	7.62	105
94-82-6						2.31	4.13	5.33	73.1

QC fields in an LCS (i.e., laboratory control sample, blank spike, Sample_type_code = LCS)

The following table shows a subset of the fields in the result file for an LCS sample. **The qc_rpd field would be blank for these rows.**

Cas_rn	Result value	qc original conc	qc spike added	qc spike measured	qc spike recovery	qc dup original conc	qc dup spike added	qc dup spike measured	qc dup spike recovery
93-76-5			5.00	5.26	105				
94-75-7			1.00	1.02	102				
94-82-6			12.5	12.9	103				

Retests

The following table shows how to report retests in an example where a sample was retested at dilution. The end user would see the first two constituents (75-25-2, and 67-66-3) in the initial test, and constituent 95-95-4 in the diluted retest. The other results would be "turned off" by setting the reportable_result field to "No".

Test_type	cas_rn	result_value	reportable_result
initial	75-25-2	1.2	Yes
initial	67-66-3	3.4	Yes
initial	95-95-4	100	No
retest	75-25-2	0	No
retest	67-66-3	0	No
retest	95-95-4	78.3	Yes

Second Columns

The following table shows how to report first and second column confirmation results. The end user would see the first and third constituents (75-25-2, and 95-95-4) as "primary" in the first column, and constituent 67-66-3 as "primary" in the second column. The other results would be "turned off" by setting the reportable_result field to "No".

column_number	cas_rn	result_value	reportable_result
1C	75-25-2	1.2	Yes
1C	67-66-3	3.4	No
1C	95-95-4	5.6	Yes
2C	75-25-2	1.3	No
2C	67-66-3	3.7	Yes
2C	95-95-4	5.4	No

Units

Units are to be reported consistently for the duration of the project. The result_unit field is required to be reported as specified in the reference values. Associated measurements (i.e., reporting detection limit, method detection limit) should be reported consistently with the result units.

Core Data Import Format

#	Attribute Name	Column Datatype	PK	Required	Attribute Definition
1	core_ID	Text(14)	PK	required	Unique core ID
2	core_date	Date		required	Date core was collected (in MM/DD/YY format).
3	core_time	Time		required	Time core was collected (in 24-hr (military) HH:MM format.
4	sampling_technique	Text(4)		required if applicable	Indicates how sample was collected. Valid values are CORE or GRAB
5	weight	Text(4)		required if applicable	The weight of the full core or grab sample
6	weight_unit	Text(4)		required if applicable	Unit of measurement for the weight of the full core or grab sample
7	northing	Text(20)		required	Northing coordinate (NY state plane east NAD83)
8	easting	Text(20)		required	Easting coordinate (NY state plane east NAD83)
9	coordinate_unit	Text(15)			Unit of measurement for the northing and easting coordinates
10	water_depth	Text(5)		required	Water depth at core collection location
11	water_depth_unit	Text(15)			Unit of measurement for the core collection location water depths
12	core_recovered	Yes/No		required	Indicates if core collection was possible at target coordinates. If “No”, target coordinates are entered in Northing and Easting fields.
13	pen_depth	Text(4)			Total penetration depth of sediment core tube
14	field_rec_depth	Text(5)			Total length of sediment core recovered
15	lab_rec_depth	Text(5)			Recovery depth measured at the field lab
16	probe_depth	Text(5)		required	Depth of penetration of sediment probe
17	prp_depth_unit	Text(15)			Units of measurement for the penetration depths of the core tube and sediment probe, and the recovery depths.
18	probe_sed_type	Text(20)		required	General sediment texture description based on probing – ‘FINE’, ‘COARSE’, ‘ROCK’
19	probe_desc	Text(255)			Additional information from sediment probing results.
20	core_tube	Text(10)			Type of core tube used to collect sediment sample – ‘LEXAN’, ‘ALUMINUM’
21	sampler	Text(30)			Name or initials of sampler.
22	sampling_company_code	Text(10)			Contractor code. For valid value list consult the reference values for the project.

Field Sample Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(20)	PK	required		Unique sample identifier. Each sample must have a unique value, including blanks and duplicates. This field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (ex: the first sample on the chain would be COC042602-001, second sample would be COC042602-002, etc.). This file should only contain field samples, including field blanks, equipment blanks, and field duplicates. This table should not include laboratory samples. **Required**
2	sample_name	Text(30)		required		Unique field sample ID. Each sample must have a unique value. **The Organization, Project, Location naming convention, as described on page 2, must be followed.**
3	sample_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of sample matrix. For example, soil samples must be distinguished from ground water samples. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g. TCLP leachates), so this field is required at the sample level. For valid value list, consult the reference values supplied for this project.
4	sample_type_code	Text(10)		required	Yes	Code which distinguishes between different types of samples. For valid value list, consult the reference values supplied for this project.

5	sample_source	Text(10)		required	Yes	This field identifies where the sample came from, either **Field** or **Lab**. In this import, this should always be **Field**.
6	parent_sample_code	Text(20)		required if applicable		Must be blank for normal field samples. The value of "sys_sample_code" that uniquely identifies the sample that was the source of this sample.
7	sample_date	Date		required		Date sample was collected (in MM/DD/YY format).
8	sample_time	Time		required		Time of sample collection in 24-hr (military) HH:MM format.
9	start_depth	Text(5)		required		Beginning depth (top) of soil sample.
10	end_depth	Text(5)		required		Ending depth (bottom) of soil sample.
11	depth_unit	Text(15)		required		Unit of measurement for the sample begin and end depths.
12	test_requested	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the reference values supplied for this project.
13	preservative_chemical	Text(50)		required if applicable		If sample is preserved, enter type of preservative in this field (use chemical symbol). If sample is unpreserved, this field must be null.
14	preservative_temperature	Text(5)		required if applicable		Temperature to which sample is cooled in the format of number and unit without the degree symbol (i.e. if temp. is 4 degrees Celcius it should be reported as “4C” not “4°C”).
15	chain_of_custody	Text(15)		required		Chain of custody identifier. A single sample may be assigned to only one chain of custody.
16	sent_to_lab_date	Date				Date sample was sent to lab (in MM/DD/YY format for EDD). Not included in the laboratory EDD.
17	custodian_initials	Text(5)				Initials of sample processing custodian
18	texture_desc	Text(11)			Yes	Uniform codes indicating sediment type or composition (primary/some/little/trace). Example: CS/--/--/OR (sample is primarily coarse sand with

						trace organics). For valid value list, consult the reference values supplied for the project.
19	num_containers	Integer		required		Number of sample containers
20	general_desc	Text(255)				General visual description information for sediment core section.
21	cultural_obs	Text(255)				Description of cultural artifacts (if any) found in the sample.
22	sample_archived	Yes/No				Indicates if a split sample was archived.
23	cooler_id	Text(30)		required		Sample container identifier.
24	epa_split	Yes/No				Indicates if the sample was chosen as a split by the EPA.
25	tat_expected	Double		required		Expected turn-around-time in number of business days for laboratory results.
26	matrix_spike_yn	Yes/No		required	Yes	“Y” if the sample was chosen for matrix spike analysis, “N” if not chosen.
27	matrix_spike_dup_yn	Yes/No		required	Yes	“Y” if the sample was chosen for matrix spike duplicate analysis, “N” if not chosen.
28	jar_lot_number	Text(30)		required		ID of the sample jar, assigned by the supplier.

Sample Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(20)	PK	required		Unique sample identifier. Each sample must have a unique value, including spikes and duplicates. Laboratory QC samples must also have unique identifiers. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (ex: COC042602-001), followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. This table should **only** contain laboratory-generated samples, including lab blanks, blank spikes, matrix spikes, matrix spike duplicates, and laboratory replicates. This table should not include field samples. **Required**
2	lab_sample_id	Text(60)		required		Laboratory sample identifier. **The Organization, Project, Location naming convention, as described on page 2, must be followed. Required**
3	sample_type_code	Text(10)		required	Yes	Code which distinguishes between different types of sample. For valid value list, consult the reference values supplied for the project.
4	sample_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of sample matrix. For example, soil samples must be distinguished from ground water samples. The matrix

						of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g. TCLP leachates), so this field is required at the sample level. For valid value list, consult the reference values supplied for the project.
5	sample_source	Text(10)		required	Yes	Must be “Lab” for internally generated laboratory QC samples. For example, a matrix spike duplicate sample would be a “Lab” sample.
6	parent_sample_code	Text(20)		required where applicable		The value of “sys_sample_code” that uniquely identifies the sample that was the source of this sample. For example, the value of this field for a laboratory replicate sample would identify the normal sample of which this sample is a replicate (same sys_sample_code as replicate without the “LR” designation). Required in the laboratory EDD for all laboratory “clone” samples (e.g., spikes and duplicates). Must be blank for samples that have no parent (e.g., lab blanks and lab control samples). This field must be filled out for those samples which have “parents.”
7	Comment	Text(255)				Sample comments as necessary (optional).
8	sample_date	Date/Time				Must be blank for laboratory generated samples. Date of sample collection in MM/DD/YY format. **Will be a blank field for this project.**
9	sample_time	Text(5)				Must be blank for laboratory generated samples. Time of sample collection in 24-hr (military) HH:MM format. **Will be a blank field for this project.**

10	standard_solution_source	Text(20)				Relevant only for laboratory-generated samples. Textual description of the source of standard solutions as needed for certain laboratory samples (e.g., LCS).

Test Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(20)	PK	required		Unique sample identifier. Each sample must have a unique value, including spikes and duplicates. Laboratory QC samples must also have unique identifiers. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (ex: COC042602-001), followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. **Required**
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the reference values supplied for this project.
3	analysis_date	Date/Time	PK	required		Date of sample analysis in MM/DD/YY format. Must refer to the beginning of the analysis for this project.
4	analysis_time	Text(5)	PK	required		Time of sample analysis in 24-hr (military) HH:MM format. Must refer to the beginning of the analysis for this project. Note that this field, combined with the "analysis_date" field is used to distinguish between retests and reruns. Please ensure that retests have "analysis_date" and/or "analysis_time" different from the original test event (and fill out the test_type field as needed).
5	total_or_dissolved	Text(1)	PK	required	Yes	It must be either "T" for total [metal] concentration, "D" for dissolved or filtered [metal] concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.

6	column_number	Text(2)	PK	required	Yes	Required, it must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable. If any "2C" tests are reported, then there must be corresponding "1C" tests present also. Also, laboratories will be reporting which of the two columns is to be considered "primary". This distinction is handled by the "reportable_result" field in the result table.
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	lab_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of lab sample matrix. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g. TCLP leachates). Valid values include “W” and “S”.
9	analysis_location	Text(2)		required	Yes	Must be either "FI" for field instrument or probe, "FL" for mobile field laboratory analysis, or "LB" for fixed-based laboratory analysis.
10	basis	Text(10)		required	Yes	It must be either "Wet" for wet-weight basis reporting, "Dry" for dry-weight basis reporting, or "NA" for tests for which this distinction is not applicable.
11	dilution_factor	Text(4)		required		Effective test dilution factor.
12	prep_method	Text(35)		required if applicable	Yes	Laboratory sample preparation method name or description. For valid values consult the reference list supplied for the project.
13	prep_date	Date/Time		required if applicable		Date of sample preparation in MM/DD/YY format. Must refer to the end of the prep for this project.
14	prep_time	Text(5)		required if applicable		Time of sample preparation in 24-hr (military) HH:MM format. Must refer to the end of the prep for this project.
15	leachate_method	Text(15)		required if		Laboratory leachate generation

				applicable		method name or description. A list of valid method names is not required for the laboratory EDD unless otherwise specified by the project manager.
16	leachate_date	Date/Time		required if applicable		Date of leachate preparation in MM/DD/YY format. Must refer to the end of the leachate for this project.
17	leachate_time	Text(5)		required if applicable		Time of leachate preparation in 24-hr (military) HH:MM format. Must refer to the end of the leachate for this project.
18	lab_name_code	Text(10)		required		Unique identifier of the laboratory. Must be consistent throughout the project.
19	data_package_level	Text(10)		required	Yes	Data package level. Values are “A”, “B”, or “AB”.
20	lab_sample_id	Text(20)		required		Laboratory sample identifier.
21	percent_moisture	Text(5)		required		Percent moisture of the sample portion used in this test; this value may vary from test to test for any sample. Numeric format is "NN.MM", i.e., 70.1% could be reported as "70.1" but not as "70.1%".
22	subsample_amount	Text(14)		required		Amount of original sample used in sample preparation.
23	subsample_amount_ unit	Text(15)		required		Unit of measurement for subsample amount.
24	analyst_name	Text(30)				Name or initials of laboratory analyst. This is an optional field for the laboratory EDD unless otherwise specified by the project manager.
25	instrument_id	Text(50)				Instrument identifier. This is an optional field for the laboratory EDD unless otherwise specified by the project manager.
26	sample_receipt_date	Date/Time		required		Must be blank for laboratory generated samples. Date of sample collection in MM/DD/YY format.
27	sample_receipt_time	Text(5)		required		Must be blank for laboratory generated samples. Time of sample collection in 24-hr (military) HH:MM format.
28	sample_delivery_group	Text(10)		required		Sample delivery group.
29	Comment	Text(255)				Comments about the test as necessary.

30	final_volume	Text(15)		required if applicable		The final amount/volume of the sample, extract, or digestate after sample preparation.
31	final_volume_unit	Text(15)		required if applicable		The unit of measure that corresponds to the final volume.

Result Import Format

#	Attribute Name	Type	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(20)	PK	required		Unique sample identifier. Each sample must have a unique value, including spikes and duplicates. Laboratory QC samples must also have unique identifiers. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (ex: COC042602-001), followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. **Required**
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the reference values supplied for the project.
3	analysis_date	Date/Time	PK	required		Date of sample analysis in MM/DD/YY format. Must refer to the beginning of the analysis for this project.
4	analysis_time	Text(5)	PK	required		Time of sample analysis in 24-hr (military) HH:MM format. Must refer to the beginning of the analysis for this project. Note that this field, combined with the "analysis_date" field is used to distinguish between retests and reruns. Please ensure that retests have "analysis_date" and/or "analysis_time" different from the original test event (and fill out the test_type field as needed).

5	total_or_dissolved	Text(1)	PK	required	Yes	It must be either "T" for total [metal] concentration, "D" for dissolved or filtered [metal] concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	Required, it must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable. If any "2C" tests are reported, then there must be corresponding "1C" tests present. Also, laboratories are reporting which of the two columns is to be considered "primary". This distinction is handled by the "reportable_result" field in the result table.
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	cas_rn	Text(15)	PK	required	Yes	Chemical Abstracts Registry Number for the parameter if available. Otherwise consult the reference values supplied for this project.
9	chemical_name	Text(60)		required	Yes	Chemical name is used only in review of EDD. For valid value list, consult the reference values supplied for the project. **Required**
10	result_value	Text(20)		required where applicable		Analytical result reported at the project specified number of significant digits. Must be blank for non-detects.
11	result_error_delta	Text(20)				Error range applicable to the result value; typically used only for radiochemistry results.
12	result_type_code	Text(10)		required	Yes	Must be either "TRG" for a target or regular result, and "SUR" for surrogates.

13	reportable_result	Text(10)		required	Yes	Must be either "Yes" for results which are considered to be reportable, or "No" for other results. This field has many purposes. For example, it can be used to distinguish between multiple results where a sample is retested after dilution. It can also be used to indicate which of the first or second column result should be considered primary. The proper value of this field in both of these two examples should be provided by the laboratory (only one result should be flagged as reportable).
14	detect_flag	Text(2)			Yes	Must be either "Y" for detected analytes or "N" for non-detects.
15	lab_qualifiers	Text(7)		required	Yes	Qualifier flags assigned by the laboratory. For valid value list, consult the reference values supplied for the project
16	organic_yn	Yes/No		required	Yes	Must be either "Y" for organic constituents or "N" for inorganic constituents.
17	method_detection_limit	Text(20)		required		Method detection limit. Required for all results for which such a limit is appropriate.
18	reporting_detection_limit	Text(20)		required		Detection limit that reflects conditions such as dilution factors and moisture content. Required for all results for which such a limit is appropriate.
19	quantitation_limit	Text(20)		required		Concentration level above which results can be quantified with confidence. It must reflect conditions such as dilution factors and moisture content. Required for all results for which such a limit is appropriate.
20	result_unit	Text(15)		required if applicable	Yes	Units of measurement for the result. For valid value list, consult the reference values supplied for the project.

21	detection_limit_unit	Text(15)		required		Units of measurement for the detection limit(s).
22	tic_retention_time	Text(8)				Retention time in seconds for tentatively identified compounds. TICs will not be used on this project.
23	result_comment	Text(255)				Result specific comments.
24	qc_original_conc	Text(14)		required where applicable		The concentration of the analyte in the original (unspiked) sample. This field is required for matrix spikes and not necessary for surrogate compounds or LCS samples (where the original concentration is assumed to be zero). If original (unspiked) sample is a non-detect, then populate this field with a "0" as opposed to the detection limit. For matrix spikes, if using an original sample result that is less than the reporting limit for background correction, then populate this field with the below reporting limit original sample result, as opposed to "0".
25	qc_spike_added	Text(14)		required where applicable		The concentration of the analyte added to the original sample. Required for matrix spikes, surrogate compounds, and LCSs.
26	qc_spike_measured	Text(14)		required where applicable		The measured concentration of the analyte. Use zero for spiked compounds that were not detected in the sample. Required for matrix spikes, surrogate compounds, and LCSs.
27	qc_spike_recovery	Text(14)		required where applicable		The percent recovery calculated. Always required for spikes, surrogate compounds, and LCSs. Report as percentage multiplied by 100 (e.g., report "120%" as "120").

28	qc_dup_original_conc	Text(14)		required where applicable		The concentration of the analyte in the original sample. Is required for matrix spike duplicates and lab replicates only. If original sample is a non-detect, then populate this field with a “0” as opposed to the detection limit. For matrix spike duplicates, if using an original sample result that is less than the reporting limit for background correction, then populate this field with the below reporting limit original sample result, as opposed to “0”.
29	qc_dup_spike_added	Text(14)		required where applicable		The concentration of the analyte added to the original sample. Required for matrix spike duplicates.
30	qc_dup_spike_measured	Text(14)		required where applicable		The measured concentration of the analyte in the duplicate (for background corrected matrix spike duplicates). Use zero for spiked compounds that were not detected in the sample. Required for matrix spike duplicates and lab replicates.
31	qc_dup_spike_recovery	Text(14)		required where applicable		The duplicate percent recovery calculated. Always required for spike or LCS duplicates, surrogate compounds, and any other spiked and duplicated sample. Also complete the qc_spike_recovery field. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
32	qc_rpd	Text(8)		required where applicable		The relative percent difference calculated. Required for duplicate samples as appropriate. Report as percentage multiplied by 100 (e.g., report "120%" as "120").

33	qc_spike_lcl	Text(8)		required where applicable		Lower control limit for spike recovery. Required for spikes, spike duplicates, surrogate compounds, LCS and any spiked sample. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
34	qc_spike_ucl	Text(8)		required where applicable		Upper control limit for spike recovery. Required for spikes, spike duplicates, surrogate compounds, LCS and any spiked sample. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
35	qc_rpd_cl	Text(8)		required where applicable		Relative percent difference control limit. Required for any duplicated sample. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
36	qc_spike_status	Text(10)		required where applicable		Used to indicate whether the spike recovery was within control limits. Use the "*" character to indicate failure, otherwise leave blank. Required for matrix spikes, surrogate compounds, and LCSs.
37	qc_dup_spike_status	Text(10)		required where applicable		Used to indicate whether the duplicate spike recovery was within control limits. Use the "*" character to indicate failure, otherwise leave blank. Required for any spiked and duplicated sample.
38	qc_rpd_status	Text(10)		required where applicable		Used to indicate whether the relative percent difference was within control limits. Use the "*" character to indicate failure, otherwise leave blank. Required for any duplicated sample.

Batch Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(20)	PK	required		Unique sample identifier. Each sample must have a unique value, including spikes and duplicates. Laboratory QC samples must also have unique identifiers. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a three digit number that is typed on the Chain-of-Custody to the left of each sample, followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. **Required**
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the reference values supplied for this project.
3	analysis_date	Date/Time	PK	required		Date of sample analysis in MM/DD/YY format. May refer to either beginning or end of the analysis long as it is consistent throughout the project.
4	analysis_time	Text(5)	PK	required		Time of sample analysis in 24-hr (military) HH:MM format. May refer to either beginning or end as long as it is consistent throughout the project. Note that this field, combined with the "analysis_date" field is used to distinguish between retests and reruns. Please ensure that retests have "analysis_date" and/or "analysis_time" different from the original test event (and fill out the test_type field as needed).
5	total_or_dissolved	Text(1)	PK	required	Yes	It must be either "T" for total [metal] concentration, "D" for dissolved or filtered [metal] concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	If required, then it must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable. If any

						"2C" tests are reported, then there must be corresponding "1C" tests present. Also, laboratories will be reporting which of the two columns is to be considered "primary". This distinction is handled by the "reportable_result" field in the result table.
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	test_batch_type	Text(10)	PK	required	Yes	Lab batch type. Valid values include "Prep", "Analysis", and "Leach". Additional valid values may optionally be provided by the project manager. This is a required field for all batches.
9	test_batch_id	Text(20)		required		Unique identifier for all lab batches. Must be unique within a database. For example, the same identifier can not be used for a prep batch and an analysis batch.