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QUALITY ASSURANCE PROJECT PLAN — DRAFT ADDENDUM

ATTACHMENT K

Standard Operating Procedures (SOPs)

Addendum to Tasks 19-22 QAPP (5/23/2001) To Support Centredale RI/FS

SDMS DocID 35829

ATTACHMENT K

Standard Operating Procedures (SOPs)

(not paginated)

STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHOD 8260B, 624 AND 524.2

(SUPERSEDES: REVISION 1)

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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°C (40°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 ± 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°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.

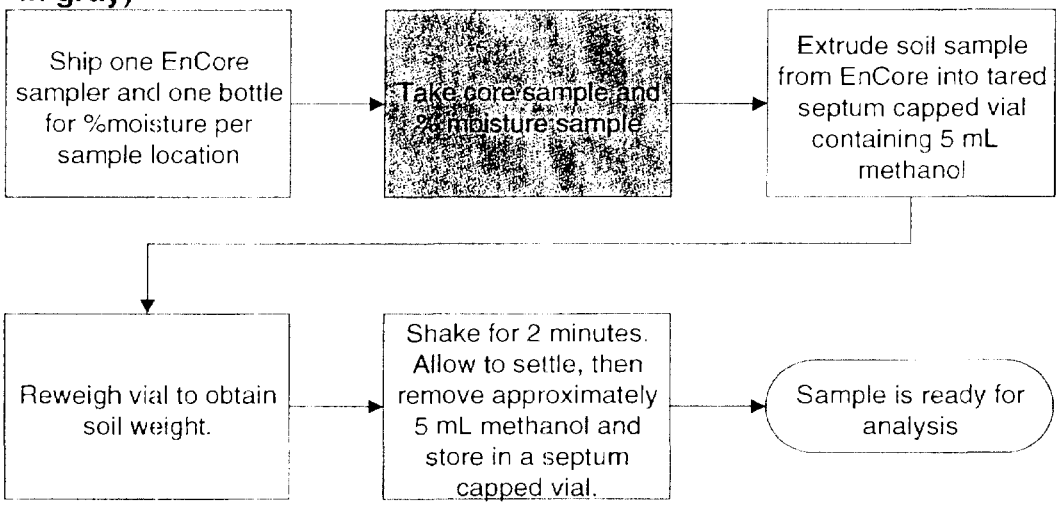
8.9 Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

8.10 Medium level solid extracts are aliquoted into 2 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

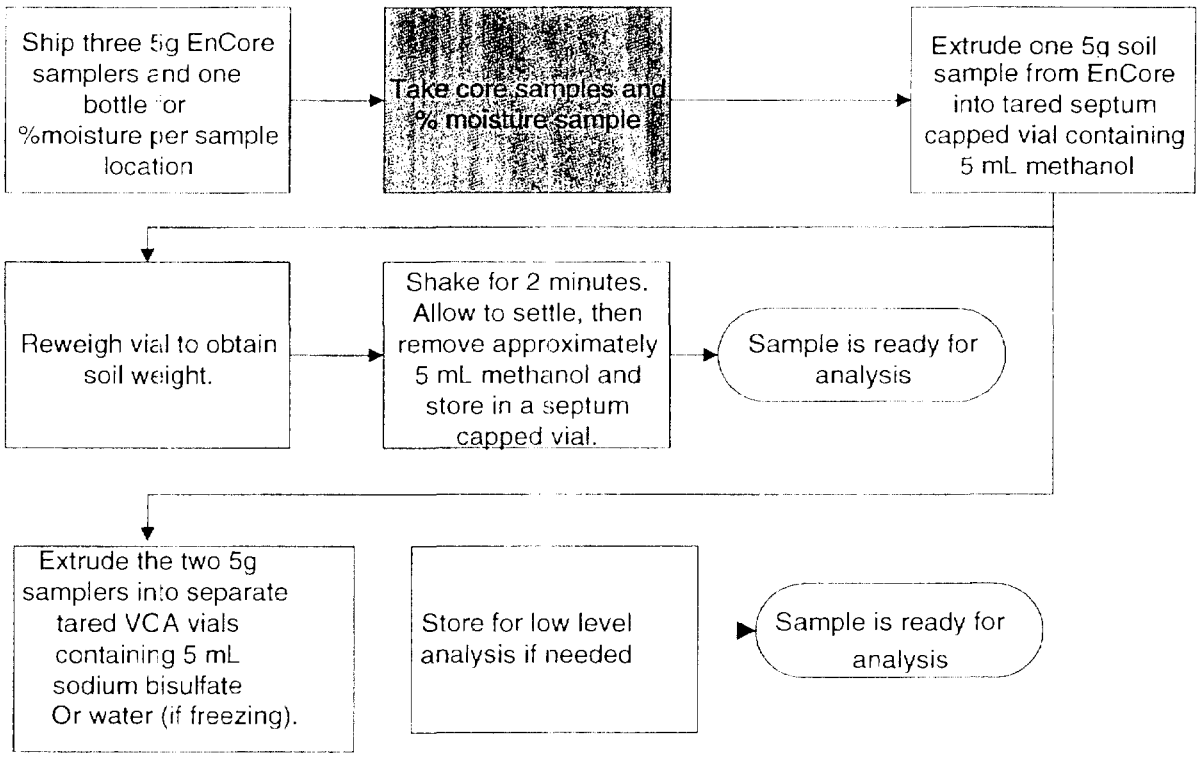
8.11 The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time 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.

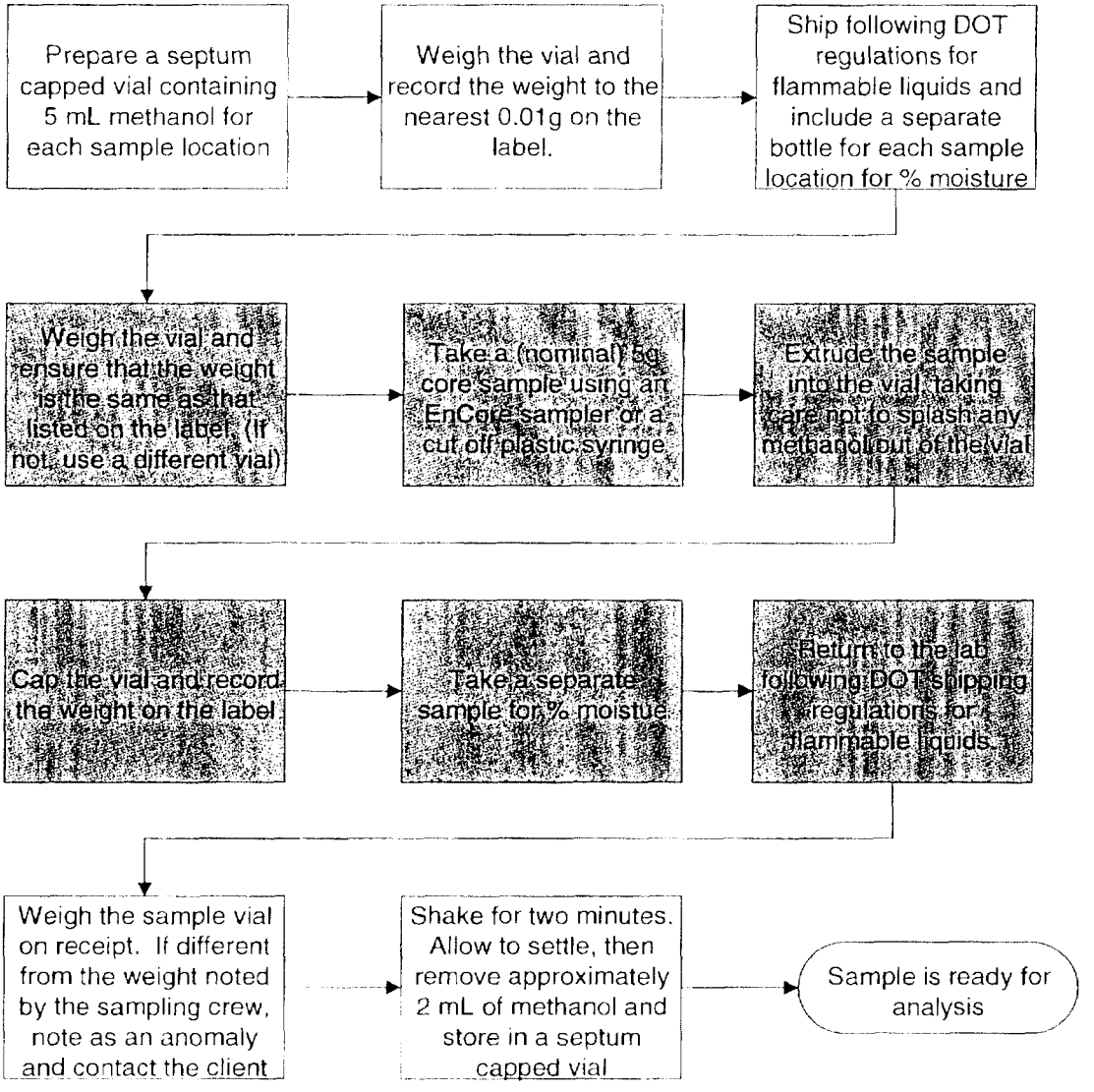
EnCore procedure when low level is not required (field steps in gray)



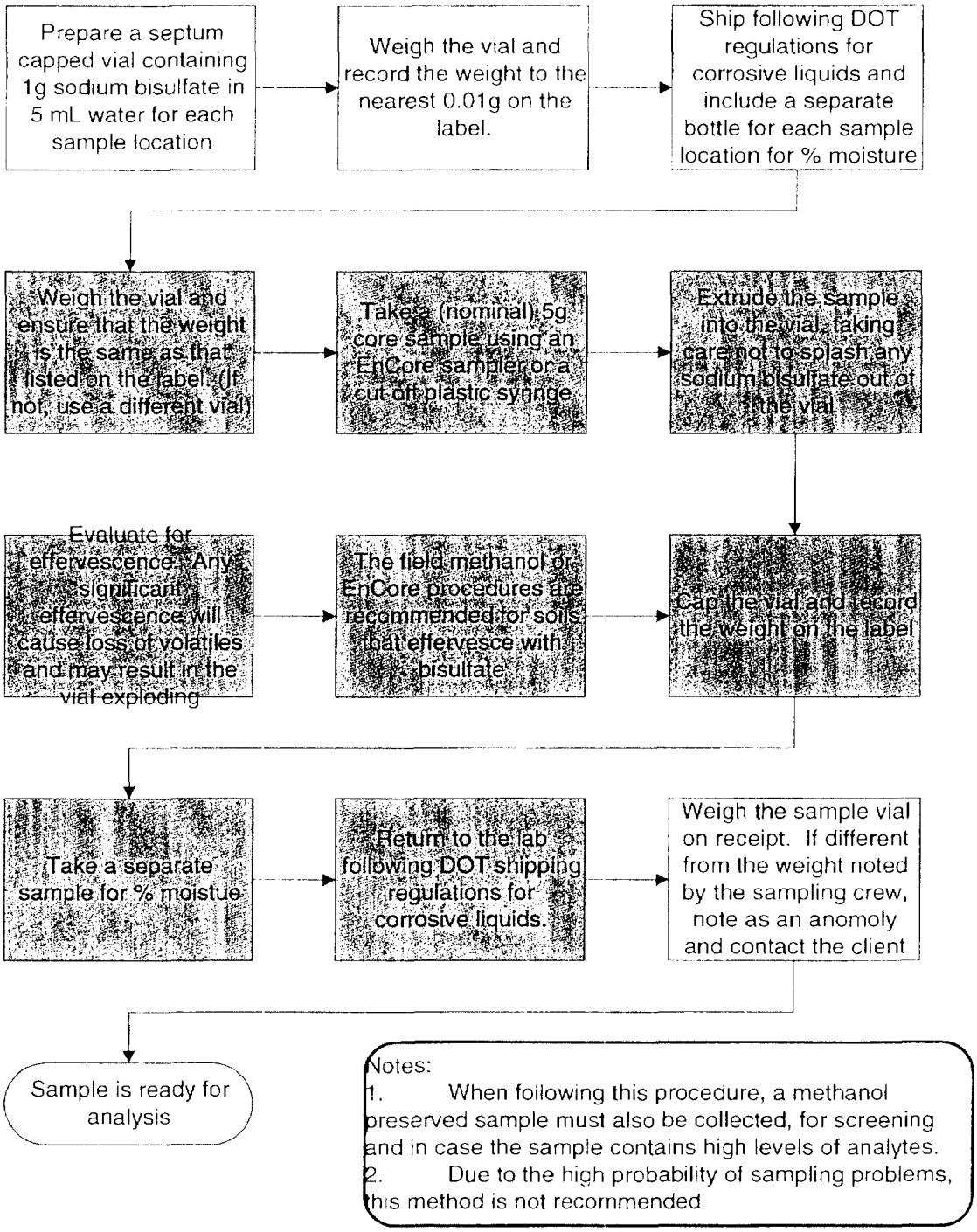
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



Notes:
1. When following this procedure, a methanol preserved sample must also be collected, for screening and in case the sample contains high levels of analytes.
2. Due to the high probability of sampling problems, this method is not recommended

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 ≤ 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 TCLP 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 $\leq$ 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

$$\%RSD = \frac{\textbf{Standard Deviation}}{\overline{RF_i}} \times 100$$

$\overline{RF_i}$ = **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

$$\% \text{ Drift} = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100$$

Where

$C_{expected}$ = Known concentration in standard

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

$$\text{Concentration } \mu g / L = \frac{x}{RF}$$

12.3.6.2 Calculation of concentration using Linear fit

Equation 7

$$\text{Concentration } \mu g / L = A + Bx$$

12.3.6.3 Calculation of concentration using Quadratic fit

Equation 8

$$\textbf{Concentration } \mu g / L = A + Bx + Cx^2$$

x is defined in equations 8, 9 and 10

A is a constant defined by the intercept

B is the slope of the curve

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:

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)

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

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:

A_x, I_s, D_f, A_{is}, same as for water.

V_t = Volume of total extract, mL

V_a = Volume of extract added for purging, µL

W_s = Weight of sample extracted, g

$$D = \frac{100 - \%\text{moisture}}{100}$$

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:

A_x, I_s, A_{is}, same as for water.

D is as for medium level soils

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

$$\mathbf{RPD} = \frac{|\mathbf{MSR - MSDR}|}{\frac{1}{2}(\mathbf{MSR + MSDR})} \times 100$$

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

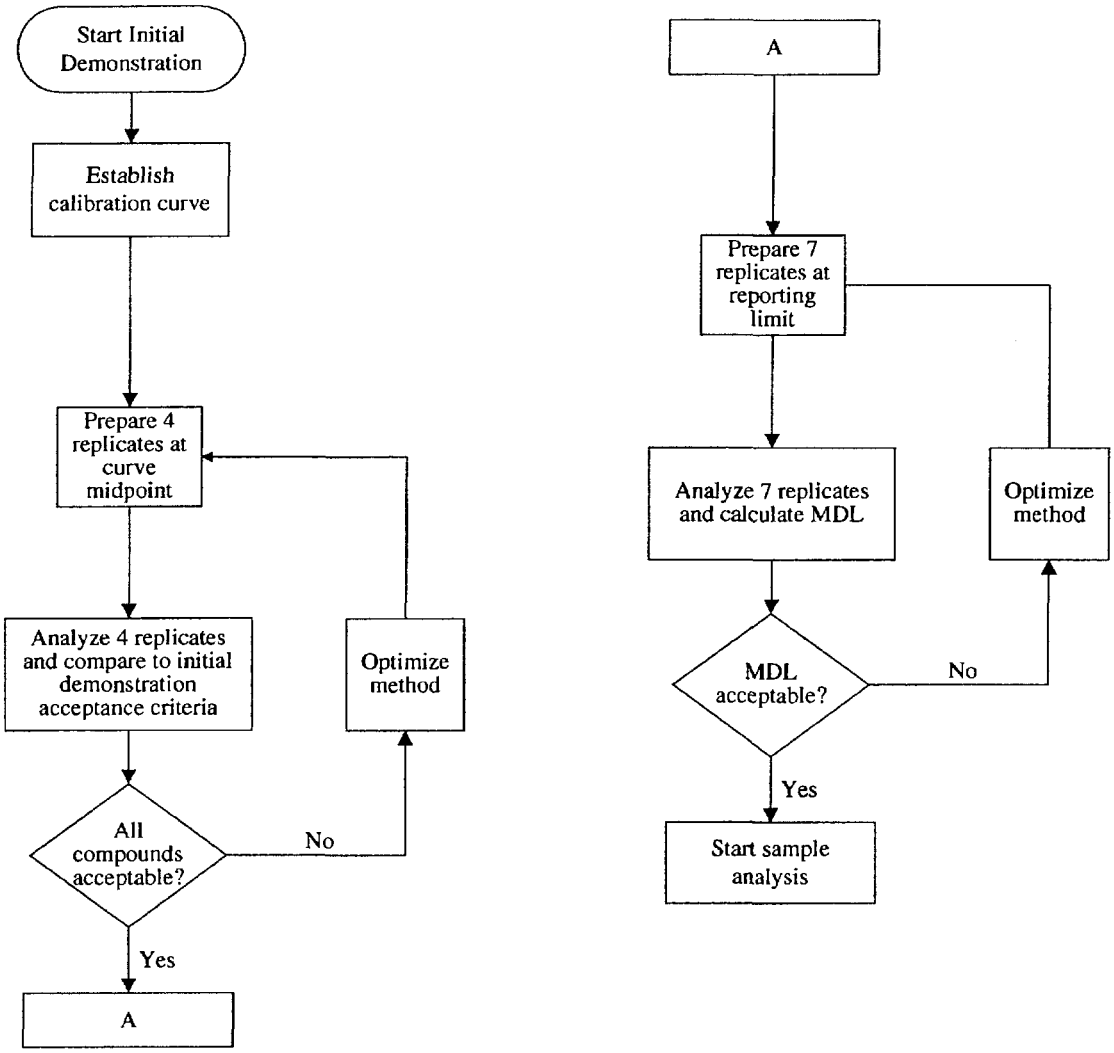


Table 1

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	10	2	10	500
Chloromethane	74-87-3	10	2	10	500
Bromomethane	74-83-9	10	2	10	500
Vinyl chloride	75-01-4	10	2	10	500
Chloroethane	75-00-3	10	2	10	500
Trichlorofluoromethane	75-69-4	10	2	10	500
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	2.5	0.5	2.5	125
Methyl *tert*-butyl ether (MTBE)	1634-04-4	20	5	20	1000
cis-1,2-Dichloroethene	156-59-2	2.5	0.5	2.5	125
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

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
4-Methyl-2-pentanone	108-10-1	20	5	20	1000
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	10	2	10	500
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

Table 5

Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Benzene	71-43-2	X	X	X	X	X
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 and Method 624.

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.

4) The surrogates for Method 524 will be at 2 ppb.

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 25 mL purge.

2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by the QA dedartment.

3) Full analyte spikes may also be used at the laboratories option or at client request. Method 524.2 will be spiked at 2 ppb for all compounds of interest.

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
2-Hexanone	43	58	57, 100

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
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.

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	0.5	10	2	10	500
Chloromethane	74-87-3	0.5	10	2	10	500
Bromomethane	74-83-9	0.5	10	2	10	500
Vinyl chloride	75-01-4	0.5	10	2	10	500
Chloroethane	75-00-3	0.5	10	2	10	500
Trichlorofluoromethane	75-69-4	0.5	10	2	10	500
Acetone[1]	67-64-1	10	20	10	20	1000
Methylene chloride	75-09-2	0.5	5	2	5	250
1,1-Dichloroethene	75-35-4	0.5	5	1	5	250
1,1-Dichloroethane	75-34-3	0.5	5	1	5	250
trans-1,2-Dichloroethene	156-60-5	0.5	2.5	0.5	2.5	125
Methyl *tert*-butyl ether (MTBE)[1]	1634-04-4	0.5	20	5	20	250
2,2-Dichloropropane	590-20-7	0.5	5	1	5	250
cis-1,2-Dichloroethene	156-59-2	0.5	2.5	0.5	2.5	125
1,2-Dichloroethene (Total)	540-59-0	1	5	1	5	250
Chloroform	67-66-3	0.5	5	1	5	250
Bromochloromethane	74-97-5	0.5	5	1	5	250
1,2-Dichloroethane	107-06-2	0.5	5	1	5	250
Dibromomethane	74-95-3	0.5	5	1	5	250
2-Butanone[1]	78-93-3	10	20	5	20	1000
1,1,1-Trichloroethane	71-55-6	0.5	5	1	5	250
Carbon tetrachloride	56-23-5	0.5	5	1	5	250
1,1-Dichloropropene	563-58-6	0.5	5	1	5	250
Bromodichloromethane	75-27-4	0.5	5	1	5	250
1,2-Dichloropropane	78-87-5	0.5	5	1	5	250
1,3-Dichloropropane	142-28-9	0.5	5	1	5	250
cis-1,3-Dichloropropene	10061-01-5	0.5	5	1	5	250
Trichloroethene	79-01-6	0.5	5	1	5	250
Dibromochloromethane	124-48-1	0.5	5	1	5	250
1,2-Dibromoethane	106-93-4	0.5	5	1	5	250
1,2,3-Trichloropropane	96-18-4	0.5	5	1	5	250
1,1,2-Trichloroethane	79-00-5	0.5	5	1	5	250
Benzene	71-43-2	0.5	5	1	5	250
trans-1,3-Dichloropropene	10061-02-6	0.5	5	1	5	250
Bromoform	75-25-2	0.5	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	10	20	5	20	1000
2-Hexanone[1]	591-78-6	10	20	5	20	1000
Tetrachloroethene	127-18-4	0.5	5	1	5	250
Toluene	108-88-3	0.5	5	1	5	250
1,1,2,2-Tetrachloroethane	79-34-5	0.5	5	1	5	250
Chlorobenzene	108-90-7	0.5	5	1	5	250
1,1,1,2-Terrachloroethane	630-20-6	0.5	5	1	5	250
Ethylbenzene	100-41-4	0.5	5	1	5	250
Styrene	100-42-5	0.5	5	1	5	250
m and p Xylenes		1	2.5	0.5	2.5	125
o-xylene	95-47-6	0.5	2.5	0.5	2.5	125
Total xylenes	1330-20-7	3	5	1	5	250
Isopropylbenzene	98-82-8	0.5	5	1	5	250
Bromobenzene	108-86-1	0.5	5	1	5	250
n-Propylbenzene	103-65-1	0.5	5	1	5	250
2-Chlorotoluene	95-49-8	0.5	5	1	5	250
4-Chlorotoluene	106-43-4	0.5	5	1	5	250
1,3,5-Trimethylbenzene	108-67-8	0.5	5	1	5	250
tert-Butylbenzene	98-06-6	0.5	5	1	5	250
1,2,4-Trimethylbenzene	95-63-6	0.5	5	1	5	250
sec-butylbenzene	135-98-8	0.5	5	1	5	250
1,3-Dichlorobenzene	541-73-1	0.5	5	1	5	250
1,4-Dichlorobenzene	106-46-7	0.5	5	1	5	250
1,2-Dichlorobenzene	95-50-1	0.5	5	1	5	250
4-Isopropyltoluene	99-87-6	0.5	5	1	5	250
n-Butylbenzene	104-51-8	0.5	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	1	5	1	5	250
1,2,4-Trichlorobenzene	120-82-1	0.5	5	1	5	250
Napthalene	91-20-3	0.5	5	1	5	250
Hexachlorobutadiene	87-68-3	0.5	5	1	5	250
1,2,3-Trichlorobenzene	87-61-6	0.5	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.

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.

20.8 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, gases (20ppb), 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	2
Carbon tetrachloride	1
Chlorobenzene	1
Chloroethane	2
2-Chloroethyl vinyl ether	2
Chloroform	1
Chloromethane	2
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	2
Vinyl chloride	2

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

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Revision No: 6.0
Revision Date: 03/25/2002

STL STANDARD OPERATING PROCEDURE

TITLE: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000B, 8021B, 8081A, 8082 and 8151A, SW-846,

WITH LAB SPECIFIC APPENDICES FOR 8141A & 8310

(SUPERSEDES: Revision 5.2)

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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). Volatile analytes are prepared for analysis using purge and trap methodology (Appendix A).

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. Stock standards for method 8021B are stored at -10 to -20°C. Other stock standard solutions are stored at ≤6°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. Volatile Calibration Standards

The procedure for preparation of volatile 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 ≤6°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 ≤6°C and analyzed within 40 days of the end of the extraction. Volatile sample storage conditions and holding times are given in Appendix A.

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). For low level volatiles, the method blank consists of reagent water. For medium level volatiles, the method blank consists of methanol as described in Appendix A. 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).

9.6.2. 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.

9.6.3. Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

9.6.4. 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:

$$Average\ response\ factor = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

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 ± 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 ≤ 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 ± 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 ± 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

In general, volatiles analytes are introduced using purge and trap as described in Appendix A. 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,* the 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:

$$RPD = \frac{R_1 - R_2}{\frac{1}{2}(R_1 + R_2)} x\,100$$

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

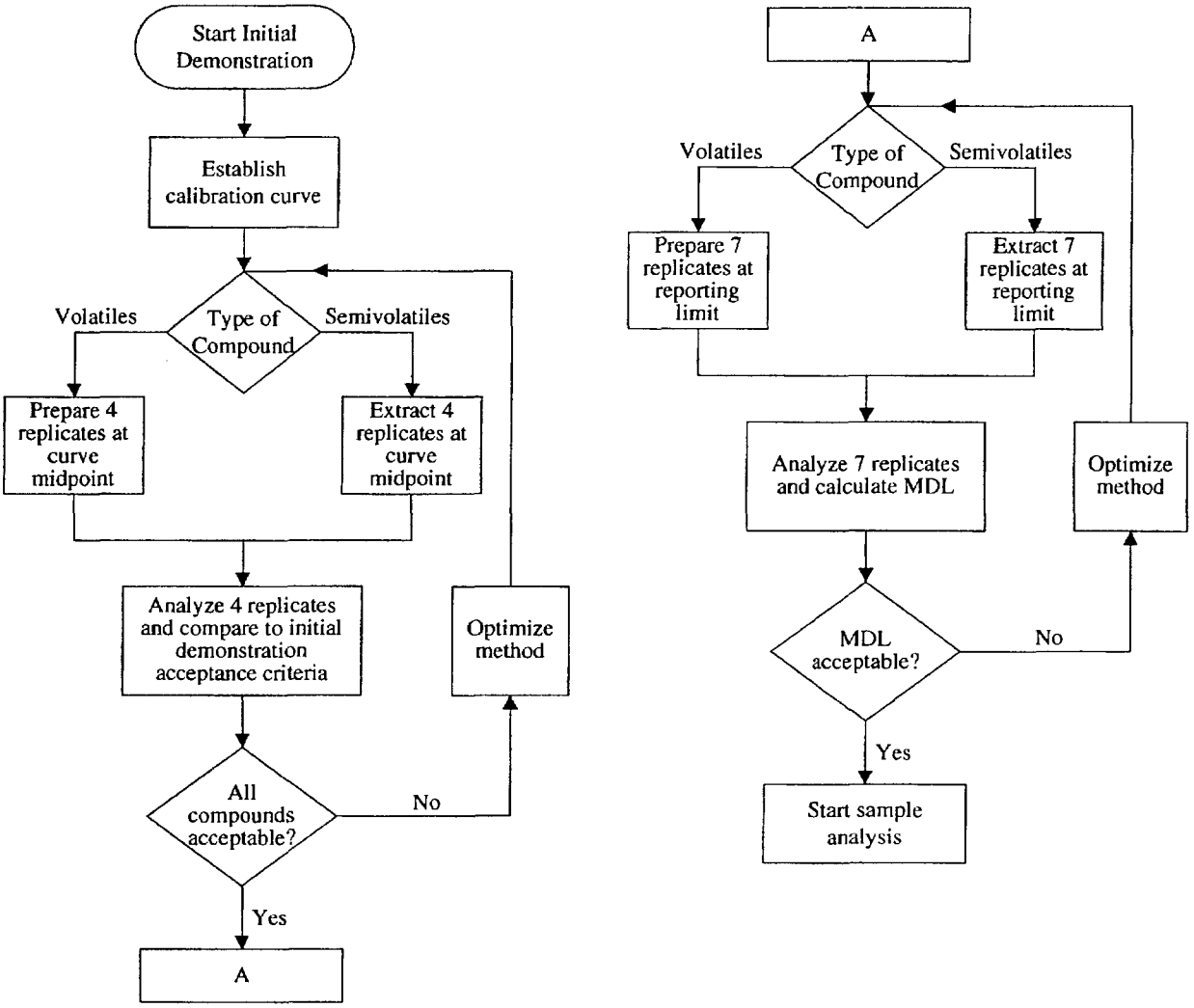
The calibration criteria in section 10.11 have been rewritten to improve consistency with SW-846 and to improve clarity.

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.

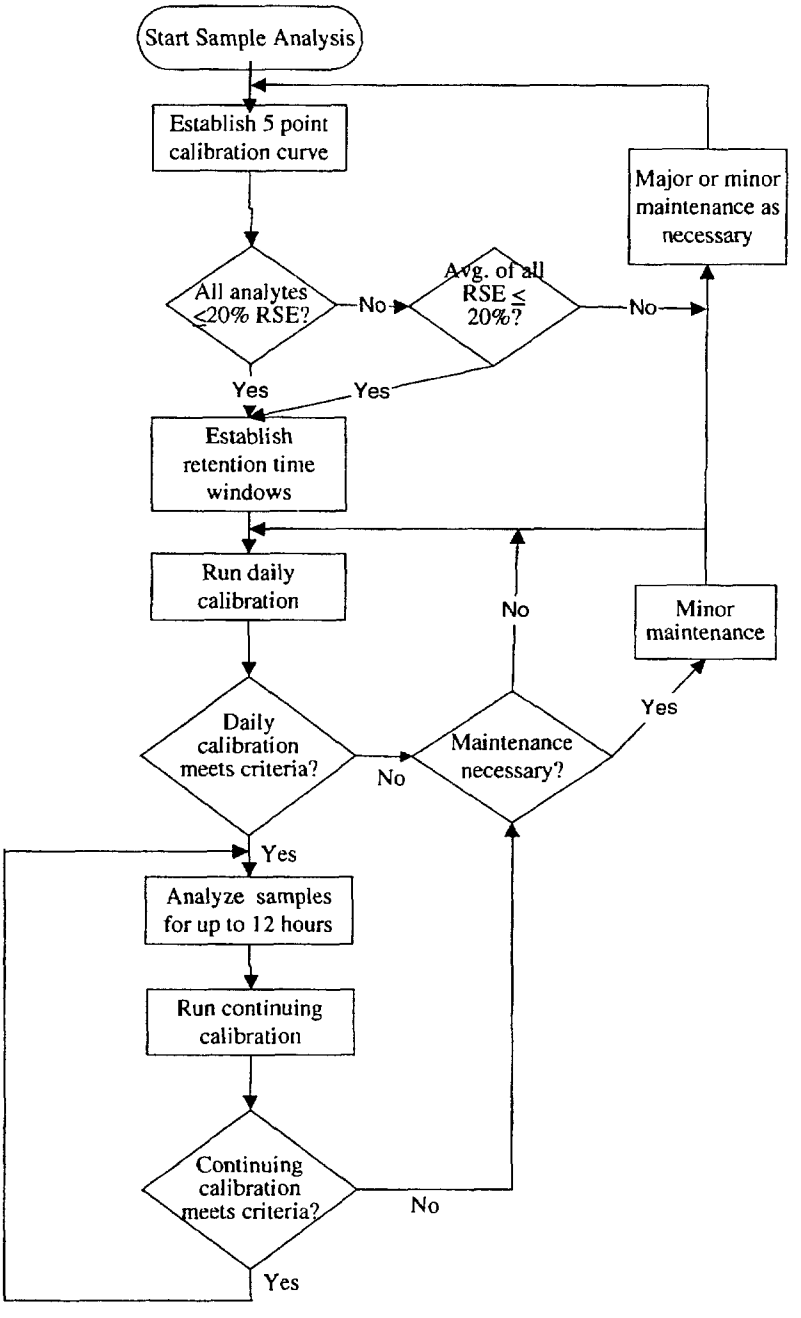
17.4. Flow Diagrams

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

1.1. This method describes sample preparation and extraction for the analysis of volatile organics by a purge and trap procedure, following method 8021B. However, where required by a client QAPP this section may also be used to analyze aromatic volatiles by discontinued methods 8020A and 8010B. All requirements of the 8000B section of this SOP must be met except when superseded by this Appendix. Refer to Table A-1 for the individual analytes normally determined by these procedures.

1.2. Compounds within the scope of this method have boiling points below 200°C and are soluble or slightly soluble in water. Classes of compounds best suited to purge-and-trap analysis include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3. Water samples and soils samples with low levels of contamination may be analyzed directly by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in soil may be determined by the medium level methanol extraction procedure.

1.4. This method also describes the preparation of water-miscible liquids, non-water-miscible liquids, solids, wastes, and soils/sediments for analysis by the purge-and-trap procedure.

2. SUMMARY OF METHOD

2.1. An inert gas is bubbled through the sample at ambient temperature or at 40°C (40°C required for low level soils), and the volatile components are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. Analytes are detected using a photoionization Detector, an electrolytic conductivity detector or a combination of both.

2.2. For soil samples, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water. It is then analyzed by purge-and-trap GC following the normal water method. If very low detection limits are needed for soil samples then direct purge using sodium bisulfate preservation may be necessary.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this SOP.

4. INTERFERENCES

4.1. Refer to section 4 of the method 8000B part of this SOP for general information on chromatographic interferences.

4.2. Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.3. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

4.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the system may be required.

4.5. When utilizing an autosampler system which has multiple ports for sample analysis, it is likely that only a single stage or port may be contaminated by a highly concentrated sample. If a port is suspect, a water blank should be analyzed to verify lack of contamination. If the water blank and subsequent blanks on that port show contamination consistent with the concentrated sample, further maintenance is required. This may include replacing or cleaning the multi-port valve, transfer lines, etc.

4.6. A holding blank is kept in the sample refrigerator. This is analyzed and replaced every 14 days. If the holding blank does not meet the method blank criteria, the source of contamination must be found and corrected. Evaluation of all samples analyzed in the 14 day period prior to the analysis of the contaminated holding blank is required.

4.7. Acidification of samples may result in hydrolysis of 2-chloroethyl vinyl ether.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B section of this SOP for general safety requirements.

5.2. Often, purge vessels on purge-and-trap instrumentation are pressurized by the time analysis is completed. Therefore, vent the pressure prior to removal of these vessels to prevent the contents from spraying out.

5.3. The toxicity or carcinogenicity of each chemical used in this procedure has 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:

Methanol -- Flammable and toxic

5.4. Methanol shall not be used in a CaptAir hood.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes -- 10µL, 25µL, 100µL, 250µL, 500µL, and 1000µL. These should be equipped with a 20 gauge (0.006" ID) needle. These will be used to measure and dispense methanolic solutions and aqueous samples.

6.2. Gas tight syringes -- 5 mL and 25 mL. Used for measuring sample volumes.

6.3. Purge and Trap Apparatus -- A device capable of extracting volatile compounds, trapping on a sorbent trap, and introducing onto a gas chromatograph.

6.4. Purge and Trap Autosampler -- In order to maintain high sample throughput, an autosampler is highly recommended.

6.5. Trap -- The trap used is dependent on the class of compound to be analyzed. Refer to Table A-2 for suggested traps for specific tests.

6.6. Purge Vessels -- These are dependent on the purge and trap unit/autosampler used. Both disposable culture tubes (needle sparge units) and specially designed vessels with fritted bottoms may be used. Follow the manufacturer's suggestions for configuration.

6.7. Columns - Refer to Table A-2 for details of columns.

6.8. Volumetric flasks, Class A: 5 mL to 250 mL

6.9. pH paper

6.10. Balance capable of weighing to 0.01g for samples.

7. REAGENTS AND SUPPLIES

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Organic Free Water

Organic free water is defined as water in which an interferent is not observed at the reporting limit of the compounds of interest. Suggested methods for generating organic free water include:

- Filtration through a carbon bed.
- Continuously sparging water with helium or nitrogen.
- Use of commercial water purification systems.

Other methods may be used, so long as the requirement that the water not show any interferences is met. The procedure used should be documented in a lab specific attachment.

7.3. Sodium Bisulfate

7.4. Methanol -- Purge and Trap Grade

7.5. Standards

Refer to tables A-5 and A-6 for details of surrogate, matrix spiking and internal standards. Calibration standard levels are not specified, since they may depend on the sensitivity and linear range of specific detectors. However, the low level standard must be equivalent to the reporting limits specified in Table A-1.

7.5.1. Volatile standards are prepared by injecting a measured volume of the stock standard into a syringe containing the appropriate volume of organic free water. The calibration standard is then loaded into the purge device.

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 < 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 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 a 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). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.)

8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.4%) which can be neglected, into the calculations.

8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 25 mL methanol or 20 µL spike to 5 mL methanol).

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a VOA vial by adding 5 mL purge and trap grade methanol. (If a 25 g sample is to be used, add 25 mL methanol to the VOA vial).

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.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.)

8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.4%) which can be neglected, into the calculations.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 25 mL methanol or 20 µL spike to 5 mL methanol).

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (methanol preserved) 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 a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal the vial and attach a label. The label must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.01g 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 on the label.

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°C until analysis.

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. 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.

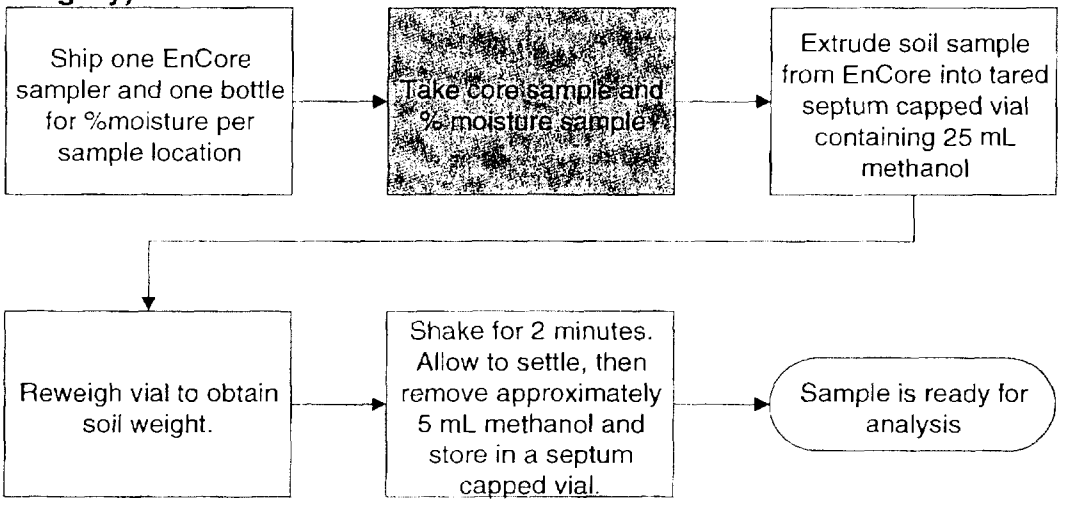
8.8. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

8.9. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

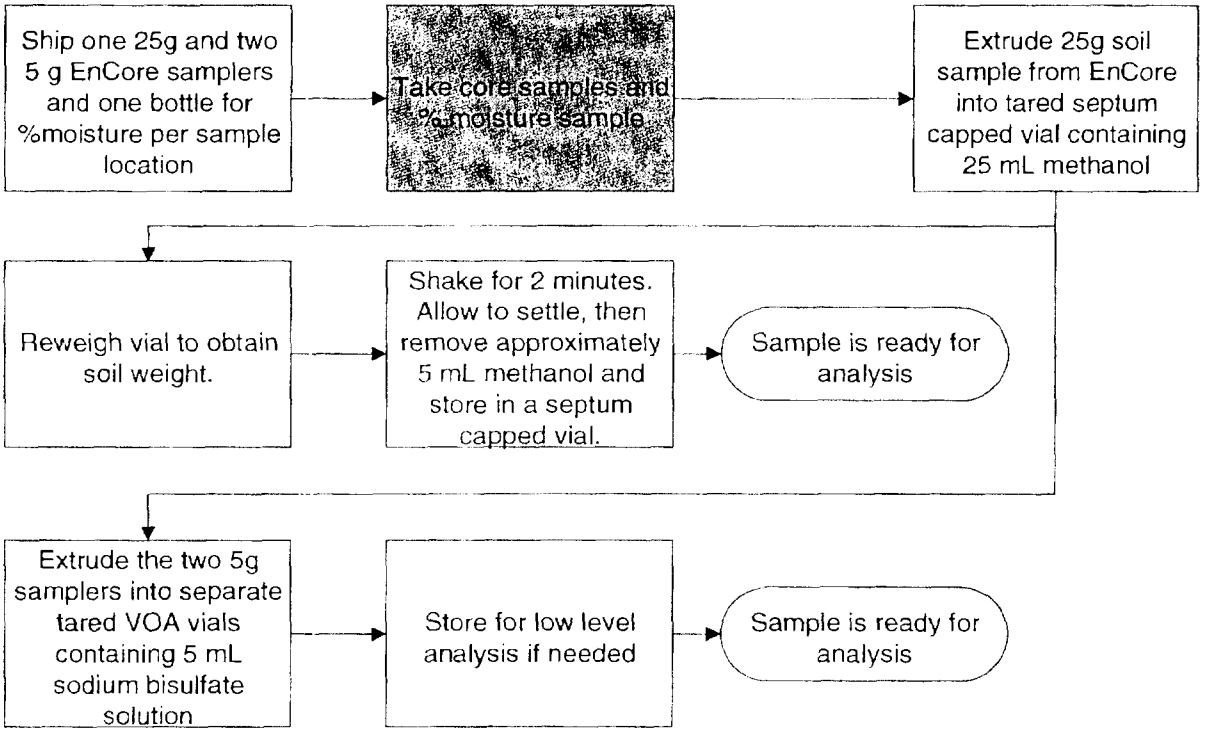
8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.11. 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.

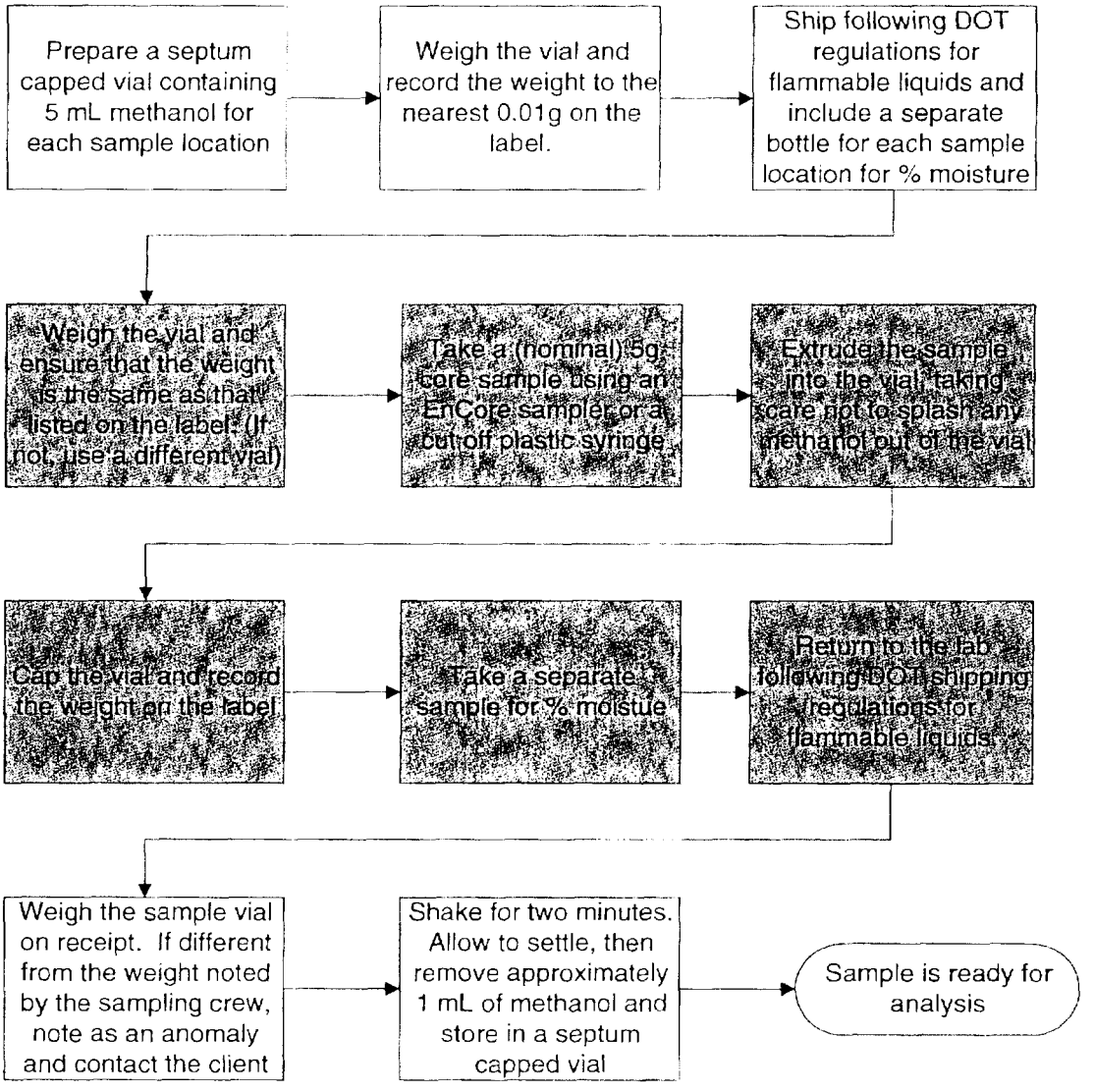
EnCore procedure when low level is not required (field steps in gray)



EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Refer to the method 8000B section of this SOP, section 9, for general quality control procedures, including batch definition, requirements for method blanks, LCS, matrix spikes, surrogates, and control limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to the method 8000B section of this SOP, section 10, for general calibration procedures.

10.2. Gas Chromatograph Operating Conditions

Various column configurations are possible. If dual column confirmation is necessary, the sample may be split using a Y splitter at the injector end to direct the sample to two columns and two detectors. For simultaneous determination of aromatic and halogenated volatiles, a single column is used and the PID and ELCD detectors are connected in series.

10.2.1. Refer to Table A-2, A-3 and A-4 for GC operating conditions.

10.3. Initial Calibration

10.3.1. Refer to Section 10 of the 8000B section of this SOP for details of initial calibration criteria.

10.3.2. Low level soil samples must be purged at 40°C, therefore the calibration curve must also be purged at 40°C. In addition, the low level soil calibration solutions should contain approximately the same amount of sodium bisulfate as the samples.

10.3.3. The low level calibration must be at the reporting limit or below. The remaining standards encompass the working range of the detector.

10.3.4. Calibrate the instrument using the same volume that will be used during sample analysis.

10.4. Calibration Verification

10.4.1. A mid level calibration standard is used for the calibration verification. The gases have 20 % D criteria rather than the 15% used for other analytes.

10.4.2. A calibration verification run is performed after every 10 samples for this method.

10.4.3. Bracketing of samples with calibration verification runs is only necessary for external standard analysis.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a 12 hour calibration that meets % difference criteria from an existing initial calibration.

11.3. Confirmation

The PID and ELCD detectors are sufficiently selective that second column confirmation is not always necessary. Requirements for second column confirmation should be decided in

consultation with the client. If the PID and ELCD are used in series confirmatory information for many analytes can be gained by comparing the relative response from the two detectors.

11.4. Aqueous Sample Analysis (Purge and Trap units using sparge vessels)

11.4.1. Depending on the sensitivity of the instrument and capabilities of the purge and trap device, 5, 10, 20, or 25 mL sample volumes may be analyzed. A 5 mL sample volume is recommended.

11.4.2. Rinse a 5 mL (or 25 mL for larger sample volumes) gas-tight syringe with organic free water. Fill the syringe with the sample to be analyzed, and compress to volume.

11.4.3. Check and document the pH of the sample remaining in the VOA vial after loading the syringe.

11.4.4. This procedure invalidates the contents of the VOA vial for further analysis, unless an aliquot is transferred to a smaller VOA vial with no headspace (e.g., 20 mL) at the same time the analysis aliquot is removed.

11.4.5. Spike with the appropriate volume of surrogate/internal standard solution and spike solution (if required) through the barrel of the syringe. The method blank is spiked with surrogates only, the LCS and matrix spikes with the surrogate and matrix spiking solutions. Refer to Tables A-5 and A-6 for volumes and concentrations of spiking solutions.

11.4.6. Load onto the purge and trap device and start the run.

11.4.7. If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample has a high response for a compound, analysis should be followed by an organic free water blank. It is recognized that during automated unattended analysis, this may not occur. If any potential carryover hits are present in samples following highly contaminated samples, the sample must be reanalyzed to determine if any of these hits are a result of carryover or are actually present in the sample.

11.4.8. Dilutions may be made in gas tight syringes unless the volume of sample used is less than 5 µL, in which case dilution in volumetric flasks will be necessary.

11.4.8.1. Spike with the same volume of surrogate/internal standard solution as used for undiluted samples prior to loading onto the purge and trap device.

11.4.8.2. For Matrix spike / matrix spike duplicates where the sample requires dilution, the sample is spiked <u>after</u> the dilution is performed.

11.5. Aqueous and Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

11.5.1. 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.

11.5.2. 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.

11.5.3. 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.

11.5.4. Check the pH of the sample remaining in the VOA vial after analysis is completed.

11.6. 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 reagent water 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.

11.6.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.6.2. 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.

11.6.3. Connect the purge vessel to the purge and trap device.

11.6.4. 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.) (See Tables A-5, A-6, A-7 and A-8.) Add directly to the sample from 11.6.2.

11.6.5. The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.

11.6.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.6.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect. If external standard calibration is used, samples with surrogate recovery below the control limit should be reanalyzed once to confirm matrix effect.

11.7. Methanol Extract Soils

11.7.1. 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.

12. DATA ANALYSIS AND CALCULATIONS

Refer to section 12 of the 8000B section of this SOP.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the 8000B section of this SOP are 70-130%, with %RSD $\leq$ 25% The spiking level should be 20 µg/L. These limits are for guidance, and certain "difficult" analytes may fall outside this range. Any outliers must be discussed with STL's Director of Quality Assurance and/or Director of Technology before proceeding with sample analysis.

14. POLLUTION PREVENTION

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 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

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Sections 5000, 5030B, 5035 and 8021B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.2. Modifications from previous revision

17.2.1. No revisions were made to this appendix.

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 A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
Halogenated volatiles by 8021B	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chloroethane	70-00-3	1.0	1.0	50
	2-Chloroethyl vinyl ether	110-75-8	5.0	5.0	250
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	Dibromochloromethane	124-48-1	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-45-4	1.0	1.0	50
	cis-1,2 Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	Dichloromethane(DCM)	75-09-2	5.0	5.0	250
	1,2-Dichloropropane	78-87-5	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
Additional halogenated volatiles	Benzyl Chloride	100-44-7	5.0	5.0	250
	Bromobenzene	108-86-1	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
BTEX by 8021B	Benzene	71-43-2	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50

Table A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	Chlorobenzene	108-90-7	1.0	1.0	50
	1,2-Dichlorobenzene	75-34-3	1.0	1.0	50
	1,3-Dichlorobenzene	107-06-2	1.0	1.0	50
	1,4-Dichlorobenzene	75-45-4	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Additional aromatic and unsaturated volatiles	1,2,4 Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5 Trimethylbenzene	108-67-8	1.0	1.0	50
	Acetone	67-64-1	10	10	500
	MEK (2-butanone)	78-93-3	5.0	5.0	250
	MIBK (4-methyl-2-pentanone)	108-10-1	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	Styrene	100-42-5	1.0	1.0	50
	Methyl tert-butyl ether (MTBE)	1634-04-4	1.0	1.0	50
Combined halogenated and aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50
	Bromobenzene	108-86-1	1.0	1.0	50
	Bromochloromethane	74-97-5	1.0	1.0	50
	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	n-butylbenzene	104-51-8	1.0	1.0	50
	sec-Butylbenzene	135-98-8	1.0	1.0	50
	tert-Butylbenzene	98-06-6	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chlorodibromomethane	124-48-1	1.0	1.0	50
	Chloroethane	75-00-3	1.0	1.0	50
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	2-Chlorotoluene	95-49-8	1.0	1.0	50
	4-Chlorotoluene	106-43-4	1.0	1.0	50
	1,2-Dibromo-3-Chloropropane(DBCP)	96-12-8	1.0	1.0	50
	1,2-Dibromoethane(EDB)	106-93-4	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-35-4	1.0	1.0	50
	cis-1,2-Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	1,2-Dichloropropane	78-87-5	1.0	1.0	50

Table A-1
Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	1,3-Dichloropropane	142-28-9	1.0	1.0	50
	2,2-Dichloropropane	590-20-7	1.0	1.0	50
	1,1-Dichloropropene	563-58-6	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	Ethylbenzene	100-41-4	1.0	1.0	50
	Hexachlorobutadiene	87-68-3	1.0	1.0	50
	Isopropylbenzene	98-82-8	1.0	1.0	50
	p-Isopropyltoluene	99-87-6	1.0	1.0	50
	Methylene Chloride	75-09-2	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	n-Propylbenzene	10306501	1.0	1.0	50
	Styrene	100-42-5	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	1,2,3-Trichlorobenzene	87-61-6	1.0	1.0	50
	1,2,4-Trichlorobenzene	120-82-1	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
	1,2,4-Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5-Trimethylbenzene	108-67-8	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50

Table A-2
Recommended Conditions for Aromatic Volatiles

Parameter	Recommended Conditions
Temperature program	50°C, 1min, 10°C/min to 200°C, 1min
Column 1	Rtx-502.2 or DB-502.2 60m x 0.53mm 3.0um
Column 2	Rtx-1 or DB-1 60m x 0.53mm 3.0 um
Carrier gas	Helium or hydrogen
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-3
Recommended Conditions for Method Halogenated Volatiles

Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-4
Recommended Conditions for Method Combined Aromatic and Halogenated Volatiles

Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-5
Surrogate and Internal Standard Concentrations

Standard	Components	Working Solution µg/mL	Spike amount µL (for 5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic volatiles IS/SS	4-Chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Halogenated volatiles IS/SS	4-chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Combined Aromatic and halogenated volatiles IS/SS	Fluorobenzene (SS)	20	5	20
	1,4-Dichlorobutane (SS)	20	5	20
	1-Chloro-4-fluorobenzene (IS)	40	10	40

It may be necessary to select different surrogates in order to minimize sample interferences. 1-chloro-4-fluorobenzene and 4-chlorotoluene are fairly well resolved from analytes listed in this SOP. However 4-chlorotoluene may sometimes be requested as a target analyte. Other surrogates that may be considered, and issues associated with their use are:

Bromochloromethane: Elutes very close to chloroform and cis-1,2-dichloroethene on the 502.2 column. May be a target analyte.

1,2-Bromochloroethane:

1-Chloro-2-fluorobenzene: Elutes close to ethylbenzene on DB-1 or Rtx-1 and close to m,p-xylene on 502.2

a,a,a-Trifluorotoluene: Good for aromatic volatiles, coelutes or very close to trichloroethene

Bromofluorobenzene: Close to 1,1,2,2-trichloroethane and 1,2,3-trichloropropane on the 502.2 column. Good on DB-1 or Rtx-1.

2-Bromo-1-chloropropane: May coelute with 1,1,2-trichloroethane

Table A-6
Concentrations for LCS and MS/MSD compounds

Standard	Components	Working Solution µg/mL	Spike amount µL (5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
Halogenated	Chlorobenzene	20	5	20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20
Combination aromatic / halogenated	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20

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

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This Appendix is to be applied when SW-846 Method 8082 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). The PCBs are determined and quantitated as Arochlor mixes.

Table C-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.

Note: SW-846 method 8082 provides incomplete guidance for determination of individual PCB congeners. This SOP does not include directions for congener specific analysis.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of PCBs. The PCBs are injected onto the column and separated and detected by electron capture detection. 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 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.

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 C-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. All standards for this method must be replaced

7.2. Refer to Table C-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Other surrogates may be used at client request. Refer to Table C-4 for details of surrogate standards.

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. Initial Calibration

10.2.1. Refer to Table C-5 for the initial calibration analytical sequence.

10.2.2. The response for each Arochlor will be calculated by the procedures described in the general method for GC analysis, with the following modifications.

10.2.3. A five point calibration of the Arochlor 1016/1260 mix is generated with at least mid level single points for the other Aroclor mixes. The average response factor is used to quantitate Arochlors 1260 and 1016, other Arochlors are quantitated from the mid level single point.

10.2.4. The analyst may include a full 5 point calibration for any of the Arochlors with the initial calibration.

10.2.5. The high and low standards for the initial 5 point calibration of 1016 / 1260 define the acceptable quantitation range for the other Arochlors. If any Arochlor is determined above this concentration the extract must be diluted and reanalyzed.

10.2.6. If the analyst knows that a specific Arochlor is of interest for a particular project, that Arochlor may be used for the five point calibration rather than the 1016 / 1260 mix.

10.2.7. The surrogate calibration curve is calculated from the Aroclor 1016/1260 mix. Surrogates in the other calibration standards are used only as retention time markers.

10.2.8. Two options are possible for quantitation of Aroclors. The same quantitation option must be used for standards and samples.

10.2.8.1. Multiple peak option

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 Aroclor, 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.)

10.2.8.2. 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.

10.3. 12 hour Calibration

The 12 hour calibration verification 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 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 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.

10.3.1. At a minimum, the 12 hour calibration includes analysis of the Arochlor 1260 / 1016 mix.

10.3.2. It is adequate to verify calibration with a mixture of Aroclors 1016 and 1260. If a specific Aroclor is expected, it should be included in the daily calibration check.

10.3.3. The retention time windows for any analytes included in the daily calibration are updated.

10.3.4. For this method samples must be bracketed with successful calibration verification runs.

10.4. Calibration verification

The Arochlor 1260/1016 calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

10.4.1. A mid level standard is used for the calibration verification.

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 C-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table C-5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Arochlors

Retention time windows are used for identification of Arochlors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification 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.

A clearly identifiable Arochlor pattern serves as confirmation of single column GC analysis. However, if the pattern is not clear, or if no historical data for the site is available, then second column confirmation must be performed.

12.2. Quantitation of Arochlors

Use 3-10 major peaks or total area for quantitation

If the analyst believes that a combination of Aroclor 1254 and 1260, or a combination of 1242, 1248 and 1232 is present, then only the predominant Arochlor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well separated, Aroclor patterns are present, then both Aroclors are quantitated and reported.

12.2.1 Laboratory uses 3-5 major peaks.

12.3. If there are no interfering peaks within the envelope of the Arochlor, 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.

12.4. Second column confirmation of Aroclors will only be performed when requested by the client, or if the pattern is not clear or there is no historical data leading to a suspicion that Arochlors may be present. The appearance of the multiple peaks in the sample usually serves as a confirmation of Aroclor 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.

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 recovery of 70-130%. The spiking level should be equivalent to a mid level calibration.

13.2. Method detection limits (MDL) are determined for Arochlor 1016 and 1260. Arochlor 1016 represents an Arochlor consisting primarily of low chlorinated congeners while Arochlor 1260 represents an Arochlor consisting primarily of high chlorinated congeners. The same reporting limit is applied to all Arochlors, and must be supported by both MDLs.

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 8082

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Method 8082 includes limited direction for congener specific quantitation. This is outside the scope of this SOP.

17.2. Modifications from Previous Revisions

No changes were made to this Appendix

17.3. Tables

Table C-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aroclor-1016	1.0	33	1000
Aroclor-1221	1.0	33	1000
Aroclor-1232	1.0	33	1000
Aroclor 1242	1.0	33	1000
Aroclor-1248	1.0	33	1000
Aroclor-1254	1.0	33	1000
Aroclor-1260	1.0	33	1000

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 C-2

Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	DB-5 or Rtx-5 30m x 0.32mm id, 0.5µm
Column 2	DB-1701 or Rtx 1701 30m x 0.32 mm id, 0.25µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	1-2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table C-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[1]
Aroclor 1016/1260	100	200	500	1000	2000	4000
Aroclor 1242[2]			500			
Aroclor 1221 +1254[2]			500			
Aroclor 1232[2]			500			
Aroclor 1248[2]			500			
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] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.
[2] Aroclors may be quantitated within the range 100 to 2000 ng/mL (4000ng/mL if the level 6 1016/1260 standard is included). If the Aroclor is more concentrated, it must be reanalyzed at a dilution.

Table C-4			
LCS/Matrix Spike and Surrogate Spike levels for Aroclor analysis with Acid Cleanup µg/L or µg/kg			
	Aqueous	Soil	Waste
Aroclor 1016/1260	10	333	10,000
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table C-5
Suggested Analytical Sequence

Initial Calibration

Injection #		
1	Solvent blank (optional)	
2	Aroclor 1016/1260	Level 1
3	Aroclor 1016/1260	Level 2
4	Aroclor 1016/1260	Level 3
5	Aroclor 1016/1260	Level 4
6	Aroclor 1016/1260	Level 5
7	Aroclor 1232	Level 3
8	Aroclor 1242	Level 3
9	Aroclor 1248	Level 3
10	Aroclor 1221/1254	Level 3
11	Solvent blank	
12-31	Sample 1-20 (or as many samples as can be analyzed in 12 hours	
	Solvent blank (optional)	
32	Aroclor 1016/1260	Level 3

etc

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 Aroclor 1260 / 1016 mix. Mid level standards of any other Aroclors expected to be present in the samples are also injected.

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

PITTSBURGH SPECIFIC APPENDIX FOR THE ANALYSIS OF ORGANOPHOSPHOROUS PESTICIDES BY SW-846 METHOD 8141A

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Proprietary Information Statement:

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1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8141 is applied to the analysis of organophosphorous pesticides by GC/FPD. This Appendix is applicable to extracts derived from any matrices which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001)

1.2. Table B-1 lists compounds which are routinely determined by this method and their associated 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.

2. SUMMARY OF METHOD

2.1. This method presents conditions for the analysis of prepared extracts of organophosphorous pesticides. The pesticides are injected onto the column and separated and detected by Flame Photometric detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

3.1. 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 flame photometric detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding sample/reagent contact with plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups have not been determined for this method.

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 flame photometric 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

Triphenyl phosphate and Tributyl phosphate are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

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 using both columns.

10.3. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.3.1. Refer to Table B-7 for the initial calibration analytical sequence.

10.3.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4. 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.

10.4.1. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.5. Continuing Calibration

The mid-level 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. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.5.1. 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

No cleanup procedure has been determined.

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. Surrogate recovery results are calculated and reported for Triphenyl phosphate and Tributylphosphate. Corrective action is only necessary if Triphenyl phosphate and Tributyl phosphate are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Current laboratory performance limits are listed in Tables B-5a and B-5b. 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 8141A

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
Dimethoate	1	33
Disulfoton	1	33
Famphur	1	33
Methyl parathion	1	33
O,O,O-Triethyl phosphorothioate	1	33
Parathion	1	33
Phorate	1	33
Tetraethyldithiopyrophosphate	1	33
Thionazin	1	33
Azinphos-methyl	1	33
Bolstar	1	33
Chlorpyrifos	1	33
Coumaphos	1	33
Demeton (total)	1	100
Demeton-O	1	33
Demeton-S	1	33
Diazinon	1	33
Dichlorvos	1	33
EPN	1	33
Ethoprop	1	33
Ethyl parathion	1	33
Fensulfothion	1	33
Fenthion	1	33
Malathion	1	33
Merphos	1	33
Mevinphos	1	33
Monocrotophos	1	33
Naled	1	33
Ronnel	1	33
Stirophos	1	33
Sulfotepp	1	33
Tokuthion	1	33
Trichloronate	1	33

Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	250°C
Temperature program	110C for .5 min, 3.0°C/min to 250°C, , 2.84 min hold
Column 1	DB608 30m x 0.53mm id, 1μm
Column 2	DB1701 30m x 0.53 mm id, 1μm
Injection	2μL
Carrier gas	Helium
Make up gas	Helium

Table B-3					
Calibration Levels ng/mL					
	Level 1	Level 2	Level 3	Level 4	Level 5
Dimethoate	.2	.5	1.0	2.0	4.0
Disulfoton	.2	.5	1.0	2.0	4.0
Famphur	.2	.5	1.0	2.0	4.0
Methyl parathion	.2	.5	1.0	2.0	4.0
O,O,O-Triethyl phosphorothioate	.2	.5	1.0	2.0	4.0
Parathion	.2	.5	1.0	2.0	4.0
Phorate	.2	.5	1.0	2.0	4.0
Tetraethyldithiopyrophosphate	.2	.5	1.0	2.0	4.0
Thionazin	.2	.5	1.0	2.0	4.0
Tributyl phosphate	.2	.5	1.0	2.0	4.0
Triphenyl phosphate	.2	.5	1.0	2.0	4.0
Azinphos-methyl	.2	.5	1.0	2.0	4.0
Bolstar	.2	.5	1.0	2.0	4.0
Chlorpyrifos	.2	.5	1.0	2.0	4.0
Coumaphos	.2	.5	1.0	2.0	4.0
Demeton (total)	.2	.5	1.0	2.0	4.0
Demeton-O	.2	.5	1.0	2.0	4.0
Demeton-S	.2	.5	1.0	2.0	4.0
Diazinon	.2	.5	1.0	2.0	4.0
Dichlorvos	.2	.5	1.0	2.0	4.0
EPN	.2	.5	1.0	2.0	4.0
Ethoprop	.2	.5	1.0	2.0	4.0
Ethyl parathion	.2	.5	1.0	2.0	4.0
Fensulfothion	.2	.5	1.0	2.0	4.0
Fenthion	.2	.5	1.0	2.0	4.0
Malathion	.2	.5	1.0	2.0	4.0
Merphos	.2	.5	1.0	2.0	4.0
Mevinphos	.2	.5	1.0	2.0	4.0
Monocrotophos	.2	.5	1.0	2.0	4.0
Naled	.2	.5	1.0	2.0	4.0
Ronnel	.2	.5	1.0	2.0	4.0
Stirophos	.2	.5	1.0	2.0	4.0
Sulfotepp	.2	.5	1.0	2.0	4.0
Tetraethyl pyrophosphate	.2	.5	1.0	2.0	4.0
Tokuthion	.2	.5	1.0	2.0	4.0
Trichloronate	.2	.5	1.0	2.0	4.0

1 Standards may be split into multiple mixs if resolution of all compounds on both columns is not obtained.
Note: Component mixes of a CCAL should be run sequentially. The ccal evaluation is performed on the sum of the mixes, rather than by mix. Ie. the CCAL = sum of the component mixes.

Table B-5a					
Aqueous LCS/Matrix Spike and Surrogate Spike levels µg/L					
		LCS		MSD	
Compound	ug/L	LCL	UCL	LCL	UCL
Dimethoate	10	46	153	70	192
Disulfoton	10	17	185	36	130
Famphur	10	14	165	59	131
Methyl parathion	10	36	159	65	157
O,O,O-Triethyl phosphorothioate	10	65	141	60	172
Parathion	10	13	150	65	144
Phorate	10	35	152	54	154
Tetraethyldithiopyrophosphate	10	75	140	51	158
Thionazin	10	69	149	56	136
Tributyl phosphate	10	30	150	30	150
Triphenyl phosphate	10	25	152	25	152

Table B-5b					
Soil LCS/Matrix Spike and Surrogate Spike levels µg/mg					
		LCS		MSD	
Compound	ug/kg	LCL	UCL	LCL	UCL
Dimethoate	33	65	135	45	170
Disulfoton	33	66	133	26	136
Famphur	33	42	162	31	178
Methyl parathion	33	64	144	56	150
O,O,O-Triethyl phosphorothioate	33	58	131	48	130
Parathion	33	58	141	58	145
Phorate	33	71	135	51	140
Tetraethyldithiopyrophosphate	33	69	144	63	143
Thionazin	33	68	140	64	136
Tributyl phosphate	33	30	150	30	150
Triphenyl phosphate	33	20	151	20	151

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)
Calibration Mix A
Calibration Mix B
Calibration Mix C
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:

Calibration Check Mix

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.

Tables B8 & B9 Laboratory Control Limits and Control Compound List (STL Reference Data Summary) See Attachments: current print outs from LIMS system.

PITTSBURGH SPECIFIC APPENDIX FOR THE ANALYSIS OF PAHs by HPLC SW-846 METHOD 8310

Prepared by: _____

Reviewed by: _____
Technology 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 Appendix describes procedures to be used when SW-846 Method 8310 is applied to the analysis of Polynuclear Aromatic Hydrocarbons by HPLC. This Appendix is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (C-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.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of Polynuclear Aromatic Hydrocarbons. The extracts are injected onto the column and separated and detected by ultraviolet(UV) and fluorescence 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 HPLC analysis arise from many compounds amenable to HPLC that give a measurable response on the UV and fluorescence 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. 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 have not been determined for this method.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. UV and fluororescence detectors are 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

Benzo(e)pyrene and p-terphenyl are the surrogate standards. Refer to tables B-5 for details of surrogate standards.

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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 HPLC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both detectors.

10.3. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.3.1. Refer to Table B-8 for the initial calibration analytical sequence.

10.3.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4. 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.

10.4.1. .

10.4.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.5. Continuing Calibration

The mid-level 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. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.5.1. 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. C-OP-0001.

11.3. Cleanup

No cleanup procedure has been determined.

11.4. Suggested HPLC 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

Both the fluorescence detector and the UV detector are used for qualitative determination and confirmation of the presence of target compounds, however each target compound is quantitated using only one detector. Table B-1 presents the detectors used for quantitating each compound.The MDL studies are performed on both detectors. The highest MDL will be used for reporting "J"-Values. In the instance where there is no detection of any compounds on the UV detector, the Flourescence Detector results will not be submitted.

12.1. Surrogate recovery results are calculated and reported for Benzo(e)pyrene and p-terphenyl. Corrective action is only necessary if Benzo(e)pyrene and p-terphenyl are both outside of acceptance limits.

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 8310

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 and Detectors

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	Detectors
Carbazole	1.0	33	UV/Flourescence
Naphthalene	1.0	33	UV/Flourescence
Acenaphthene	1.0	33	UV/Flourescence
Acenaphthylene	1.0	33	UV
Anthracene	.2	6.7	UV/Flourescence
Benzo(a)anthracene	.2	6.7	UV/Flourescence
Benzo(b)fluoranthene	.2	6.7	UV/Flourescence
Benzo(k)fluoranthene	.2	6.7	UV/Flourescence
Benzo(g,h,i)perylene	.2	6.7	UV/Flourescence
Benzo(a)pyrene	.2	6.7	UV/Flourescence
Chrysene	.2	6.7	UV/Flourescence
Fluoranthene	.2	6.7	UV/Flourescence
Fluorene	.2	6.7	UV/Flourescence
Indeno(1,2,3-cd)pyrene	.2	6.7	UV/Flourescence
Pyrene	.2	6.7	UV/Flourescence
Phenanthrene	.2	6.7	UV/Flourescence
Dibenzo(a,h)anthracene	.2	6.7	UV/Flourescence
1-methylnaphthalene	1.0	33	UV/Flourescence
2-methylnaphthalene	1.0	33	UV/Flourescence

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	1.0 mL
Low-level Soil	30 g	1.0 mL
High-level soil / waste	1 g	1.0 mL

Table B-2	
Parameter	**Recommended Conditions**
Mobile phase program	Time 0min:solvent A 50% solvent B 50% flow 1.5 ml/min Time 7min:solvent A 65% solvent B 35% flow 1.5 ml/min Time 10min:solvent A 75% solvent B 25% flow 1.5 ml/min Time 15min:solvent A 85% solvent B 15% flow 1.5 ml/min Time 20min:solvent A 95% solvent B 5% flow 1.5 ml/min
Column 1	Hypersil PAH 150mm x 4.6mm ID
Injection	20µL
Solvent A	CH3CN
Solvent B	H2O

Table B-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	
Individual Mix						
Carbazole	1	4	7.5	10	20	
Naphthalene	1	4	7.5	10	20	
Acenaphthene	1	4	7.5	10	20	
Acenaphthylene	1	4	7.5	10	20	
Anthracene	.2	.8	1.5	2	4	
Benzo(a)anthracene	.2	.8	1.5	2	4	
Benzo(b)fluoranthene	.2	.8	1.5	2	4	
Benzo(k)fluoranthene	.2	.8	1.5	2	4	
Benzo(g,h,i)perylene	.2	.8	1.5	2	4	
Benzo(a)pyrene	.2	.8	1.5	2	4	
Chrysene	.2	.8	1.5	2	4	
Fluoranthene	.2	.8	1.5	2	4	
Fluorene	.2	.8	1.5	2	4	
Indeno(1,2,3-cd)pyrene	.2	.8	1.5	2	4	
Pyrene	.2	.8	1.5	2	4	
Phenanthrene	.2	.8	1.5	2	4	
Dibenzo(a,h)anthracene	.2	.8	1.5	2	4	
1-methylnaphthalene	1	4	7.5	10	20	
2-methylnaphthalene	1	4	7.5	10	20	
p-terphenyl	1	4	7.5	10	20	
Benzo(e)pyrene	1	4	7.5	10	20	

Table B-5		
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg		
	Aqueous	Soil
Carbazole	6.25	208
Naphthalene	6.25	208
Acenaphthene	6.25	208
Acenaphthylene	6.25	208
Anthracene	1.25	41.7
Benzo(a)anthracene	1.25	41.7
Benzo(b)fluoranthene	1.25	41.7
Benzo(k)fluoranthene	1.25	41.7
Benzo(g,h,i)perylene	1.25	41.7
Benzo(a)pyrene	1.25	41.7
Chrysene	1.25	41.7
Fluoranthene	1.25	41.7
Fluorene	1.25	41.7
Indeno(1,2,3-cd)pyrene	1.25	41.7
Pyrene	1.25	41.7
Phenanthrene	1.25	41.7
Dibenzo(a,h)anthracene	1.25	41.7
1-methylnaphthalene	6.25	208
2-methylnaphthalene	6.25	208
p-terphenyl	10	333
Benzo(e)pyrene	10	333

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)

Individual mix All levels

Solvent blank
Up to 20 samples unless 12 hours comes first)
Solvent blank (optional)
Individual mix Mid level (Continuing calibration)
Samples
After 12 hours:

Individual mix [1]

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 ..

Tables B8 & B9 Laboratory Control Limits and Control Compound List (STL Reference Data Summary) See Attachements: current print outs from LIMS system.

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: SAMPLE RECEIVING AND CHAIN OF CUSTODY

(SUPERSEDES: SOP NO.: PITT-QA-0051 Rev. 4.2 2/25/00)

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. PURPOSE

1.1. This SOP details procedures for receiving samples into the laboratory and describes laboratory custody practices.

1.2. This protocol described here complies with accepted laboratory custody procedures and regulatory requirements, e.g. NYSDEC ASP.

2. RESPONSIBILITIES

2.1. It is the responsibility of the Sample Receiving Department to receive samples in full compliance with this SOP. Sample receiving duties of the sample custodian (and other designated individuals) are described in the "PROCEDURE" section. Following this SOP assures that all samples are properly received and will always be under the custody of a person or stored in a secure area while at the laboratory.

2.1.1. For the purpose of this SOP, a sample is under custody if:

2.1.1.1. It is in your possession, or

2.1.1.2. It is in your view after being in your possession, or

2.1.1.3. It was in your possession and you locked it up, or

2.1.1.4. It is in a designated secure area. (Secure areas shall be accessible only to authorized personnel.)

2.2. It is the responsibility of each analyst or any STL staff member to maintain sample custody for all entrusted samples as described herein in full compliance with this SOP.

2.3. It is the responsibility of the laboratory director, QA manager, and supervisors to assure that operations are conducted in full compliance with this SOP. It is also their responsibility to supply training, materials, and equipment so that the laboratory staff can comply with all SOP requirements.

3. SAFETY

3.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates. The following requirements must be met:

3.2. 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 become contaminated will be removed and discarded, other gloves will be cleaned immediately.

3.3. 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:

3.3.1. The following materials are known to be corrosive: Sodium Hydroxide (NaOH), Sulfuric Acid (H_2SO_4), Hydrochloric Acid (HCl), and Nitric Acid (HNO_3)

3.4. 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. If waste is generated during operations, it will be segregated and disposed of according to the facility hazardous wastes procedures as appropriate. The Environmental Health and Safety Coordinator will be contacted if related information is required.

3.5. The preparation of any standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

3.6. 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.

4. PROCEDURE

4.1. Samples will be received at the laboratory facility during normal working hours (8 a.m. to 5 p.m.). If sample receipt is anticipated outside normal working hours, the project manager must notify and coordinate sample receipt with the sample custodian, who in turn will designate personnel to receive the samples. The sample custodian examines the shipping container (cooler, box, or other shipping container) and completes the header information on a Cooler Receipt Form (see "APPENDICES," Section 6.2). Information recorded at this time will include: client name and project, quote number, STL lot number, the date the shipping container was received and temperature checked, and the date that the shipping container was unpacked.

4.1.1. The temperature of the cooler may be taken either by using an enclosed temperature blank, if supplied, or by inserting a thermometer between samples in the cooler (the thermometer must not come in contact with the ice). If the temperature of the cooler is not 4°C ±2°C, this must be noted on a Condition Upon Receipt Variance Report (see "APPENDICES," Section 6.3). The temperature will be recorded on the Cooler Receipt Form. The reading that is recorded will take into consideration the relevant thermometer correction factor.

4.1.2. Other information to be noted at this time is: presence/absence of custody seal(s) on the shipping container(s), and their condition.

4.2. The sample custodian opens the shipping container and removes the entire contents, assuring that all enclosed samples and documents are retained. After reviewing the entire contents of the shipping container and carefully checking sample integrity (intact, broken, leaking, etc.), labels, and shipment completeness, the remaining information is placed on the Cooler Receipt Form (see "APPENDICES," Section 6.2).

4.3. The sample custodian must compare the field chain(s) of custody, the sample labels, and airbills or bills of lading. If there are any inconsistencies between the forms, the discrepancies are documented on the Condition Upon Receipt Variance Report (see "APPENDICES," Section 6.3). If samples are received out of holding time, a Nonconformance Memo must be completed and the project manager notified. The project manager then notifies the client and a decision is made concerning whether to proceed with analysis.

4.4. The sample custodian measures the pH of preserved aqueous samples (with the exception of samples that have been submitted for the testing of volatile organic compounds). This is done by placing a few drops of the sample on *narrow*-range pH paper using *either a disposable cup (for DOD clients) or* a clean disposable Pasteur pipette. This measurement determines whether the sample has been properly preserved. (For Oil & Grease pour in cap and then pipette.) The used pipette is then discarded. **Note:** The pH of samples to be analyzed for VOAs will be measured by the volatiles analytical group after removing an aliquot for analysis.

4.5. For all potentially chlorinated samples the sample custodian checks for residual chlorine by testing the sample with KI-starch paper. If residual chlorine is present, the sample custodian must indicate so on the sample condition upon receipt form and issue a NCM. Also, the client, the PM, and the group responsible for analysis of the sample must be notified. Steps for removal of residual chlorine are included in the SOP for the method the sample is to be analyzed by.

4.6. An access-based program is utilized to determine samples ready for disposal. A report is generated listing samples to be disposed. Once sample disposal date has been entered into computer system (Quantims), a sample disposal report is generated and put into a disposal logbook. The disposal logbook is kept in sample receiving for reference.

4.7. If all samples recorded on the field chain(s) of custody were received by the laboratory and there are no problems observed with the sample shipment, the sample custodian signs the

field chain(s) of custody in the "Received for Laboratory by:" box on the document. Problems such as broken bottles and pH or temperature outside criteria are noted on the Condition Upon Receipt Variance Report (see "APPENDICES," Section 6.3). *Where approved by the project manager, unpreserved samples will be preserved by the sample custodian. This action will be documented on the Condition Upon Receipt Variance Report.. Whenever lab reagents are used to make a preservative adjustment, record the reagent, lot number and amount of reagent added.*

4.8. The project manager's Quote form (the LIMS description of the sampling program) is reviewed to assure that the field chain(s) of custody is in agreement. If the documents do not agree, the project manager is notified of the discrepancy. Samples are not logged in until all discrepancies are resolved.

4.9. If it has been necessary to complete a Condition Upon Receipt Variance Report, this will be forwarded to the project manager for review. The project manager will determine the action required and contact the client as necessary or otherwise agreed.

4.10. Once the project manager has resolved any discrepancies between the field chain(s) of custody and Quote and has taken the appropriate action for any Condition Upon Receipt Variance Report which has been generated, the samples are logged in using the Laboratory Information Management System (LIMS). A unique laboratory identification number is assigned to each sample (i.e., C6B060001-001: C denotes Pittsburgh; 6 references the year [1996]; B signifies the month [February]; 06 means the sixth day of the month; 0001 is the first lot logged in; and -001 is the first sample of that lot).

4.11. The Sample Control person will enter each sample into the laboratory computer (QuantIMS), where a unique lot number is assigned to each project received, and sequential sample numbers are designated for each client identification within the lot.

4.11.1. **Lot Numbers**: The lot number is nine characters in length and is based on the date of receipt. Lot number A5J010021 is described as follows:

A - STL location where the samples were received.
(A = North Canton, B = Tampa, C = Pittsburgh, etc.)
5 - Last digit of the year (i.e. 1995).
J - Month (i.e. A = January, B = February, J = October, etc.)
01 - The next 2 numeric characters identify the day of the month, in this case, the first day of the month.
0021 - The next 4 numeric characters are the sequential assignment of numbers specific to each lot received. Each day the first lot logged in receives the number "0001", the second lot receives the number "0002", etc..
For example:
If four bottles were submitted under Client ID numbers AB100-AB103 and the laboratory identification number generated by the computer is A2K100001, then the assigned laboratory number recorded on the Sample Log-In Sheet would be as follows:

Client ID Sample Number	Assigned Laboratory Number
AB 100	A2K100001-001
AB 101	A2K100001-002
AB 102	A2K100001-003
AB 103	A2K100001-004

4.11.2. **Sample Numbers**: The samples in each lot are assigned a sample number that is attached to the lot number and are reset at each new lot. For example: the first and second samples in the lot above are labeled A5J010121-001 and A5J010121-002.

4.11.3. **Sample Suffixes**: Each sample also has a 1 character field (which is not a required field for all samples) called the suffix which identifies the sample as specified below.

Client Sample	No. Suffix
Method Blank	B
Laboratory Control Sample	C
Laboratory Control Sample Duplicate	L
Matrix Spike	S
Matrix Spike Duplicate	D
Sample Duplicate	X
Serial Dilution	P
Sample Confirmation	Y
Post Digestion Spike	Z
Re-analysis	I

Example: A5J010121-001X is a sample duplicate for sample A5J010121-001.

4.11.4. **Work Order Numbers**: Each test requested by the client for an individual sample receives an individual 8 digit work order number assigned by QuantIMS. Work order number A5WE1-2-1C is described as follows:

A5WE1 - In addition to the three digit sample (i.e. - 001 and - 002), the first 5 characters of the work order number also identifies each unique sample. This identification is generated in QuantIMS using a sequential logic.
2 - The "modifier" indicates the type of run. In this case this is the second time the sample had to be run. If it needs reprepared and run again, the number would indicate a "3". The original analysis work order number assigns "1" to the modifier position.
1C - The "suffix" is the identification of the specific test for that sample. The suffix in this case is not always sequential, but is unique to the test to be performed on the sample.

4.12. Worksheets and sample container labels are printed. The sample custodian will assure that each sample container is labeled with a unique laboratory identification number that cannot be accidentally removed in the laboratory.

4.12.1. The label will contain the following information:

4.12.1.1.The laboratory information management system unique Lab ID number.

4.12.1.2.Sampling date.

4.12.1.3.Client ID.

4.12.1.4.Storage location.

4.12.1.5.Client code.

4.12.1.6.Number and size of bottles received.

4.13. The sample custodian will put the samples into secure storage areas. Samples for tests other than volatile organics are placed on numbered shelves inside secure walk-in refrigerators. Samples received for volatile organics are placed in separate secure refrigeraters which have been designated for volatile sample storage only and are located within the volatiles lab area. From the time of log-in and refrigerator assignment by the sample receiving personnel, the volatiles personnel become the designated sample custodians for the volatile samples. As custodians they must document custody within their workgroup. In both cases temperature is maintained at 4°C ±2°C. The storage location for all received samples is entered in the laboratory information management system.

4.14. The sample custodian files the shipping documents, field chain(s) of custody, Quote, related correspondence, cooler receipt form, analytical summary, along with preliminary invoice. The summary and supporting documentation are reviewed for accuracy by the sample custodian and placed in a project folder before being submitted to Project Management. Laboratory information management system worksheets are generated by the sample custodian and distributed to the analytical group leaders.

4.15. Internal Chain of Custody

4.15.1. The sample custodian transfers the custody of requested raw samples to the analytical staff using a Sample Custodian Removal Request (see "APPENDICES," Section 6.4) which lists the laboratory identification number of the samples being transferred. The sample custodian checks that the sample labels and Sample Custodian Removal Request are in agreement, dates, records the time of transfer (using military time), and signs the Sample Custodian Removal Request as having relinquished the samples. The analyst will then sign the Sample Custodian Removal Request as having received the listed samples.

4.15.2. The Sample Custodian Removal Request form must accompany the raw samples while they are being analyzed. The analyst may transfer the samples to a second analyst using a second Sample Custodian Removal Request form which has been generated listing the samples and purpose of the transfer. All samples listed on the initial Sample Custodian Removal Request must be present and listed on the second Sample Custodian Removal Request. Transferring less than all of the samples listed on the initial Sample Custodian Removal Request is prohibited. If only several of the samples listed on the initial form are required, then all samples on the initial form will be returned to the laboratory sample custodian who will relinquish only those samples required, as described in the above section. The relinquishing analyst assures that all samples are present and correctly identified on the second Sample Custodian Removal Request before signing, dating, and recording the time of transfer (military time) on the second Sample Custodian Removal Request form. The second analyst signs the second Sample Custodian Removal Request form to accept the samples. The

original Sample Custodian Removal Request from the laboratory sample custodian must be relinquished to the second analyst and will remain with the samples.

4.15.3. Custody of raw samples may be maintained if the analyst receiving custody as described above places the samples in a secure storage area accessible only to authorized personnel for the purpose of analysis. Storage conditions must be such that the integrity of the sample will be maintained for the required analyses.

4.15.4. Raw samples (whether the containers have sample volume remaining or are empty) shall be returned to the sample custodian with the original Sample Custodian Removal Request and any additional Sample Custodian Removal Requests which were required to document subsequent transfers. The Sample Custodian Removal Request must be reconciled with the samples being returned before the sample custodian accepts receipt of the samples. (The sample custodian will not accept the samples unless <u>all</u> of the containers listed on the Sample Custodian Removal Request are present.) The analyst then signs as relinquishing the samples, and sample custodian accepts custody of returned raw samples by signing, dating, and recording the time of receipt (using military time) on the Sample Custodian Removal Request that documents the most recent transfer of the samples.

4.15.5. The sample custodian will record which samples have been completely expended in analyses by making an entry on the Sample Custodian Removal Request.

4.15.6. Custody information for extracts, distillates, and digestates prepared from raw samples shall be recorded on the sample preparation benchsheet used to document the preparation. (A Sample Custodian Removal Request will not be used for sample preparations.) The individual who has conducted the preparation is responsible for completing custody transfer information. The relinquishing analyst assures that all sample preparations are present and correctly identified before signing, dating, and recording the time of transfer (military time) on the benchsheet. Prepared samples are transferred to and kept in a secure area accessible only to authorized personnel for the purpose of analysis. If further custody transfers are necessary, these are recorded in a similar manner on the same benchsheet. The benchsheet with completed custody information must accompany the prepared samples whenever custody transfers are necessary.

4.16. Samples will be properly disposed of by the sample custodian thirty days after the final report unless the laboratory has been otherwise notified in writing. All samples in a single STL laboratory lot will be disposed of at the same time, and a record documenting the lot disposal will be kept in a logbook maintained by the sample custodian.

4.17. The temperature of each walk-in cooler is monitored daily Monday through Saturday using a calibrated mercury bulb thermometer. A seven day recording chart which monitors temperatures on a weekly basis is also in each cooler.

4.18. **Cooler Handling Procedure**: All coolers should be rinsed out after receipt and unloading. If a cooler smells or is visibly soiled it should be soaped and warm water rinsed. If a cooler cannot be cleaned up or remains odorous after cleaning, it should be discarded.

4.19. Any deviation from the conditions and handling described in the "PROCEDURES" section will be documented using a Nonconformance Memo (NCM) with distribution to the Project Manager and Quality Assurance Department. Corrective action must be fully explained in the Nonconformance.

5. DEFINITIONS

5.1. Custody: The definition of custody may be found in Section 2.1.1.

5.2. Internal Chain of Custody: Records generated by various departments internal to the laboratory and which document custody of samples or sample preparations for transfers within the laboratory.

5.3. LIMS: Laboratory Information Management System. The computer system used to track information about samples after being received by the laboratory.

6. APPENDICES

6.1. Disaster Recovery Plan Appendix

6.2. Cooler Receipt Form, Page 1 of 2 (example form).
Cooler Receipt Form, Page 2 of 2 (example form).

6.3. Condition Upon Receipt Variance Report (example form).

6.4. Sample Custodian Removal Request (example form).

6.5. Holding Time Tables 8.5-1 through 8.5-5, taken from the STL Quality Assurance Management Plan, Revision No. 3, Nov 2, 1998, pages 110-135 of 192. Please note, client specific or project specific holding times would supersede the holding times listed in these tables.

Disaster Recovery Plan Appendix

1. When sample location transfers are required due to cooler malfunction or power failure, all transfers must be properly documented as described in the above SOP sections. Sample security must be properly maintained with access to samples limited, controlled, and documented. Temperature of the relocated samples will be documented and controlled to 4°C ±2°C.

2. In the event of a power failure limiting available cold storage capacity to less than that required to adequately store all samples at the necessary temperature, backup refrigeration trucks will be called to give assistance on site to store samples and maintain proper temperature at 4°C ±2°C. Trucking companies that could be called are:
   Thermo King Transport Refrigeration
   Ryder Trucks
   Budget Trucks

3. If refrigeration trucks are not available during a power failure, dry ice will be used to maintain proper temperature.

4. When cooling units malfunction, a local heating, ventilation, and air conditioning contractor will immediately be called to correct the problem. Sample receiving will coordinate all service calls using a 24-hour servicing company to minimize impact on sample integrity.

Cooler Receipt Form

STL Pittsburgh

Client: _____ Project: _____ Quote: _____

Cooler Rec'd & Opened for Temp. Check on: _____

Coolers Opened and Unpacked on: _____ By: _____

(Signature)

STL Pittsburgh Lot Number: _____

		Yes	No
1.	Were custody seals on the outside of the cooler? _____	___	___
	If YES, how many and where? Quantity __ Location _____		
	Were signatures and date correct? _____	___	___
2.	Were custody papers included inside the cooler? _____	___	___
3.	Were custody papers properly filled out (ink, signed, match labels)? _____	___	___
4.	Did you sign the custody papers in the appropriate place? _____	___	___
5.	Was shippers packing slip attached to this form? _____	___	___
6.	Were packing materials used? _____	___	___
	If YES, what type? _____		
7.	Were the samples chilled? (Record temperatures on reverse side.) _____	___	___
8.	Were the samples appropriately preserved? _____	___	___
9.	Were all bottles sealed in separate plastic bags? _____	___	___
10.	Did all bottles arrive in good condition (unbroken)? _____	___	___
11.	Were all bottle labels complete (sample ID, preservatives, etc.)? _____	___	___
12.	Did all bottle labels and/or tags agree with custody papers? _____	___	___
13.	Were correct bottles used for tests indicated? _____	___	___
14.	Were all VOA vials checked for the presence of air bubbles? _____	___	___
15.	Was a sufficient amount of sample sent in each bottle? _____	___	___

16. Samples received by: FEDEX UPS CLIENT DROP-OFF OTHER AIRBORNE

Explain any discrepancies: _____

_____

_____

_____

Lab Sample Receiver: _____

Was contacted on _____ by _____ to resolve discrepancies.

Cooler Receipt Form

STL Pittsburgh

P: Preserved

UP: Unpreserved

Sample ID	TMET PH<2	DMET PH<2	HG PH<2	NUT(1) PH<2	CN PH>12	OG TPHC PH<2	PHEN PH<2	SULF PH>12	TOC PH<2	TOX PH<2	VOA PNUP	Metals PH<2			

(1) "NUT" could include sample bottles for ammonia, chemical oxygen demand, nitrate/nitrite, TKN, or total phosphorus

Comments: _____

Cooler Number	Temperature

Bottle Type	Lot Number*

* Please use an indelible if bottle lot number was covered by the label.

Condition Upon Receipt Variance Report
STL Pittsburgh Laboratory

Client: _____ Date: _____
Project No.: _____ Initiated by: _____
Analysis Requested: _____ RFA/COC: _____
Client Sample Numbers Affected: _____

Condition/Variance (Check all that apply):

1. ☐ Not enough sample received for proper analysis. Received approx. _____
2. ☐ Sample received broken/leaking.
3. ☐ Sample received without proper preservative.
   - ☐ Cooler temperature not within 4°C ± 2°C
     - Record temperature: _____
     - ☐ pH _____
     - ☐ other _____
4. ☐ Sample received in improper container.
5. ☐ Sample received without proper paperwork. _____
6. ☐ Paperwork received without sample.
7. ☐ No sample ID on sample container.
8. ☐ Custody tape disturbed/broken/missing.
9. ☐ Sample splits performed by lab.
10. ☐ Volatile sample received with approximately _____ cm headspace.
11. ☐ Sample ID on container does not match on paperwork. Explain: _____
12. ☐ All coolers on airbill not received with
13. ☐ Other (explain below): _____

Notes: _____

Corrective Action:

☐ Client's Name: _____ Informed verbally on: _____ By: _____

☐ Client's Name: _____ Informed in writing on: _____ By: _____

☐ Sample(s) processed "as is" _____

☐ Sample(s) on hold until _____ Analyst: _____

Sample Control Supervisor Review: _____ Date _____

Project Management Review: _____ Date _____

COC/Sample Request

STL Pittsburgh
450 William Pitt Way
Pittsburgh, Pennsylvania 15238
412/820/9380 FAX:412/820-2080

Project Name

Site

Lot Number/Sample Number	Analysis	Matrix

Raw Sample	Raw Relinquished by				Raw Received by			
	Date	Time	Analyst	Location	Date	Time	Analyst	Location

Quanterra
Environmental Services

Controlled Copy
Copy No.: _____

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

Title: Glassware Clean-Up for Organic/Inorganic Procedures

(SUPERSEDES: None)

Prepared by: _____ 2/27/98

Reviewed by: _____ (for LM, EF & RR) 2/27/98
Technical Specialist

Approved by: _____ 2/27/98
Quality Assurance Manager

Approved by: _____ 2/27/98
Environmental, Health and Safety Coordinator

Approved by: _____ 2/27/98
Laboratory Director

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1. SCOPE AND APPLICATION

1.1 The following procedures must be followed to ensure all glassware being cleaned is free of contamination. Laboratory coat, safety glasses and gloves must be worn at all times when cleaning glassware.

2. SUMMARY OF METHOD

2.1 This procedure describes the glassware cleaning practices at the Quanterra Pittsburgh laboratory.

3. DEFINITIONS

3.1 Not applicable.

4. INTERFERENCES

4.1 Not applicable.

. SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates. The following requirements must be met:

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 become 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: Refer to method SOPs associated with the glassware being washed.

5.3.2 Chemicals known to be **flammable** are: Refer to method SOPs associated with the glassware being washed.

5.3.3 The following materials are known to be corrosive: Sodium Hydroxide (NaOH), Sulfuric Acid (H_2SO_4)

5.4 Exposure to chemicals must be maintained **as low as reasonably achievably**, 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 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6 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.

6. EQUIPMENT AND SUPPLIES

6.1 Autoclave.

6.2 Muffle oven.

6.3 180 ° C oven

6.4 Dessicator

7. REAGENTS AND STANDARDS

7.1 Soap.

7.2 DI water.

7.3 Super-Q water.

7.4 Chromic acid, it is received in a safe plastic container.

7.5 Nitric acid diluted (1: 5).

7.6 Sulfuric acid (1:4).

7.7 Aluminum foil.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Not applicable.

9. QUALITY CONTROL

9.1 Any blank contamination due to unclean glassware is subject to repreparation and reanalysis of samples.

9.2 Nonconformance & Corrective Action

9.2.1 Any deviation from this SOP is considered a nonconformance and will be documented by a Nonconformance Memo.

10. CALIBRATION AND STANDARDIZATION

10.1 Not applicable

11. PROCEDURE

.2. DATA ANALYSIS AND CALCULATIONS

12.1 **Metals and Inorganic prep:**

12.1.1 Wash with soap and water.

12.1.2 Rinse with tap water.

12.1.3 Glassware must be rinsed once with DI water and once with 20 percent nitric acid (HNO_3) before the final DI rinse.

12.1.4 Rinse with DI water three times.

12.2 **General Chemistry:**

12.2.1 **Evaporating Dishes (TDS, TS):**

12.2.1.1 Scour out residue with soap and water.

12.2.1.2 Soak in chromic acid or 1:1 HCL for one hour, if needed.

12.2.1.3 Rinse three times with tap water.

12.2.1.4 Rinse three times with DI water.

12.2.1.5 Dry upside down in 180°C oven, overnight.

12.2.1.6 Remove from oven and store in dessicator.

12.2.2 Boiling Flasks (125 mL w/round glass top):

12.2.2.1 Proceed as in 12.2.1.1 - 12.2.1.4.

12.2.2.2 Place flask in muffle oven ~ 550 °C for 2 hours

12.2.2.3 Store in dessicator

12.2.3 B.O.D. bottles (300 mL round glass top):

12.2.3.1 Rinse once with tap water.

12.2.3.2 Rinse with 1:1 HCL or Chromic Acid.

12.2.3.3 Rinse with tap water three times.

12.2.3.4 Rinse with DI water three times.

12.2.3.5 Bottles may be placed in 180°C oven overnight to dry.

12.2.4 Phosphate: C.O.D. FLASKS (125 mL Erlenmeyer w/round glass top):

12.2.4.1 Rinse once with tap water.

12.2.4.2 Soak for two hours in 1:1 HCL or chromic acid.

12.2.4.3 Rinse three times with tap water.

12.2.4.4 Rinse three times with DI water.

12.2.4.5 Cover tops with aluminum foil.

12.2.4.6 Phosphate glassware is stored separately.

12.2.5 Surfactant glassware (125, 250, 500 mL separatory funnels):

12.2.5.1 ***Do not use any detergent !!***

12.2.5.2 Rinse with 1:1 HCL or Chromic Acid

12.2.5.3 Rinse three times with tap water.

12.2.5.4 Rinse three times with DI water.

12.2.6 Phenol flasks, 1000 mL separatory funnels, Cyanide flasks:

12.2.6.1 Wash with soap and water (if needed).

12.2.6.2 Rinse with 1:1 HCL or chromic acid.

12.2.6.3 Rinse three times with tap water.

12.2.6.4 Rinse three times with DI water.

12.3 Mercury BOD bottles:

12.3.1 Same procedure as Metals glassware.

12.3.2 Do not autoclave.

12.4 **Organic Glassware Cleanup**: (for base neutrals/acids, herbicides, pesticides & PCBs) (LAB COATS, SAFETY GLASSES AND GLOVES MUST BE WORN).

12.4.1 Rinse with last solvent used (must be done by technician or chemist after use).

12.4.2 Wash with soap and water.

12.4.3 Rinse with tap water.

12.4.4 Rinse three times with DI water.

12.4.5 Let dry.

12.4.6 All glassware in baked in a muffle furnace at 400 °C for two hours before use.

12.5 VOA glassware cleaning procedure:

12.5.1 Tubes: Tubes are cleaned using dishwashing detergent and rinsed with tap water. Then they are baked in oven (180°C) for at least 1 hour before being used again.

12.5.2 Volumetrics: Volumetrics are cleaned by rinsing with tap water after use and put in oven (180°C) for at least 1 hour before being used again.

12.5.3 Pipettes: Pipettes are placed in oven (180°C) after each use. They remain in oven for at least 1 hour before being used again.

12.5.4 Syringes: Syringes for samples (5 mL and 25 mL) are cleaned before each use by rinsing at least 3 times with Super-Q water. Other syringes (1000 µl, 500 µl, 25 µl, and 10 µl) are cleaned by rinsing with methanol before each use.

13. METHOD PERFORMANCE

14. POLLUTION PREVENTION

15. WASTE MANAGEMENT

16. REFERENCES

16.1 Quanterra Pittsburgh, Laboratory Specific Attachment, Quality Assurance Manual, Current Revision.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1 Training Qualifications

17.1.1 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. The group/team leader must document the training and submit to the QA/QC Coordinator for inclusion in associate training files.

17.2 Records Management/Documentation

17.2.1 All records will be managed and kept in accordance with Quanterra policy QA-008.

Organics Bench Sheet
Refer to SOP for additional details

Organic Glassware Cleanup: (for base neutrals/acids, herbicides, and pesticides) (LAB COATS, SAFETY GLASSES AND GLOVES MUST BE WORN).

1. Rinse with last solvent used (must be done by technician or chemist after use).
2. Wash with soap and water.
3. Rinse with tap water.
4. Rinse three times with DI water.
5. Let dry.
6. All glassware in baked in a muffle furnace at 400 °C for two hours before use.

VOA glassware cleaning procedure:

1. Tubes: Tubes are cleaned using dishwashing detergent and rinsed with tap water. Then they are baked in oven (180°C) for at least 1 hour before being used again.
2. Volumetrics: Volumetrics are cleaned by rinsing with tap water after use and put in oven (180°C) for at least 1 hour before being used again.
3. Pipettes: Pipettes are placed in oven (180°C) after each use. They remain in oven for at least 1 hour before being used again.
4. Syringes: Syringes for samples (5 mL and 25 mL) are cleaned before each use by rinsing at least 3 times with Super-Q water. Other syringes (1000 µl, 500 µl, 25 µl, and 10 µl) are cleaned by rinsing with methanol before each use.

(bench sheet may be posted in laboratory by the group leader. the location of the posted copies must be recorded below by the group leader. Posted copy must be initialed and dated by the group leader)

Location	Posted by	Date

Metals Glassware Cleaning Bench Sheet
Refer to SOP for additional details
(bench sheet may be posted in laboratory by the group leader)

Metals and Inorganic prep:

1. Wash with soap and water.
2. Rinse with tap water.
3. Glassware must be rinsed once with DI water and once with 20 percent nitric acid (HNO_3) before the final DI rinse.
4. Rinse with DI water three times.

Mercury BOD bottles:

1. Wash with soap and water.
2. Rinse with tap water.
3. Glassware must be rinsed once with DI water and once with 20 percent nitric acid (HNO_3) before the final DI rinse.
4. Rinse with DI water three times.

(bench sheet may be posted in laboratory by the group leader. the location of the posted copies must be recorded below by the group leader. Posted copy must be initialed and dated by the group leader)

Location	Posted by	Date

Inorganic Glassware Cleaning Bench Sheet page one of two
Refer to SOP for additional details
(bench sheet may be posted in laboratory by the group leader)

General Chemistry:

Evaporating Dishes (TDS, TS):

1. Scour out residue with soap and water.
2. Soak in chromic acid or 1:1 HCL for one hour, if needed.
3. Rinse three times with tap water.
4. Rinse three times with DI water.
5. Dry upside down in 180°C oven, overnight.
6. Remove from oven and store in dessicator.

Boiling Flasks (125 mL w/round glass top):

1. Proceed as in 12.2.1.1 - 12.2.1.4.
2. Place flask in muffle oven ~ 550 °C for 2 hours
. Store in dessicator

B.O.D. bottles (300 mL round glass top):

1. Rinse once with tap water.
2. Rinse with 1:1 HCL or Chromic Acid.
3. Rinse with tap water three times.
4. Rinse with DI water three times.
5. Bottles may be placed in 180°C oven overnight to dry.

Phosphate: C.O.D. FLASKS (125 mL Erlenmeyer w/round glass top):

1. Rinse once with tap water.
2. Soak for two hours in 1:1 HCL or chromic acid.
3. Rinse three times with tap water.
4. Rinse three times with DI water.
5. Cover tops with aluminum foil.
6. Phosphate glassware is stored separately.

Inorganic Glassware Cleaning Bench Sheet page two of two
Refer to SOP for additional details
(bench sheet may be posted in laboratory by the group leader)

Surfactant glassware (125, 250, 500 mL separatory funnels):

1. *Do not use any detergent !!*
2. Rinse with 1:1 HCL or Chromic Acid
3. Rinse three times with tap water.
4. Rinse three times with DI water.

Phenol flasks, 1000 mL separatory funnels, Cyanide flasks:

1. Wash with soap and water (if needed).
2. Rinse with 1:1 HCL or chromic acid.
3. Rinse three times with tap water.
4. Rinse three times with DI water.

(bench sheet may be posted in laboratory by the group leader. the location of the posted copies must be recorded below by the group leader. Posted copy must be initialed and dated by the group leader)

Location	Posted by	Date

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: EMPLOYEE ORIENTATION AND TRAINING

(**SUPERSEDES**: Revision No. 0)

Prepared by: Sevdâ K. Aleckson, Assistant Director, Quality Assurance

Reviewed by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Corporate Management

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1. PURPOSE

1.1. To provide guidance in the establishment and maintenance of a formal, documented training program for all Quanterra® laboratory and administrative support personnel. The training program is designed to provide a means for demonstrating competency, experience, and data quality and for stimulating professional development.

2. RESPONSIBILITIES

2.1. This SOP is applicable to all permanent or temporary technical and administrative support staff. Responsibilities of key staff members are as follows:

2.1.1. *Associate* -- Each Quanterra® associate shall ensure that training received, as described in this SOP, is documented and that the documents are maintained in that associate's training file. Also, when formal external training is received, the associate shall forward pertinent records to the training files.

2.1.2. *Laboratory Manager* -- The Laboratory Manager is responsible for ensuring that the training requirements are implemented as delineated in this SOP. The Laboratory Manager is also responsible for ensuring that sufficient time is allocated to laboratory training and making final decisions on the qualifications of any trainee, if questions arise.

2.1.3. *Quality Assurance Manager (QA) (or designee)* -- The QA Manager or designee is responsible for conducting orientation and on-going training in QA/QC policies and practices as described in this SOP. It is also the responsibility of the QA Manager or designee to maintain the documentation of training performed under this SOP at each Quanterra® facility.

2.1.4. *Environmental Health & Safety (EH&S) Coordinator or Radiation Safety Officer (RSO)* -- The EH&S Coordinator or RSO is responsible for training new or transferred associates in accordance with the requirements of this SOP and with the Quanterra® EH&S Procedures. The EH&S Coordinator or RSO will ensure that necessary documentation is maintained and accessible for review by auditors. Documents will be archived according to Quanterra® filing procedures or electronically.

2.1.5. *Laboratory Technical Manager* -- Determines qualification required for technical positions and evaluates job candidates against those requirements. Certifies the qualification of laboratory personnel.

2.1.6. *Management/Management Group (Department Manager/Supervisor/Group or Team Leader)* -- The Management Group is responsible for ensuring that all new and existing analysts and support staff in their group receive adequate on-the-job training and complete the initial and on-going proficiency demonstration requirements specified in this SOP. In addition, these individuals are responsible for continuously reviewing the analysts' performance and determining if additional training is required. This can be accomplished through the on-going peer or secondary technical reviews.

2.1.7. *Trainer* -- The trainer is responsible for providing the trainees with the instructions necessary to perform a given task in accordance with the appropriate SOPs and regulations. The trainer is also responsible for notifying the appropriate parties of the training that is to be conducted or has been conducted, as appropriate. The Trainer must forward all training documents to associate's training files. If required, QA or EH&S shall ensure the trainer meets the requirements for teaching the class.

3. SAFETY

3.1. Typical office dependent safety precautions must be adhered to in performing this SOP. If personnel are required to perform any portion of the procedure in laboratory areas, appropriate personal protective equipment and precautions must be utilized.

4. PROCEDURE

4.1. Overview

4.1.1. Orientation and training are provided to achieve initial proficiency, maintain proficiency, and to promote continuous improvement. In general, new and transferred personnel are oriented and trained in the following subjects as they relate to his/her job requirements:

- Quanterra® EH&S Procedures,
- Quanterra® Radiation Safety (as applicable to facilities where radioanalytical work is performed),
- Quanterra® QA Program Elements, and
- Job-Specific Technical Procedures.

4.2. Determination of Qualifications

4.2.1. Quanterra® shall identify basic job descriptions for all laboratory positions. These job descriptions shall provide the minimum qualifications for education and experience, knowledge and skills that are necessary for an associate to perform at a satisfactory level.

4.2.1.1. A hard copy or electronic version of the current Quanterra® job description shall be included in the associate's training file or with Human Resources.

4.2.1.2. An associate's performance shall be compared with the requirements of his/her job description annually as part of the associate's annual performance review that is conducted with the associate's supervisor.

4.2.2. A copy of the associate's resume may be included in the associate's training file or maintained in electronic format. The associate is responsible for ensuring the accuracy of the following information in the resume: academic credentials, employment history and experience and professional registrations.

4.3. Orientation to Environmental Health & Safety and Radiation Safety

4.3.1. In accordance with the Chemical Hygiene Plan (CHP), it is Quanterra® policy to fully instruct all personnel who are exposed or potentially exposed to hazardous substances in basic safety operations prior to their initial work assignments.

4.3.2. Each newly hired associate shall receive an EH&S Orientation as applicable to their job assignments to be conducted by the EH&S Coordinator or designee prior to being exposed to hazardous material or samples. **NOTE**: The EH&S training will also include fire safety and evacuation procedures as well as the elements in **Table 1**.

4.3.3. At each laboratory where radioanalytical tests are performed, radiation safety training covering basic radiation theories and safety will be conducted by the RSO, as indicated in Quanterra® Procedure EHS 150, prior to the individual handling potentially radioactive samples or being occupationally exposed to radioactive material. In addition, all personnel requiring routine access to the radioanalytical sections of the laboratories are required to receive radiation protection training.

4.3.4. The EH&S Coordinator shall include in this orientation areas described in **Table 1** in accordance with Quanterra's® Environmental Health & Safety Procedure EHS050.

TABLE 1. REQUIRED ENVIRONMENTAL HEALTH & SAFETY TRAINING ELEMENTS

Training Areas	Frequency	Applicable Regulations
Chemical Hygiene Plan & Hazard Communication	Annually or if the person changes to a job where this training is required (e.g., from admin. to laboratory operations)	29 CFR 1910.1450
Transportation of Hazardous Materials	Annually (Any person who ships or receives hazardous materials or supervises a person who ships or receives hazardous materials)	49 CFR 172.704
Facility Contingency Plan (or Emergency Procedures)	Annually, or when the procedure is changed, if more frequent	
Hazardous Waste handling	Annual (facility procedures for lab personnel; RCRA training for people shipping the wastes)	40 CFR 265.16
General Employee Radiation Protection Training	Annual (in facilities with radioactive material license)	10CFR 20.
Bloodborne Pathogens	Annual (Emergency Response Team members, or people who could handle human blood)	29 CFR 1910.1030

4.3.5. Upon completion of the orientation, the associate shall take an exam prepared by the EH&S Coordinator and/or the RSO, as an indication that the contents of the training program is understood.

4.3.6. The Transportation of Hazardous Materials Orientation shall be conducted <u>within 90 days</u> of the laboratory associate's being assigned responsibility for shipping and receiving.

4.3.7. Upon completion of the training, the EH&S Coordinator and/or the RSO shall submit the required safety training documents to the training files.

4.4. Orientation to Quality Assurance Program Requirements

4.4.1. Each newly hired associate shall receive a Quality Orientation.

4.4.2. The Quality Orientation shall be conducted by the QA Manager or designee <u>within the first two weeks</u> of the laboratory associate's report-to-work date.

4.4.3. The QA Manager or designee shall provide orientation covering the following QA-related items as they apply to associate's assigned responsibilities:

- Quanterra® Quality Policy as described in the Quality Assurance Management Plan (QAMP)
- Quanterra's® Ethics Policy on Data Integrity & Meeting Client/Contract Requirements
- Quanterra® Quality Documents
- Nonconformance & Corrective Action Identification and Documentation
- Proper Record Keeping Practices
- Key elements of Quanterra® QC Program Policy QA-003

4.4.4. In addition, the QA Manager or a designee shall provide other training in matters related to QA Program requirements on an annual basis. This will include the updates to the QAMP or specific topics as related to the key Quanterra® QA Program elements. On-going QA training may be conducted in a meeting format, through publishing updated QA materials, or via presentations using computer media. Required QA on-going training shall be identified for each area within the laboratory.

4.4.5. The QA orientation or on-going QA training shall be documented using a written exam, a checklist, or a preprinted form. EXAMPLE forms that may be used for this purpose are illustrated in **Appendix A**.

4.5. On-the-Job Technical Training

4.5.1. On-the-job training shall be conducted by the Operations Management Group (e.g., Supervisor, Group/Tcam Leader, or an experienced peer) immediately upon assignment of the laboratory associate to a given analytical preparation or determinative method.

4.5.2. The analyst shall become familiar with the procedure by reading the applicable standard operating procedure (SOP). The trainee shall receive one-on-one instructions in performing the procedure from an experienced peer designated by management. The trainee shall work under supervision until the appropriate supervisor deems his/her work satisfactory.

4.5.3. On-the-job training documents shall be forwarded to the analyst's training files.

4.5.4. Authorization to work on client samples ***independently*** shall be granted when requirements specified in the following section are met. **NOTE**: Work may be performed by a trainee prior to the successful method proficiency completion only under the supervision of a qualified peer designated by management.

4.6. Demonstration of Analyst Proficiency

4.6.1. Initial Demonstration of Proficiency

4.6.1.1. An analyst must successfully prepare and/or analyze four consecutive laboratory control samples (LCSs) or a blind performance evaluation (PE) sample (if available) or if specified, meet EPA method requirements for number of proficiency samples. It is not necessary that each LCS be part of the same QC batch.

4.6.1.2. Each LCS must consist of a spiked aliquot of a control matrix (i.e., aqueous and/or solid , if available, and where there is a substantial difference in the methodology).

4.6.1.3. Control limits for accuracy and precision specified in the method SOPs or established by the laboratories will be used to assess the acceptability of data.

4.6.1.4. As appropriate, an associate must also demonstrate familiarity with proper documentation practices including but not limited to standards traceability, data review, nonconformance documentation, proper error correction protocols, and sample and document chain-of-custody procedures. Proficiency in performing these tasks can be accomplished by observation of the trainee by a supervisor, group leader, or a qualified peer.

4.6.1.5. If the results of QC samples do not meet the requirements specified in this SOP, the analysis must be repeated until the associate is able to independently demonstrate acceptable performance on another set of QC sample analyses.

4.6.2. On-going Demonstration of Proficiency and Retraining

4.6.2.1. The Operations Management Group is responsible for monitoring the associate's performance and evaluate his/her ability to perform adequately on each method. On-going proficiency can be demonstrated annually by (1) by the preparation and/or analysis of four consecutive LCS samples with acceptable results within laboratory-established

control limits. This activity may be documented as part of the technical data review process; or (2) a blind PE sample can be obtained from a regulatory authority, a client or generated internally. Examples of acceptable blind PE samples include: WP/WS Studies, NELAC-approved PT studies, PEs submitted by the state agencies and the clients, double-blind PEs submitted by Quanterra® Corporate QA staff, or single blind PEs purchased from external vendors; or (3) successful analysis of a blind performance sample on a similar test method using the same technology (e.g., GC/MS volatiles by purge and trap for 524.2, 624, CLP and 5035 [8260]) would only require documentation for one of the test methods.

4.6.2.2. If internal (i.e., single blind) or external PE samples are used to establish proficiency, data must be compared against vendor's certified acceptance criteria or published study limits, respectively.

4.6.2.3. If the results of QC samples do not meet the requirements specified in this SOP, the analysis must be repeated until the associate is able to independently demonstrate acceptable performance on another set of QC sample analyses.

4.6.3. Documentation of Technical Proficiency

4.6.3.1. Acceptable performance shall be documented. The EXAMPLE forms provided in Appendix B can be used for this purpose. At any time an associate is no longer able to perform adequately, remedial training must be provided and proficiency process must be repeated and documented as described in Section 4.6.

4.7. External Training

4.7.1. In the interest of maximizing professional development and the long-term effectiveness of associates to meet projected needs, formal training in special fields may be provided through local institutions, training courses offered by the instrument vendors, scientific meetings, instructional workshops, and the U.S. Environmental Protection Agency (EPA).

4.7.2. The associate shall forward a copy of any certificate of training to the training files.

4.8. Requirements for Trainers

4.8.1. In all cases, training will be conducted by qualified staff selected on the basis of knowledge, experience, and proven competency. Technical, procedure-specific training may be conducted by experienced personnel familiar with the procedure, including the Laboratory Manager, Department Manager, Group Supervisors, Technical Specialist, and Associates who have either developed the procedure (SOP) or have already been qualified to perform the procedure. For administrative, health and safety, and QA-related procedures, the Department Manager, Health and Safety Manager, and QA Manager or a designee may conduct training as well as qualified associates who have either written the SOP or have already been qualified to perform the procedure. If required, the trainer shall take the necessary steps to meet the requirements for teaching the class.

4.9. Transfer of Analysts Between Facilities

4.9.1. An associate may be trained at one facility and transferred to another facility for temporary or permanent assignment. In the case of permanent assignment, the associate's training records must be transferred to the new location. As deemed necessary by the Management Group, the associate may need to further demonstrate acceptable performance as outlined in section 4.6 as part of the first set of samples analyzed at his/her new location.

4.9.2. The laboratory operations groups must maintain the analytical data generated during this process in the data archives.

4.9.3. A new Health and Safety orientation must be conducted with the employee per section 4.3 for the new facility.

4.10. Documentation for Technical Training Sessions

4.10.1. To demonstrate each associate's participation in a training course, the following minimum level of information must be included in the training files:

- The date of training,
- The name of trainer,
- The name of trainee (associate),
- The course/training session title which links to a reference set of training materials, and
- For technical training in analytical methods, attach qualifying data or include applicable references to the qualifying data such as a project number or

analytical/QC batch to reference any analytical raw data substantiating successful training.

4.11. Maintenance of Training Records

4.11.1. At a minimum, a training file shall be maintained for each associate in the QA office or in an area designated by the Laboratory Manager. Evidence or documentation of external training activities (if any) must also be kept for reference purposes. Training records must be maintained and managed under routine Quanterra® policies.

4.11.2. Each Quanterra® associate's training file shall include the following types of information:

- General (e.g., resume, job description, ethics related training)
- Health & Safety and Radiation Safety (if applicable)
- Quality Assurance
- Technical Proficiency Demonstration
- Professional Development (if applicable)

NOTE: All documentation for the above may be maintained in electronic files rather than as hard copy in individual's training file.

4.11.3. A database, <u>although</u> <u>not</u> <u>required</u>, can be used to record and monitor training for each associate and to notify management when retraining is necessary.

4.11.4. EH&S training files must be maintained in a such a manner as to be readily accessible on request (to auditors, clients, associates, or representatives) without being mixed with training records from other disciplines.

4.12. **Certification of Lead Auditor:** Quanterra's® requirement for lead auditor certification is described in Appendix C.

5. DEFINITIONS

5.1. *Orientation* -- The process by which an individual becomes acquainted with existing systems, environment, and conditions.

5.2. *On-the-job Training* -- A mechanism to help an associate to develop skills and introduction to local procedures.

5.3. *Technical Proficiency* -- A process by which analyst and method performance is demonstrated on the basis of generating acceptable QC data and consistent with Quanterra® QA policies.

6. REFERENCES

6.1. Quanterra® Incorporated Quality Assurance Management Plan (QAMP) (current version).

6.2. Quanterra® Policy QA-003: Quanterra® Quality Control Program (current version).

6.3. U.S. EPA Interim Draft Requirements for Quality Management Plans (EPA-QA-R-2, July 92).

6.4. Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs (ANSI/ASQC-E4-1994, January 95).

6.5. DOE Order 5700.6C for Quality Assurance (1991).

6.6. Quanterra® Procedure EHS150, "Training Requirements," current revision.

6.7. Current NELAC (National Environmental Accreditation Committee) Standards.

7. APPENDICES

Appendix A: *EXAMPLE* Quality Assurance Orientation and Training

Appendix B: *EXAMPLE* Technical Proficiency Documentation
EXAMPLE Analyst Assessments & Initial/On-going Demonstration of Capability Certification Statement

Appendix C: Certification of Lead Auditor and Quanterra® Certification of Qualification for Lead Auditor form

APPENDIX A

EXAMPLE

QUALITY ASSURANCE ORIENTATION & TRAINING

Type of Training: ❑ Orientation ❑ Annual Refresher ❑ Remedial

Employee Name (print): _____ **Date:** _____

Department: _____ **Job Title:** _____

I have received and completed the required Quality Orientation/Training as described below. This training included the following key elements of the Quanterra® QA Program:

- ❑ Quanterra® Quality Assurance Management Plan (QAMP)
- ❑ Quanterra's® Ethics Policy on Data Integrity & Meeting Client Requirements
- ❑ Quanterra® Quality Documents
- ❑ Nonconformance & Corrective Action Identification and Documentation
- ❑ Proper Record Keeping Practices
- ❑ Key Elements of Quanterra® QC Program Policy QA-003
- ❑ Other *(Specify)*: _____

Employee: _____ **Date:** _____.

QA Manager (or designee): _____ **Date:** _____.

Distribution: *Associate* *Training File*

APPENDIX B

EXAMPLE

TECHNICAL PROFICIENCY DOCUMENTATION

Type of Training: ❑ Initial ❑ On-going ❑ Remedial

I verify that _____ has been trained and met the technical proficiency
(Analyst Name)
requirements specified in the SOP: CORP-QA-0013 for the following ***required*** procedure(s) or analytical method(s):_____.

- ❑ Completed four consecutive LCSs with achieved acceptable target analyte recoveries and concentrations within method- and/or laboratory-established control limits.
  *(Project/Batch IDs:*_____*)*.
- ❑ Successfully prepared and/or analyzed an *internal* "blind" performance check sample. *(Reference:* _____*)*.
- ❑ Successfully prepared and/or analyzed the following *external* performance evaluation sample *(Reference:*_____*)*.
- ❑ Individual was observed while performing the procedure in conformance with the SOP(s) delineated above.
- ❑ Other(*Specify)*:_____.

NOTE: The analyst also certifies by signing this form that he/she has read and understands the applicable safety requirements in the SOP(s) indicated above to perform this activity.

Analyst: _____ **Date:** _____.

Approved By: _____ **Date:** _____.
(Supervisor/Manager)

Reviewed By: _____ **Date:** _____.
(QA Department)

Distribution: *Associate* *Supervisor/Manager* *Training File*

APPENDIX B

(Continued)

EXAMPLE

Quanterra® Inc.

Analyst Assessments & Initial/On-going Demonstration of Capability Certification Statement

Date:	
Laboratory Name:	
Laboratory Address:	
Analyst(s) Name(s):	**Group:**
Project Number(s	**QC Lot Number(s):**
Matrices:	
SOP Number/Method Number/Analyte/Class of Analytes/Measured Parameters:	

We, the undersigned, CERTIFY that:

1. The analyst(s) identified above, using the cited test method, which is in use at this facility for the analyses of samples under the Quanterra® Incorporated Quality Assurance Program, have met the Initial/On-going Demonstration of Capability.

2. The test method was performed by the analyst(s) identified on this certification.

3. A copy of the test method and the laboratory-specific SOPs are available for all personnel on-site.

4. The data associated with the initial/on-going demonstration capability are true, accurate, complete and self-explanatory (*).

5. For initial demonstration of method, all raw data (including a copy of this certification form) necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well organized and available for review by authorized inspectors. A copy of the QA Data Review Checklist used to document this review is available in the QA files.

Technical Director's Name	**Signature**	**Date**
Quality Assurance Manager's Name	**Signature**	**Date**

* *True: Consistent with supporting data.*
Accurate: Based on good laboratory practices consistent with sound scientific principles/practices.
Complete: Includes the results of all supporting performance testing.
Self-explanatory: Data properly labeled and stored so that the results are traceable and require no additional explanation.

APPENDIX C
Certification of Lead Auditor

1.0 **General**

1.1 The auditor with direct responsibility for conducting a quality assurance systems audit or evaluation is designated as QA Lead Auditor. QA Lead Auditors shall have the training and experience necessary to direct all phases of a systems audit or evaluation, as described in the Quanterra® QAMP. The Corporate Quality Assurance Director is responsible for determining that the auditor has the necessary technical expertise to conduct the audit.

1.2 The Corporate Quality Assurance Director, who shall approve the selection of lead auditors, shall evaluate the training and experience necessary for qualifications as a QA lead auditor.

1.3 QA Auditors may include members of Quanterra® Corporate Quality Assurance Group, Quanterra® Quality Assurance Managers, or other qualified personnel and is a voluntary program.

1.4 QA Lead Auditor shall participate in the Quanterra® Quality Assurance training program.

1.5 This same approach may be used for certifying EH&S auditors.

2.0 **Certification Requirements for Analytical/Environmental Quality Assurance Auditing**:

2.1 To qualify as a lead auditor, to perform audits in a full-service analytical/environmental laboratory, the auditor shall meet the minimum defined certification requirements described below. The qualifications of the lead auditor or potential lead auditor will be documented on the Quanterra® Certification of Qualification for Lead Auditor form.

2.2 Lead auditors must accumulate a minimum of 10 credits under the following certification system:

2.1.1 Education (4 credits maximum)

- Associate Degree, 1 credit (2 credits if the degree is technical in nature), or
- Bachelor's Degree, 2 credits (3 credits if the degree is technical in nature), or
- Master's Degree, 1 additional credit if the degree is technical in nature.

APPENDIX C
(Continued)
Certification of Lead Auditor

2.1.2 Experience (9 credits maximum)

- Technical experience in science, engineering, or construction; 1 credit for each full year up to a maximum of 5 credits
- If 2 or more years of this experience have been in an environmental field, 1 additional credit, or
- If 2 or more years of this experience have been quality assurance, 2 additional credits, or
- If 2 or more years of this experience have been in auditing, 3 additional credits, or
- If 2 or more years of this experience have been in environmental quality assurance, 3 additional credits, or
- If 2 or more years of this experience have been in environmental quality assurance auditing, 4 additional credits.

2.1.3 Other Credentials of Professional Competence (2 credits maximum)

- Certification of professional competency in engineering, science, or quality assurance by a state agency or national professional/technical society, 2 credits.

2.1.4 Rights of Management (2 credits maximum)

- The Quanterra® Corporate Quality Assurance Director or Corporate EH&S Director, as appropriate, may grant up to 2 credits based upon demonstrated capability or other performance factors applicable to auditing which may not be explicitly cited in this procedure.

2.3 Lead auditors must also participate in a minimum of three audits or evaluations within the 3-year period immediately prior to initial certification.

2.4 Lead auditors must successfully pass a formal examination. This examination may be either written or oral, and should cover applicable aspects of audits or evaluations as described in the QAMP. The Corporate QA Director is responsible for preparing and administering the examination and evaluating the examination results for Quality Auditors. The Corporate EH&S Director is responsible for preparing and administering the examination and evaluating the examination results for EH&S Auditors. Evidence of the examination shall be documented in the appropriate laboratory training records.

APPENDIX C
(Continued)
Certification of Lead Auditor

3.0 **Maintenance of Auditor Certification**

3.1 The proficiency of QA Lead Auditor shall be maintained through active participation in quality assurance systems audits or evaluations and the preparation and review of standards and procedures. The proficiency of EH&S Lead Auditor shall be maintained through active participation in EH&S audits or evaluations and the preparation and review of procedures.

3.2 Evaluation of proficiency maintenance shall be conducted on a yearly basis by the Corporate QA Director or Corporate EH&S Director, as appropriate, and shall be documented on the Quanterra® Certification of Qualification for Lead Auditor form. This form will be included in the individual's training records.

APPENDIX C
(Continued)
Quanterra® Certification of Qualification for Lead Auditor

Name:	Location:	Date:

Qualification Point Requirements		Credits
Education - University/Degree/Date	4 Credits Max.	
1- Undergraduate Level		
2. Graduate Level		
Experience - Company/Dates	9 Credits Max.	
1- Technical (0-5) points		
2- Analytical Environmental Industry (0-1 point) OR		
3- Quality Assurance (0-3 points) OR		
4- Auditing (0-4 point)		
Professional Accomplishment - Certificate/Date	2 Credits Max.	
1- Society		
2- Other		
Management - Justification/Evaluator/Date	2 Credits Max.	
Explain: Evaluated By: (Name & Title) Date:		
	Total Credits	

Audit Training/Participation	
Audit Communication Skills	
Evaluated By: (Name & Title)	Date:
Audit Training Courses	

Course Topic or Title	Date
1.	
2.	
3.	

Audit Participation (If more than 4 audits performed, list them using additional form on page 2)

Location	Type of Audit	Date (s)
1.		
2.		
3.		
4.		
Examination Lead Auditor Certification Examination	Passed	Date:

Auditor Qualified Certified By: (Signature & Title)	**Date Certified:**

APPENDIX C
(Continued)
Quanterra® Certification of Qualification for Lead Auditor

Audit Participation Continued (Performed the following audits)

Location	Type of Audit	Date (s)
5.		
6.		
7.		
8.		
9.		
10.		
11.		
12.		
13.		
14.		
15.		
16.		
17.		
18.		
19.		
20.		

Annual Evaluation Year	1998	1999	2000	2001	2002
Authorized Signature and Date					

STL STANDARD OPERATING PROCEDURE

TITLE : EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, 8151A AND 600 SERIES METHODS.

(SUPERSEDES: Revision 2)

Prepared by: Richard Burrows

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Manager

Proprietary Information Statement:

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Appendix A Extraction Procedure for Chlorinated Acid Herbicides Based on Method 8151A 55

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1. SCOPE AND APPLICATION

This SOP describes procedures for preparation (extraction and cleanup) of semivolatile organic analytes in aqueous, TCLP leachate, and soil matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1. Extraction procedures for the following determinative methods are covered:
8081A, 8141A, 8151B, 8270C, 8310
608, 610, and 625

1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.3. Other extraction procedures (PFE, SPE, accelerated Soxhlet, etc.) may be used but are not currently covered in this SOP.

2. SUMMARY OF METHOD

2.1. Separatory Funnel Extraction

A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2. Continuous Liquid/Liquid Extraction

A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with methylene chloride for 18-24 hours.

2.3. Sonication Extraction

A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using an ultrasonic horn.

2.4. Soxhlet Extraction

A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is extracted with refluxing solvent.

2.5. Cleanup and Concentration

Procedures are presented for removing interferents from sample extracts, and for drying and concentration of the extract to final volume for analysis.

2.6. Phenoxy acid herbicide extractions

Procedures for the extraction and cleanup of phenoxy acid herbicides are presented in Appendix A.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All 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. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

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:

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 become contaminated will be removed and discarded, other gloves will be cleaned immediately. Viton gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone]. When good manual dexterity is needed, for example, when handling small quantities/containers, disposable gloves (such as latex or N-DEX®) shall be used. While these gloves protect against splashes, they give little or no protection against contact with large quantities of solvent, and no protection against spills or immersion.

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 MSDS files maintained in the laboratory. The following specific hazards are known:

> Chemicals that have been classified as **carcinogens** or **potential carcinogens** under OSHA include methylene chloride, PCBs, certain pesticides.

The following materials are known to be **corrosive**: Concentrated sulfuric acid, sodium hydroxide, 1N nitric acid.
Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

Chemicals known to be **flammable** are: Diethyl ether, acetone, hexane, 2-propanol.
Mercury is a highly toxic compound that must be handled with care. The analyst must be aware of the appropriate handling and clean-up techniques before handling this material.

5.4. Exposure to hazardous 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 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 operations will permit. Use of methylene chloride for glassware cheaning should be avoided as far as possible. If more thn 500 mL of Methylene chloride is spilled, evacuate the area until the area has been cleaned by a Hazardous Material Team.

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.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2. Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
Separatory Funnel: 2 L	√				
Separatory Funnel Rack	√				
Balance: >1400 g capacity, accurate ±1 g	√	√			
pH indicator paper, wide-range: covers extraction pH	√	√			
Graduated cylinder: 1 liter. (other sizes may be used)	√	√			

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
Erlenmeyer Flask or Fleaker: 125 & 300 mL (other sizes optional)	√		√		
Solvent Dispenser Pump or 100 mL Graduated Cylinder	√		√		
Continuous Liquid/Liquid Extractor		√			
Round or flat Bottom: 250, 500 mL or 1 L		√			
Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent).		√		√	√
Cooling Condensers		√		√	
Heating Mantle: Rheostat controlled		√		√	
Auto-timer for heating mantle		√		√	
Beakers: 250 & 400 mL, graduated			√		
Balance: >100 g capacity, accurate ±0.1 g			√	√	
Soxhlet Extractor				√	
Sonicator (at least 300 watts)			√		
Sonicator horn, 3/4 inch			√		
Kuderna-Danish (K-D) Apparatus: 500 mL					√
Concentrator Tube: 10 mL, attached to K-D with clips					√
Snyder Column: Three-ball macro					√
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.					√
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap					√
Nitrogen Blowdown Apparatus					√
Nitrogen: reagent grade.					√
Culture tubes: 10 mL, 16 mmx100 mm					√
Syringe: 1 mL	√	√	√	√	
Phase Separation Paper	√	√	√	√	
Glass Wool	√	√	√	√	
Glass Funnel: 75 X 75 mm	√	√	√	√	√
Disposable Pipets	√	√	√	√	√
Aluminum foil	√	√	√	√	√
Paper Towels	√	√	√	√	√

1.3. Equipment and Supplies for Cleanup Procedures

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	A/B
Gel permeation chromatography system (GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc. or Zymark Benchmate or equivalent).	√				
Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories,	√				

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	A/B
Richmond, CA, Catalog 152-2750 or equivalent).					
Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward.	√				
Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell.	√				
Strip chart recorder, recording integrator, or laboratory data system.	√				
Syringe: 10 mL with Luerlok fitting.	√				
Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent.	√				
Chromatographic column: 250 mm long x 10 mm ID; with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup).	√				
Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.		√			
Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.		√			
Vacuum pressure gauge.		√			
Rack for holding 10 mL volumetric flasks in the manifold.		√			
Mechanical shaker or mixer: Vortex Genie or equivalent.			√	√	
Separatory Funnels with Ground-Glass Stoppers: 250 mL					√
Erlenmeyer Flasks: 125 mL					√
Disposable Pipets		√	√	√	√
Culture tubes: 10 mL, 16 mmx100 mm	√	√	√	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
Sodium hydroxide (NaOH), Pellets: Reagent Grade	√	√			
Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	√			
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade	√	√			
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	√			
Organic free reagent water.	√	√			
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400°C a minimum of two hours.	√	√	√	√	

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
Extraction/Exchange Solvents: Methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent	√	√	√	√	√
Acetone: Used for cleaning	√	√	√	√	√

1.2. Reagents for Cleanup Procedures

REAGENTS	GPC	Florisil	Sulfur	Acid	A/B
Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (calalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.)		√			
Mercury: triple distilled			√		
Tetrabutylammonium hydrogen sulfate			√		
Sodium sulfite			√		
Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3.39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution.			√		
2-Propanol			√		
Nitric acid: 1N			√		
Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.			√		
Sulfuric acid, Concentrated				√	
Sodium hydroxide, Pellets					√
Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water					√
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade					√
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.					√

1.3. Standards

1.3.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from neats. Semivolatile stock standards are stored at $\leq 6^{o}C$. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampule is opened if purchased.) Standards must be allowed to come to room temperature before use.

1.1.2. Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

1.1.3. Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

1.1.4. GPC calibration solution - prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
Corn Oil	25.0
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard has a lifetime of 6 months.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1. Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples.

8.3.2. For TCLP leachates, extraction is initiated within seven days from when the leaching procedure is completed.

8.3.3. Analysis of the extracts is completed within forty days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an 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. See policy QA-003 for further definition of the batch.

9.2. Definition of matrix

The possible matrix types are aqueous, soil, waste and TCLP leachate.

9.3. Insufficient Sample

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. Use of a LCS pair in place of a MS/MSD must be documented.

9.4. Sample count

Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field samples are included.

9.5. Method Blank

A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the 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.

9.5.1. Aqueous Method Blanks use 1000 mL of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.2. Solid method blanks use 30 g of sodium sulfate spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.3. TCLP method blanks use 200 mL of leachate fluid (100 mL for pesticides or herbicides) spiked with the surrogates. The leachate may optionally be diluted

to 1000 mL with reagent water. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.6. 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. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.6.1. The LCS is made up in the same way as the method blank (See sections 9.5.1 - 9.5.3) but spiked with the LCS standard and the surrogates.

9.7. Surrogates

9.7.1. 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.

9.7.2. Each applicable 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.

9.8. 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 spiked aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike.

9.9. Initial Demonstration of Capability

The initial demonstration and method detection limit studies described in section 13 must be acceptable before analysis of samples may begin.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries (QAS) 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

Refer to section 11.8.1.2 for calibration of the GPC. Otherwise this section is not applicable.

11. PROCEDURE

Procedures for separatory funnel liquid/liquid extraction (11.2), continuous liquid/liquid extraction (11.3), sonication extraction (11.4), soxhlet extraction (11.5), waste dilution (11.6), extract concentration (11.7), and extract cleanup (11.8) are presented in this section.

11.1. 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 will be notified. The Nonconformance memo will be filed in the project file.
Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

11.2. Separatory Funnel Liquid/Liquid Extraction of Water Samples.

A flow chart for this procedure is included in Section 17.

11.2.1. For pesticides and TCLP leachates, measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.2.2. The normal sample volume is 1 liter. Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with reagent water, may be used for very dirty samples.

11.2.3. Weigh the sample container on a balance (± 1 g), taring the sample and container. Add 1.0 mL of the surrogate spiking solution. Also add 1.0 mL of matrix spiking solution to any matrix spike / matrix spike duplicate samples. Mix well. Transfer the sample to the separatory funnel. Rinse the sample bottle with 60 mL methylene chloride and transfer to the separatory funnel. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: If the sample bottle is completely full, it may be difficult to add the spike solutions to the bottle. In this case, transfer the sample to the separatory funnel and then add the spike.
Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.3.1. If the entire sample bottle will not be used, transfer the aliquot to the separatory funnel, then add the spiking solutions to the sample in the separatory funnel.

11.2.3.2. Sample bottles and graduated cylinders will be solvent rinsed for SW-846 methods.

Note: Alternative methods of measurement of sample volume include a) transferring the sample to a measuring cylinder. STL Pittsburgh uses this method. b) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs.

11.2.4. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The LCS is spiked with the surrogate and matrix spike solutions, the method blank only with the surrogates.

11.2.5. Use 100 mL of leachate for TCLP pesticides, and 200 mL of leachate for TCLP semivolatiles, measured in a graduated cylinder. The leachate may be made up to 1 L in volume with reagent water.

11.2.6. For a TCLP method blank, measure 100 mL (200 mL for semivolatiles) of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Add 60 mL of methylene chloride to the separatory funnel. The TCLP leachate may be diluted to approximately 1 liter before extraction if desired.

11.2.7. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.2.8. Seal and shake or rotate the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.9. Allow the organic layer to separate from the water phase until complete visible separation has been achieved (approximately 10 minutes). If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical

methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in continuous liquid-liquid extraction (Section 11.2.). If this is done, the sample must be extracted as part of a valid CLLE batch.

***Note**: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

11.2.10. Fill a funnel with 10-20 g of anhydrous sodium sulfate. The funnel can be plugged with glass wool or filter paper may be used to hold the sodium sulfate. Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

11.2.11. Repeat the extraction process two more times using fresh 60 mL portions of solvent, combining the three solvent extracts in the collection container.

11.2.12. If extraction at a secondary pH is required, adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Serially extract with three 60 mL portions of methylene chloride, as outlined in Steps 11.1.7 to 11.1.9. Collect these three extracts in the same container used for the acid fraction.

Note: Alternatively, the acid and base fractions may be kept separate. This may be required for method 625. Separate analysis of the acid and base fractions may also be required for method 625. Individual client requirements must be checked before starting the extraction.

11.2.13. Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

11.2.14. Dispose of solvent and water remaining in the extractor into the appropriate waste container.

11.2.15. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.3. Continuous Liquid/Liquid Extraction from Water Samples:

A flow chart for this procedure is included in Section 17.

11.3.1. Assemble the apparatus. Add 300-500 mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round-bottom distilling flask.

11.3.2. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.3.3. Weigh the sample container on a balance (± 1 g), taring the sample and container. Add 0.5 mL of the surrogate spiking solution. Also add 0.5 mL of matrix spiking solution to any matrix spike / matrix spike duplicate samples. Mix well. Transfer the sample to the extractor. Rinse the sample bottle with 60 mL methylene chloride and transfer to the extractor. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

Note: If the sample bottle is completely full, it may be difficult to add the spike solutions to the bottle. In this case, transfer the sample to the extractor and then add the spike.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.3.3.1. If the entire sample bottle will not be used, transfer the aliquot to the extractor, then add the spiking solutions to the sample in the extractor.

Note: **Alternative methods of measurement of sample volume include: a.) transferring the sample to a measuring cylinder.** *STL Pittsburgh uses this methods.* b.) marking a meniscus on the sample bottle and then measuring the volume of water required to fill the bottle to the meniscus after the sample is transferred. The former method is not recommended because of the risk of cross contamination while the latter is not recommended because of poor accuracy. However, either method may be necessary for specific client programs. *Please note (for aqueous samples) : Due to difficulties in handling variable amounts of sample in the QuanTIMS LIMs system, as long as the sample container amount is within 5 % of the targeted sample amount, the sample volume may be adjusted by discarding excess sample volume before rinsing the sample bottle with extraction solvent. For example, if a one liter sample bottle contains 1050 mLs, 50 mLs of sample may be discarded in order to adjust the volume of sample analyzed.*

11.3.3.1.1. Sample bottles and graduated cylinders will be solvent rinsed for SW-846 methods.

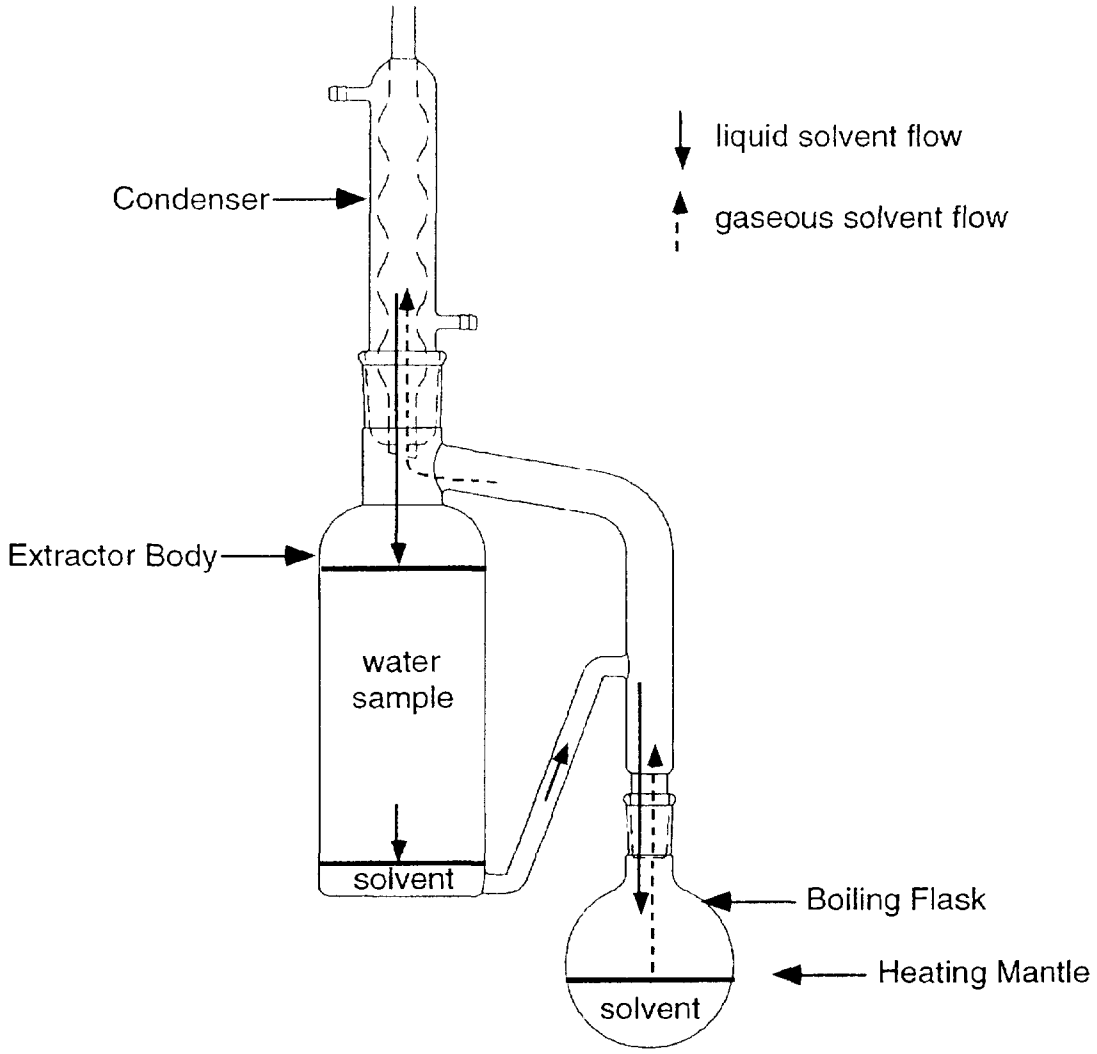
11.3.3.2. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The method blank is spiked with the surrogates, the LCS and matrix spikes with the surrogates and matrix spiking solutions. Note that

different spiking solutions are used for methods 625, 8270 and TCLP.

11.3.3.3. Use 100 mL of leachate for TCLP pesticides, and 200 mL of leachate for TCLP semivolatiles, measured in a graduated cylinder. The leachate may be made up to 1 L in volume with reagent water.

11.3.3.4. For a TCLP method blank, measure 100 mL (200 mL for semivolatiles) of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water.

11.3.3.5. Less than one liter of sample may be used, for highly contaminated samples, or if the reporting limit can be achieved with less than one liter of sample. In this event dilute the sample to about 1 liter with reagent water.



11.3.4. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.3.5. Add reagent water to the extractor body until approximately 250 mL of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation and solvent cycling. Attach cold condenser (about 10°C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours. (24 hours required for 600 series)

11.3.6. If extraction at a secondary pH is required, (see Table 1) turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and

record the adjusted pH on the benchsheet. If desired, the acid and base fractions may be kept separate by replacing the boiling flask with a clean flask and fresh solvent. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours.

Note: Alternatively, the acid and base fractions may be kept separate. This may be required for method 625. Separate analysis of the acid and base fractions may also be required for method 625. Individual client requirements must be checked before starting the extraction.

11.3.7. Turn off the heating mantle and allow the extractor to cool.

11.3.8. Place a funnel containing 10-20 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) apparatus or other glass container. The funnel can be plugged with glass wool enabling it to hold the granular anhydrous sodium sulfate or phase separation filter paper may be used.

11.3.9. Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary or advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

11.3.10. Collect the dried extract in a K-D or other glass container. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

Note: Some types of CLLE apparatus have built in drying columns. If this type of apparatus is used then a drying step subsequent to the extraction may not be necessary.

11.3.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.4. Sonication

A flow chart for this procedure is included in Section 17.

11.4.1. Determination of percent moisture (Optional - if a different group performs this test, refer to the facility SOP.)

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight (at least 12 hours) at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.4.2. Determination of pH (Optional - if a different group performs this test, refer to the facility SOP.)

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for five minutes then let stand for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.4.3. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator). Document if a water layer was discarded.

11.4.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.4.5. Weigh 30 g of sample ± 1.0 g into a 250 or 400 mL beaker. Record the weight to the nearest 0. 1 g in the appropriate column on the benchsheet. Use 30 g of sodium sulfate for the method blank and 30 g of sodium sulfate with 30 g of reagent sand for the LCS.

11.4.6. Mix weighed sample with a spatula adding enough anhydrous sodium sulfate (approximately 30 g) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)

11.4.7. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP.

11.4.8. Add 0.5 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add 0.5 mL of the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 and 5 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogate and matrix spiking solution is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.4.9. Immediately add a minimum of 100 mL of solvent to the beaker.

Solvents:

Semivolatile GC/MS	1:1 Methylene Chloride / Acetone

Organochlorine pesticides and PCBs	1:1 Methylene Chloride/ Acetone
Hydrocarbons by FID (DRO, etc.)	Methylene Chloride

Note: Steps 11.4.5 - 11.4.9 should be performed rapidly to avoid loss of the more volatile extractables.

11.4.10. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.4.11. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn. with mode switch on pulse, and percent-duty cycle knob set at 50%.

Note: Do ***not*** use ***Microtip*** probe.

11.4.12. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.4.13. Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus.

11.4.14. Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

11.4.15. Repeat the extraction two more times with additional 100 mL minimum portions of solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.4.16. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.4.17. **Sonicator Tuning**.

11.4.17.1. Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

11.5. Soxhlet

11.5.1. Determination of % moisture

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.5.2. Determination of pH

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.5.3. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client. Document on benchsheet if a water layer was discarded.

11.5.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.5.5. Weigh 30 g of sample ± 1.0 g into a beaker, recording the weight to the nearest 0.1 g on the benchsheet.. Use 30 g of sodium sulfate for the method blank and LCS. Add 30 g of anhydrous sodium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the soxhlet extractor is an acceptable alternative for the thimble.

11.5.5.1. Sample weights less than 30 g but over 5 g may be used if the appropriate reporting limits can be met.

11.5.6. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP, using sodium sulfate as the matrix. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.5.7. Add 1 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add 1 mL of the

appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 - 6 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogates and matrix spiking compounds is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.5.8. Place approximately 250 mL of solvent into a 500 mL flat bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

Solvents:

Semivolatile GC/MS	1:1 Methylene Chloride / Acetone
Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone
Hydrocarbons by FID (DRO, etc.)	Methylene Chloride

11.5.9. Allow the extract to cool after the extraction is complete, then disassemble by gently twisting the soxhlet from the flask. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

11.5.10. Collect the dried extract in a K-D or other glass container. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

11.5.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.6. Waste Dilution

11.6.1. This method is used for materials that are soluble in an organic solvent.

11.6.2. Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, then discard the solvent.

11.6.3. Tare the vial, then transfer approximately 1g of sample to the vial. Record the weight to the nearest 0.1 g.

11.6.4. Add 1 mL of surrogate solution (Table 3) For GC/MS analysis, the surrogate solution should be 10x more concentrated than the normal solution (i.e. 1000/1500 ppm). For pesticides the normal surrogate solution is appropriate.

11.6.5. Dilute to 10 mL with the appropriate solvent. (Methylene Chloride for GC/MS analysis, hexane for pesticides analysis.)

11.6.6. Add 2 g + 0.1 g sodium sulfate to the sample. Cap and shake for 2 minutes.

11.6.7. Add 4-5 g sodium sulfate to a small funnel. The funnel can be plugged with glass wool or phase separation filter paper may be used to hold the sodium sulfate.

11.6.8. Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 10 mL.

11.6.9. Label the sample, which is now ready for cleanup or analysis.

11.7. Concentration

According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.7.1. **Kuderna-Danish (KD) Method**:

11.7.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. Transfer the sample to the K-D flask.

11.7.1.2. Add one or two clean boiling chips and the extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).

11.7.1.3. Place the KD apparatus on a water bath (80-90°C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

11.7.1.4. Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (50 mL hexane, 50 mL cyclohexane, 2 mL acetonitrile or 10 mL toluene) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 mL. Refer to Table 2 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: Add an additional boiling chip with the addition of exchange solvent.

An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add 10 mL of hexane, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.7.1.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.7.1.6. If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 11.7.2

11.7.2. Nitrogen Evaporation to Final Concentration

11.7.2.1. Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

11.7.2.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C

Toluene	111°C

11.7.2.3. During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through the process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.7.2.4. An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

11.7.2.5. *Note:* The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.7.3. **Turbovap Method**

11.7.3.1. Turn on the Turbovap and adjust the water temperature to 5-10°C less than the boiling point of the solvent to be evaporated.

11.7.3.2. Switch all endpoint sensors to the "NO" position.

11.7.3.3. Adjust the water bath level

11.7.3.4. Adjust the nitrogen gas pressure to approximately 12 psi.

11.7.3.5. Transfer the extract into the Turbovap tube and load into the Turbovap. Do not fill the Turbovap tubes over approximately 3/4 full.

11.7.3.6. Reset the sensor and close the lid.

11.7.3.7. *Note:* If the extract splashes when the nitrogen flow starts, reduce the nitrogen flow or transfer a portion of the extract back into the original extract container.

11.7.3.8. As the extract concentrates, transfer the remainder of the extract into the appropriate Turbovap tube. After all of the extract has been

transferred, rinse the flask with a few mL of methylene chloride and add to the Turbovap tube.

11.7.3.9. During the concentration rinse the Turbovap tube walls with a few mL of solvent 1 or 2 times.

11.7.3.10. Concentrate the extract to slightly less than the required final volume.

11.7.3.11. If solvent exchange is required, concentrate to 1-4 mL and add 50 mL of the exchange solvent. Concentrate back down to the appropriate volume. Refer to table 2 for details of exchange solvents and final volumes.

11.7.3.12. Transfer the concentrated extract to volumetric glassware for adjustment of final volume, using a small amount of solvent to rinse the tube and complete the transfer.

Note: Water contamination from condensation during concentration is not acceptable. If water is present, remove the Turbovap tube and filter the extract through sodium sulfate. Transfer to a clean Turbovap tube and continue the concentration.

Note 2: Dark, opaque or turbid samples may not concentrate. If this occurs, set the concentrator sensor to dryness and supervise the entire concentration procedure.

11.8. Cleanup Techniques

The following techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity. *Gel Permeation Chromatography* (Section 11.8.1) is a generally applicable technique which can be used to prepare extracts for Semivolatiles (8270), PAH (8100) and pesticides (8080) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.

Florisil column cleanup (Section 11.8.2) is particularly useful for cleanup of pesticides for analysis by method 8080 and should normally be applied to these samples unless the matrix is clean. It separates compounds with a different polarity from the target analytes.

Gel Permeation Chromatography and Florisil column cleanup may both be applied to samples for analysis by method 8080. In this case the GPC should be performed first.

Sulfur cleanup (Section 11.8.3) is generally applied to samples for analysis by method 8080, since the Electron Capture Detector responds strongly to sulfur. It is performed after GPC and Florisil cleanup.

Sulfuric acid cleanup (Section 11.8.4) is applied to samples requiring analysis for Polychlorinated Biphenyls (PCBs) only. Most organic matter is destroyed by the sulfuric acid.
WARNING: Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

Acid Base Partition Cleanup (Section 11.8.5) is useful for separating organic acids and phenols from basic and neutral organics.

Silica gel cleanup (Section 11.8.6) may be used to separate polynuclear aromatic hydrocarbons from interfering aliphatic hydrocarbons prior to analysis by GC/FID.

11.8.1. **Gel Permeation Chromatography (GPC)**

Note: GPC systems include the GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc., Zymark Benchmate, or equivalent.

11.8.1.1. GPC Column Preparation

11.8.1.1.1. Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

11.8.1.1.2. Add approximately 300 mL of methylene chloride and stir gently.

11.8.1.1.3. Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

11.8.1.1.4. Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

11.8.1.1.5. Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

11.8.1.1.6. Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer

as much as possible with one continuous pour trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

11.8.1.1.7. Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

11.8.1.1.8. Push the plunger until it meets the gel, then compress the column bed about 4 cm.

11.8.1.1.9. Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

11.8.1.1.10. After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000"ID x 2") in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

11.8.1.1.11. When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride

through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

11.8.1.2. **Initial Calibration of the GPC Column**

11.8.1.2.1. Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

11.8.1.2.2. Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22°C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

11.8.1.2.3. Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in section 11.8.1.6):

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

11.8.1.2.4. A UV trace that does not meet the criteria in paragraph 11.8.1.2.3 indicates the need for system maintenance and/or the need for a new column.

11.8.1.2.5. Determine appropriate collect and dump cycles.

11.8.1.2.6. The calibrated GPC program for pesticides/PCB should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

11.8.1.2.7. For semivolatile extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

11.8.1.2.8. Reinject the calibration solution after appropriate dump and collect cycles have been set.

11.8.1.2.9. Measure and record the volume of collected GPC eluate in a graduated cylinder.

11.8.1.2.10. The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

11.8.1.3. **GPC calibration check**

Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use.

11.8.1.3.1. Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than ± 5% use this run as the start of a new initial calibration. Otherwise, proceed with the recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

11.8.1.4. **GPC Recovery Check for Pesticides/ PCBs**

11.8.1.4.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 mL of the pesticide matrix spiking solution (Table 6) to 10 mL in methylene chloride. The second mixture is prepared by diluting 1 mL of the PCB only matrix spiking solution (Table 6) to 10 mL with methylene chloride.

11.8.1.4.2. Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

Note: If the analysis is for PCBs only, then the pesticide recovery check is not necessary.

11.8.1.4.3. After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 11.7.

11.8.1.4.4. The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-110% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

11.8.1.5. **GPC Recovery Check for Semivolatiles**

11.8.1.5.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Dilute 1.0 mL of the semivolatiles matrix spiking solution (Table 6) to 10 mL in methylene chloride.

11.8.1.5.2. Load the matrix spike mixture and a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

11.8.1.5.3. After collecting the GPC recovery check fraction, concentrate to 0.5 mL, and analyze by GC/MS. Refer to the concentration section 11.7.

11.8.1.5.4. Recovery of the matrix spike analytes should be at least 60%. The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

11.8.1.6. **Sample Extract Cleanup**

11.8.1.6.1. Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to section 11.7.

11.8.1.6.2. Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal

laboratory temperature to prevent outgassing of the methylene chloride is 22°C. The normal backpressure is 6-10 psi.

11.8.1.6.3. In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

11.8.1.6.4. Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

Note: The Zymark Benchmate automatically filters the sample extracts, but manual prefiltration of very dirty extracts may be necessary.

11.8.1.6.5. Load the filtered (or unfiltered if using the Benchmate) samples into the proper sample tubes and place on the GPC.

Note: For the GPC Autoprep Model 1002A, wash the loading port with methylene chloride after loading each sample loop in order to minimize cross contamination. This step is automated on the GPC Autoprep 1002B and on the Benchmate.

11.8.1.6.6. Set the collect, dump, and wash times determined by the calibration procedure.

11.8.1.6.7. Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

11.8.1.6.8. Collect each sample in a suitable glass container. Monitor sample volumes collected.

11.8.1.6.9. Any samples that were loaded into 2 or more positions must be recombined.

11.8.1.6.10. Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration section 11.7.

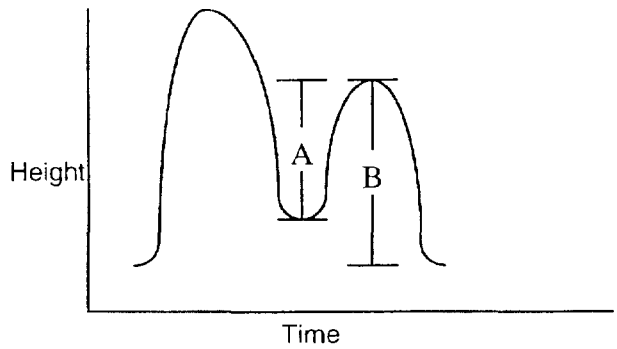
11.8.1.6.11. Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 11.7.

11.8.1.7. **Calculations**

11.8.1.7.1. Resolution

To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation



$$\% \text{ Resolution } = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak

B = peak height of smaller peak

11.8.1.7.2. Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

11.8.1.7.3. Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

11.8.2. Florisil Cartridge Cleanup

Florisil cleanup is generally used for organochlorine pesticides, although it may be applied to other analytes. Sections 11.8.2.1 through 11.8.2.8 outline the procedure for organochlorine pesticides, while section 11.8.2.9 outlines modifications required for other analytes.
Note 1: Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assembly, Zymark Benchmate, or equivalent.

Note 2: Follow the lab specific procedure when using the Zymark benchmate.

11.8.2.1. Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to Section 11.7 for details of concentration.

11.8.2.2. Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

11.8.2.3. Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

11.8.2.4. Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

11.8.2.5. Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

11.8.2.6. After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

11.8.2.7. The pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

11.8.2.8. Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the concentration section. (11.7)

Note 1: A cartridge performance standard must be run with each lot of Florisil cartridges.

Note 2: Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of GC Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks interfering with target compounds can be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

11.8.2.9. Modifications for other analyte classes

11.8.2.9.1. PCBs

Pre-elute the cartridge with 4 mL hexane. Add 2 mL of the sample extract and elute with 3 mL hexane. The eluant will contain the PCBs together with any heptachlor, aldrin, 4,4'DDE and part of any 4,4'DDT. Any BHC isomers, heptachlor epoxide, chlordane, endosulfan I and II, endrin aldehyde and endrin sulfate and methoxychlor will be retained on the column and can be eluted in a separate fraction with 8 mL 90:10 hexane:acetone if required.

11.8.3. Sulfur Removal

11.8.3.1. Sulfur can be removed by one of three methods: mercury, copper, or tetrabutylammonium sulfite (TBA) according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipet, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

11.8.3.2. Sulfur Removal with Elemental Mercury

Note: Use Mercury sparingly in order to minimize exposure and disposal costs.

11.8.3.2.1. Transfer 2 mL of sample extract into a clean concentrator tube or Teflon sealed vial.

11.8.3.2.2. Add one to three drops of mercury to the extract vial and seal.

11.8.3.2.3. Shake well for 15-30 seconds. If prolonged shaking is required, use a mechanical shaker.

11.8.3.2.4. Remove the extract from the mercury using a disposable pipette and transfer to a clean vial.

11.8.3.2.5. If black precipitate forms, sulfur was present. Shake again, then centrifuge. After centrifugation, transfer the supernate to a clean test tube and repeat. Do this until relatively little precipitate remains, or the screens indicate that cleanup is complete.

11.8.3.2.6. Properly dispose of the mercury waste.

11.8.3.3. Sulfur Removal with Copper

11.8.3.3.1. Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

11.8.3.3.2. Add approximately 2 g of cleaned copper powder (see 7.2 for copper cleaning procedure) to the sample extract tube.

11.8.3.3.3. Mix for one minute on a mechanical shaker.

11.8.3.3.4. If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

11.8.3.3.5. Transfer the supernate to a clean vial.

11.8.3.4. Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

11.8.3.4.1. Transfer 1.0 mL of sample extract into a culture tube.

11.8.3.4.2. Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

11.8.3.4.3. If a precipitate does not form, add sodium sulfite in approximately 0.1 g portions until a solid residue remains after repeated shaking.

11.8.3.4.4. Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in section 11.8.3.4.1.

11.8.4. Sulfuric Acid Cleanup

11.8.4.1. Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

Caution: There must be no water present in the extract or the reaction may shatter the sample container.

11.8.4.2. Shake or vortex for about thirty seconds and allow to settle. (Centrifuge if necessary)

11.8.4.3. Remove the sample extract (top layer) from the acid using a Pasteur pipet and transfer to a clean vial. ***CAUTION:*** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

11.8.4.4. If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

11.8.4.5. Properly dispose of the acid waste.

11.8.5. Acid/Base Partition Cleanup

11.8.5.1. Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

11.8.5.2. Add 20 mL of methylene chloride to the separatory funnel.

11.8.5.3. Slowly add 20 mL of DI water which has been previously adjusted to a pH of 12 to 13 with 10 N sodium hydroxide.

11.8.5.4. Seal and shake the separatory funnel for at least two minutes with periodic venting to release excess pressure.

CAUTION: Methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the separatory funnel has been sealed.

11.8.5.5. Allow the organic layer to separate from the aqueous phase for a minimum of ten minutes.

11.8.5.6. If an emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

11.8.5.7. Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL aliquots of dilute sodium hydroxide (pH 12-13) . Combine the aqueous extracts.

11.8.5.8. Water-soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase discard the methylene chloride and proceed to Section 11.8.5.9. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Section 11.8.5.11.

11.8.5.9. Externally cool the flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Transfer the cool aqueous phase to a clean 125 mL separatory funnel.

11.8.5.10. Add 20 mL of methylene chloride to the separatory funnel and shake for at least two minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask. Repeat the extraction two more times using fresh methylene chloride and extracting at pH 1-2. Combine the three extracts.

11.8.5.11. Dry the extract by passing through a funnel containing 10-20 g anhydrous sodium sulfate. Rinse the funnel with an additional 20-30 mL of clean methylene chloride

11.8.5.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to section 11.7 for concentration.

11.8.5.13. Dispose of solvent and water remaining in the separatory funnel into the appropriate waste container.

11.8.6. Silica Gel Cleanup

This procedure is appropriate for cleanup of extracts prior to determination of polynuclear aromatic hydrocarbons by GC/FID.

11.8.6.1. Exchange the extract solvent to cyclohexane and reduce the volume to 2 mL prior to cleanup.

11.8.6.2. Prepare a slurry of approximately 10 g of activated silica gel in about 15 mL of methylene chloride. Place this into a 10 mm ID chromatographic column. Tap the column to settle the silica gel. Add 1-2 cm of anhydrous sodium sulfate to the top of the silica gel.

11.8.6.3. Pre-elute the column with 40 mL of pentane. Elution rate should be approximately 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate to air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL of cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane elute.

11.8.6.4. Elute the column with 25 mL of methylene chloride/pentane (2:3 v/v). Since the polynuclear aromatic hydrocarbons elute in this fraction, collect the eluate and concentrate to the required volume.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Method detection limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The procedure for the determination of the method detection limit is given in STL QA Policy #: QA-005

13.2. Initial demonstration

Each laboratory must make an initial demonstration of capability for each individual method. This requires 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 spiking level should be

equivalent to a mid-level calibration. (For certain tests more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

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. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. (CORP-GC-0001, CORP-MS-0001, 0002)

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

Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Laboratory Environmental, Health and Safety Coordinator should be contacted if additional information is required.

15.1. Solvent waste must be disposed of in the clearly labeled waste cans.

15.2. Acid waste must be collected in the clearly labeled acid waste containers.

15.3. Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Methylene chloride saturated water and remaining sample after the extraction is dumped into Methylene chloride waste cans.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3510C, 3520C, 3540C, 3550B, 3600C, 3610B, 3620B, 3640A, 3650B, 3660B, AND 3665A.

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Aqueous sample volumes may be determined by weight.

17.1.3. Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.1.4. 10 g of soil is used for pH determination, rather than the 50 g suggested in the reference method. The volume of water is also adjusted to maintain the sample / water ratio specified in the method.

17.2. Modifications from previous revision

17.2.1. Some details of separatory funnel extraction and continuous liquid-liquid extraction have been changed.

17.2.2. Recovery limits for GPC cleanup have been changed.

17.2.4. A number of clarifications have been made

17.2.5. The appendix describing extraction of herbicides by method 8150 has been removed.

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
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH[2]	Secondary Ext. pH[2]
BNA: 8270[1]	1-2	11-12
625	11-12	1-2
Pest/PCB: 8080 & 608	5-9	None
OPP: 8140	6-8	None
OPP: 8141	as received	None
Hydrocarbons: 8015	as received	None
PAH: 8310, 8100 & 610	as received	None

[1] If the laboratory has validated acid only 8270C extraction for the target compound list required then the base extraction step may be omitted. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See section 13). Client acceptance should be documented before using this *option if applied to older versions of SW-846 (ie. 8270B).*

[2] *If the laboratory has validated pH up then down (As in method 625) for the 8270C target list then this order of extraction may be used for 8270C. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See section 13). Client acceptance should be documented before using this option if applied to older versions of SW-846 (ie. 8270B).*

Table 2
Exchange Solvents and Final Volumes

Final Volumes and Exchange Solvents if no cleanup is used		
Type	Exchange Solvent for Analysis	Final Volume for Analysis
Semivolatiles	N/A	1.0
Pesticides	Hexane	10.0
PAH by HPLC	Acetonitrile	Refer to facility SOP for HPLC
PAH by GC	N/A	1.0
TPH	N/A	1.0
OPP	NA	1.0

Final Volumes and exchange solvents if GPC cleanup is used			
Type	Exchange Solvent for GPC	Final Volume for GPC	Final Volume and solvent for Analysis
Semivolatiles	CH_2Cl_2	10 mL[1]	0.5 mL CH_2Cl_2
Pesticides	CH_2Cl_2	10 mL[1]	5 mL, hexane
OPP	CH_2Cl_2	10 mL	5 mL

[1] Final volume for GPC may be 4 mL if a 2 mL sample loop is used

Final volumes and exchange solvents if Florisil cleanup is used			
Type	Exchange Solvent for Florisil	Final Volume for Florisil	Final Volume and solvent for Analysis
Pesticides	Hexane	10 mL (2 mL aliquot used)	2 mL, hexane

Final volumes and exchange solvents if both GPC and Florisil cleanup are used					
Type	Exchange Solvent for GPC	Final Volume for GPC	Exchange Solvent for Florisil	Final Volume for Florisil	Final volume for analysis
Pesticides	Methylene Chloride	10 mL	Hexane	5 mL (2 mL aliquot used)	2 mL, hexane

Note:Different final volumes may be necessary to meet special client reporting limit requirements.

Note:If silica gel cleanup is performed, exchange solvent to cyclohexane prior to cleanup.

Table 3

Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA	100/150 ppm BNA	0.5
Pest	0.2 ppm DCB/TCX	1.0
Pest/PCB	0.2 ppm DCB/TCX	1.0
PCB	0.2 ppm DCB/TCX	1.0

Table 4

Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA	100/150 ppm BNA	0.5
BNA TCLP	BNA TCLP Spike	0.5
BNA NPDES	BNA NPDES Spike	0.5
Pest	0.2/0.5 ppm Pest	1.0
Pest TCLP	Pest TCLP Spike	1.0
Pest NPDES	Pest NPDES Spike	1.0
Pest/PCB	0.5 ppm pest spike	1.0
PCB	10 ppm PCB Spike	1.0

Table 5
Surrogate Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
BNA	2-Fluorobiphenyl	Methanol	100
	Nitrobenzene-d5		100
	p-Terphenyl-d14		100
	2-Fluorophenol		150
	Phenol-d6		150
	2,4,6-Tribromophenol		150
	1,2-Dichlorobenzene-d4		100
	2-Chlorophenol-d4		150
Pest/PCB	Decachlorobiphenyl	Acetone	0.2
	Tetrachloro-m-xylene		0.2

Table 6
Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
TCL BNA	Acenaphthene	Methanol	100
	4-Chloro-3-Methylphenol		150
	2-Chlorophenol		150
	1,4-Dichlorobenzene		100
	2,4-Dinitrotoluene		100
	4-Nitrophenol		150
	N-Nitroso-Di-n-Propylamine		100
	Pentachlorophenol		150
	Phenol		150

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Pyrene		100
	1,2,4-Trichlorobenzene		100
BNA TCLP	1,4-Dichlorobenzene	Methanol	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
BNA NPDES		Methanol	
	Acenaphthene		100
	Acenaphthylene		100
	Anthracene		100
	Benzo(a)anthracene		100
	Benzo(b)fluoranthene		100
	Benzo(k)fluoranthene		100
	Benzo(a)pyrene		100
	Benzo(ghi)perylene		100

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Benzyl butyl phthalate		100
	Bis(2-chloroethyl)ether		100
	Bis(2-chloroethoxy)methane		100
	Bis(2-ethylhexyl)phthalate		100
	Bis(2-chloroisopropyl)ether		100
	4-Bromophenyl phenyl ether		100
	2-Chloronaphthalene		100
	4-Chlorophenyl phenyl ether		100
	Chrysene		100
	Dibenzo(a,h)anthracene		100
	Di-n-butylphthalate		100
	1,3-Dichlorobenzene		100
	1,2-Dichlorobenzene		100
	1,4-Dichlorobenzene		100
	3,3'-Dichlorobenzidine		100
	Diethyl phthalate		100
	Dimethyl phthalate		100
	2,4-Dinitrotoluene		100
	2,6-Dinitrotoluene		100
	Di-n-octylphthalate		100
	Fluoranthene		100
	Fluorene		100
	Hexachlorobenzene		100
	Hexachlorobutadiene		100

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Hexachloroethane		100
	Indeno(1,2,3-cd)pyrene		100
	Isophorone		100
	Naphthalene		100
	Nitrobenzene		100
	N-Nitrosodi-n-propylamine		100
	Phenanthrene		100
	Pyrene		100
	1,2,4-Trichlorobenzene		100
	4-Chloro-3-methylphenol		100
	2-Chlorophenol		100
	2,4-Dichlorophenol		100
	2,4-Dimethylphenol		100
	2,4-Dinitrophenol		100
	2-Methyl-4,6-dinitrophenol		100
	2-Nitrophenol		100
	4-Nitrophenol		100
	Pentachlorophenol		100
	Phenol		100
	2,4,6-Trichlorophenol		100
Pest	Aldrin	Acetone	0.25
	gamma-BHC (Lindane)		0.25
	4,4'-DDT		0.5
	Dieldrin		0.5

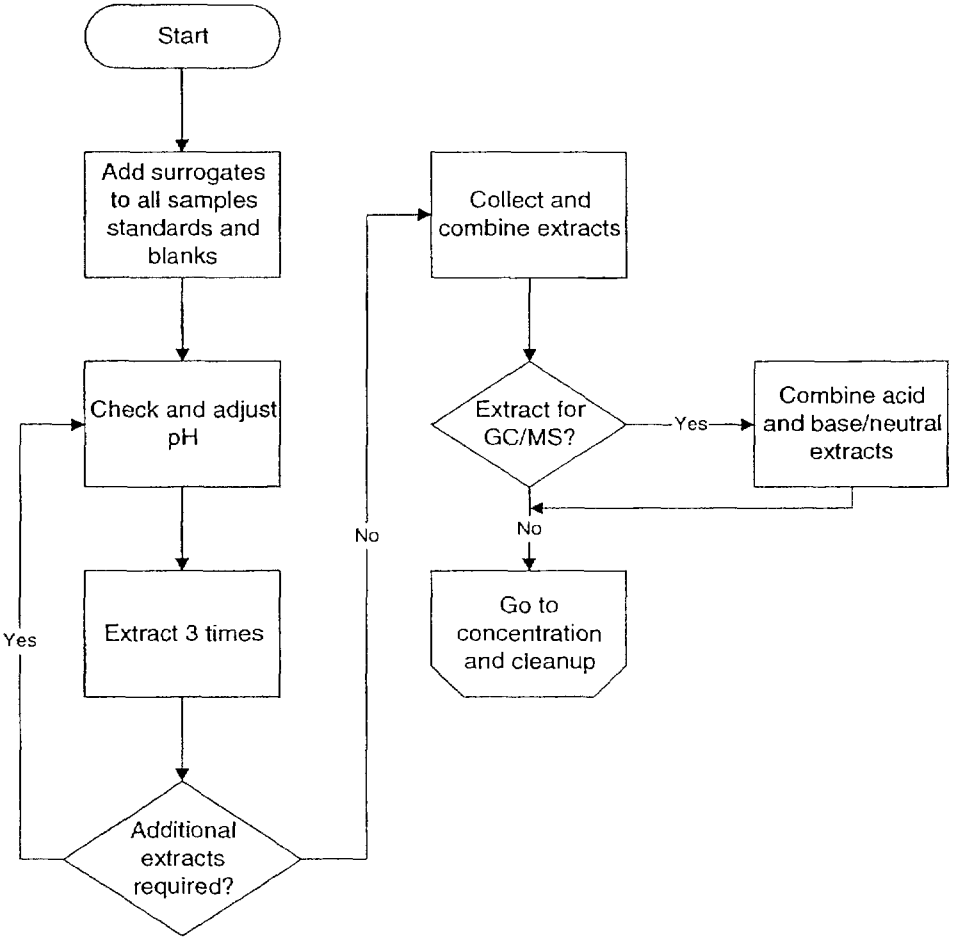
Table 6

Matrix Spike Components

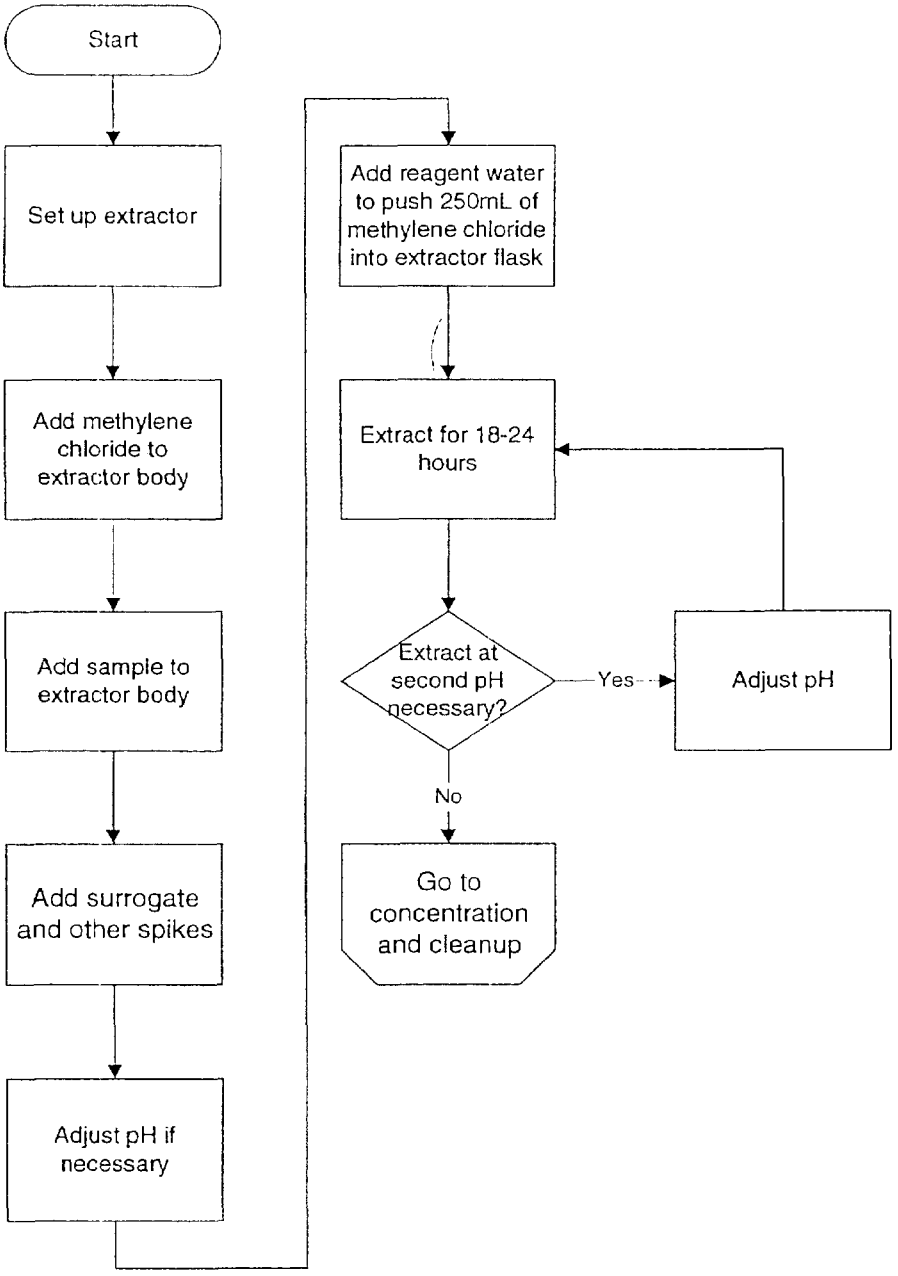
Type	Compounds	Solvent	Conc. (µg/mL)
	Endrin		0.5
	Heptachlor		0.25
Pest TCLP	Heptachlor	Acetone	0.5
	Heptachlor epoxide		0.5
	Lindane		0.5
	Endrin		0.5
	Methoxychlor		1.0
Pest NPDES	Aldrin	Acetone	0.25
	alpha-BHC		0.25
	beta-BHC		0.25
	delta-BHC		0.25
	gamma-BHC (Lindane)		0.25
	4,4'-DDD		0.25
	4,4'-DDE		0.25
	4,4'-DDT		0.25
	Dieldrin		0.25
	alpha-Endosulfan		0.25
	beta-Endosulfan		0.25
	Endosulfan Sulfate		0.25
	Endrin		0.25
	Heptachlor		0.25
	Heptachlor Epoxide		0.25
PCB only	PCB 1016/1260	Acetone	10

17.5. Flow diagrams

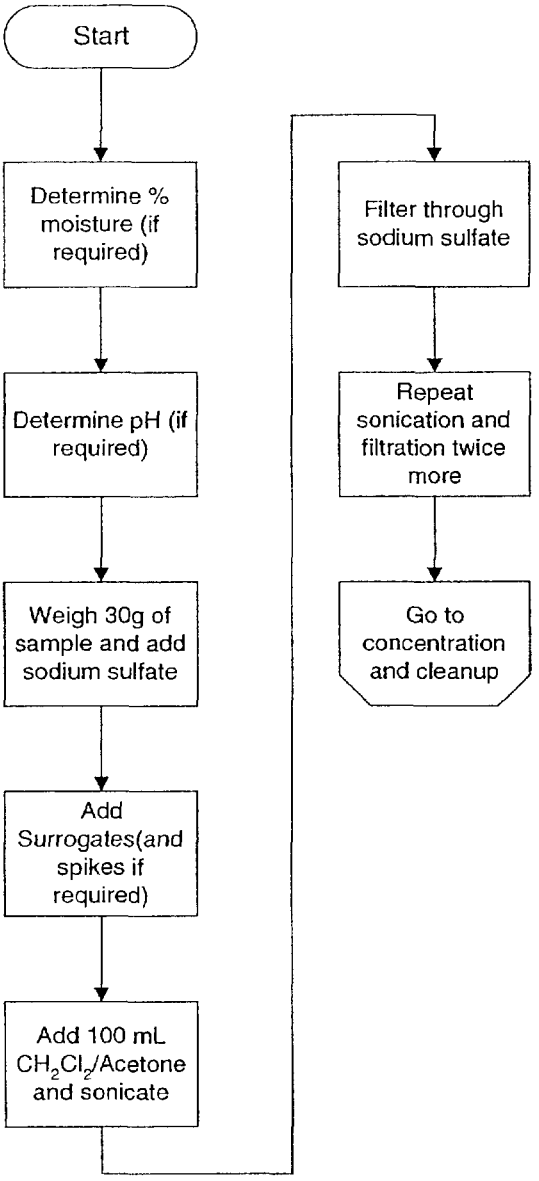
17.5.1. Separatory funnel extraction



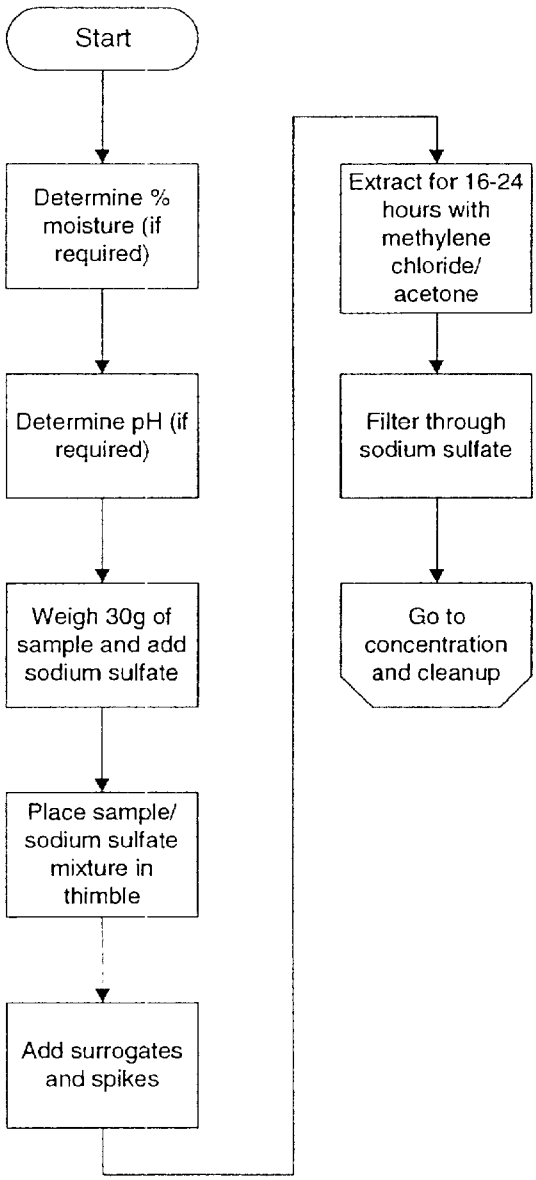
17.5.2. Continuous liquid/liquid extraction



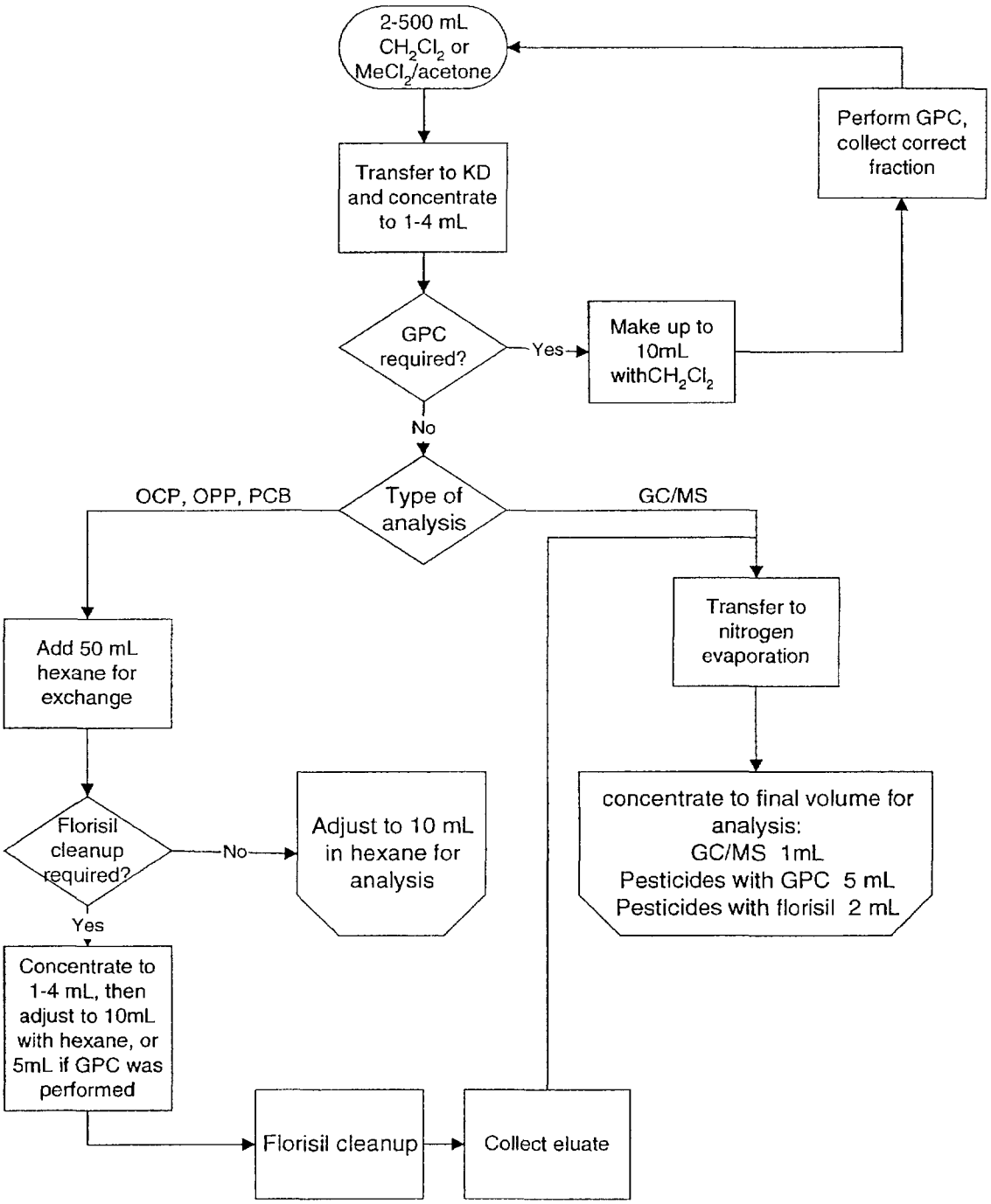
17.5.3. Sonication Extraction



17.5.4. Soxhlet extraction



17.5.5. Concentration and cleanup



18. SCOPE AND APPLICATION

This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in CORP-GC-0001, Appendix D, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8151A.

19. SUMMARY OF METHOD

This method is based on SW846 method 8151A. Aqueous samples are hydrolyzed if esters and acids are to be determined, then washed with methylene chloride by a separatory funnel extraction. After acidifying the sample the free acids are extracted into diethyl ether. Solids are extracted into methylene chloride/ acetone by sonication. If esters and acids are to be determined, the extract is hydrolyzed and extracted into diethyl ether. For both soils and aqueous samples, the free acid herbicides in the ether extract are esterified. The final volume is adjusted to prepare the extract for gas chromatography.

20. DEFINITIONS

Refer to section 3 of the main body of this SOP.

21. INTERFERENCES

Refer to section 4 of the main body of this SOP.

22. SAFETY

22.1. Refer to section 5 of the main body this SOP for basic safety information.

22.2. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free of scratches, cracks, chips and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.

22.3. Diethyl ether is extremely flammable. It also tends to form peroxides when exposed to air. The peroxides can present an explosion hazard, especially when the ether is concentrated.

22.4. Diethyl ether must be free of peroxides as demonstrated by EM (or equivalent) Quant test strips. This test can be done every time the ether is used or once per week if the bottle is marked with the test date(s).

22.5. Concentrated potassium hydroxide solution is highly caustic.

23. EQUIPMENT AND SUPPLIES

23.1. Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

23.2. Diazomethane generation apparatus

23.3. EM Peroxide test strips

24. REAGENTS AND STANDARDS

24.1. Reagents are listed in Section 7 of the main body of this SOP. Additional Reagents and standards needed for this procedure are listed below.

24.2. Reagents

24.2.1. Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

24.2.2. Sodium hydroxide solution, 6N. Dissolve 400 g NaOH in reagent water and dilute to 1.0L. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

24.2.3. Sodium hydroxide solution, 0.1N. Dissolve 4g NaOH in reagent water and dilute to 1.0L. Other volumes of solution may be made up as convenient.

24.2.4. Sulfuric acid, 1:1 Slowly add 500 mL concentrated sulfuric acid to 500 mL water. **Caution:** Considerable heat will be generated. The acid must be added to the water. Wear protective clothing and safety glasses. Other volumes of solution may be made up as convenient.

24.2.5. Diazald, 99% purity

24.2.6. 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr)$C_6H_5CH_2Br$

24.2.7. Sodium sulfate, Na_2SO_4, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 1000 g sodium sulfate with just enough diethyl ether to cover. Add 2-5 mL of concentrated sulfuric acid and mix thoroughly.

Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

24.2.8. Sodium Chloride, NaCl

24.2.9. Acidified 5% sodium sulfate solution

Add 50 g of sodium sulfate to one liter of reagent water. Add 10 mL of concentrated H_2SO_4. (This reagent may be prepared in different quantities if the proportions are kept the same).

24.2.10. Diethyl ether, reagent grade.

24.2.11. Methanol, reagent grade.

24.2.12. Silicic acid

24.3. Standards

24.3.1. Surrogate Standard

See Table A3.

24.3.2. Matrix Spike and LCS standard

See Table A4.

25. SAMPLE COLLECTION PRESERVATION AND STORAGE

25.1. Sample collection and storage is described in Section 8 of the main body of this SOP.

26. QUALITY CONTROL

26.1. Refer to Section 9 of the main body of this SOP for Quality control procedures.

27. CALIBRATION AND STANDARDIZATION

Not applicable

28. PROCEDURE

28.1. Preparation of Aqueous Samples

28.1.1. Weigh the sample bottle and pour approximately 1 liter (100 mL for TCLP leachates) into a 2 liter separatory funnel. Reweigh the bottle and record the sample volume on the benchsheet, assuming a density of 1.0. Alternatively, measure 1 liter in a graduated cylinder. If less than 1 liter was used, add reagent water to make the volume up to 1 liter.

28.1.2. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

28.1.3. Add 250 g of NaCl to the sample and shake to dissolve the salt.

28.1.4. Hydrolysis

Use this step only if herbicide esters in addition to herbicide acids are to be determined. This is normally the case. If the herbicide esters are not to be determined, omit this step and go to 11.1.10.
Add 17 mL of 6N NaOH to the sample, seal and shake. Check the pH of the sample with pH paper. If the pH of the sample is not $\geq$12 adjust to $\geq$12 by adding more NaOH. Let the sample sit at room temperature for 2 hours to complete the hydrolysis.

28.1.5. If the sample was originally in a 1 liter bottle, and the whole sample was used, add 60 mL of methylene chloride to the sample bottle. Rinse the bottle (and graduated cylinder, if used) and add the methylene chloride to the separatory funnel.

28.1.6. If the whole contents of the sample bottle were not used, add 60 mL of methylene chloride to the separatory funnel.

28.1.7. Extract the sample by shaking or rotating vigorously for 2 minutes, venting as necessary. (An automatic shaker may be used). Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.8. Discard the **methylene chloride** phase.

28.1.9. Add a second 60 mL of methylene chloride and repeat the extraction a second time, discarding the methylene chloride. Repeat the extraction a third time.

28.1.10. Add 17 mL of cold (4°C) 1:1 sulfuric acid to the sample. Seal, and shake to mix. Check the pH of the sample with pH paper. If the pH is not ≤ 2, and more acid to adjust the pH to ≤ 2.

Caution: Addition of acid may cause heat and / or pressure build up.

28.1.11. Add 120 mL diethyl ether to the sample and extract by shaking or rotating vigorously for 2 minutes, venting as necessary. (An automatic shaker may be used). Allow the organic layer to separate from the aqueous layer. If a emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.12. Drain the aqueous layer into a clean flask or beaker. Collect the ether phase in a clean flask or bottle containing approximately 10g of acidified anhydrous sodium sulfate.

28.1.13. Return the aqueous phase to the separatory funnel, add 60 mL diethyl ether and repeat the extraction procedure a second time., combining the ether extracts. Repeat the extraction a third time with 60 mL diethyl ether. Discard the aqueous phase after the third extraction.

28.1.14. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken.

28.1.15. Proceed to section 11.5, concentration.

28.2. Extraction of soil and sediment samples

28.2.1. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator). Document if a water layer was discarded.

28.2.2. Weigh 50.0 g of moist solid sample into an clean glass jar. Use 50 g of sodium sulfate for the Method Blank and 50g Ottawa sand for the LCS. Acidify the sample with 5 mL of concentrated HCl.

28.2.3. There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

28.2.4. After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS are not determined.)

28.2.5. Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

28.2.6. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

28.2.7. Add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker.

28.2.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

28.2.9. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn with mode switch on pulse, and percent-duty cycle knob set at 50%.

28.2.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

28.2.11. Place the prepared funnel on a collection apparatus. If the herbicide esters are *not* to be determined, the collection apparatus is a bottle or flask containing approximately 10g of anhydrous acidified sodium sulfate. If the herbicide esters *are* to be determined, (normally the case) the collection apparatus is glassware suitable for the hydrolysis step, typically a KD flask or Turbovap tube.

28.2.12. Decant and filter extracts through the prepared funnel into the collection apparatus.

28.2.13. Repeat the extraction two more times with additional 100 mL minimum portions of methylene chloride / acetone each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

28.2.14. If the herbicide esters are not to be determined, dry the extract as described in 11.4.2 or go to cleanup, section 11.3. If the herbicide esters are to be determined (normally the case) proceed to section 11.2.15

28.2.15. Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Check the pH with pH paper. If the pH is not $\geq$12, adjust with additional KOH.

28.2.16. Heat on a water bath at 60-65°C for 2 hours. Allow to cool. Higher temperatures, up to 90°C, may be used if needed to remove the ether layer within 2 hours.

28.2.17. Transfer the solution to a separatory funnel and extract three times with 100 mL portions of methylene chloride. **Discard the methylene chloride phase.** The aqueous solution contains the herbicides.

28.2.18. Adjust the pH of the solution to $\leq$2 with 1:1 sulfuric acid.

28.2.19. Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

28.2.20. Proceed to section 11.3, Cleanup, if required, or Section 11.4, Extract drying.

28.3. Cleanup

This cleanup step may be necessary if the procedure for determining the herbicide acids only is being followed. (See section 11.2.14) It is not normally required if the acids and esters are being determined. (The usual case.) If cleanup is not required, proceed to section 11.4, Extract drying.

28.3.1. Prepare 45 mL of basic extraction fluid by mixing 30 mL of reagent water with 15 mL of 37% KOH. Use three 15 mL portions of this fluid to partition the extract from section 11.2.12 or 11.2.20, using a small separatory funnel. **Discard the organic phase.**

28.3.2. Adjust the pH of the solution to ≤ 2 with cold (4°C) sulfuric acid. (1:1). Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

Caution: Addition of acid may cause heat and / or pressure build up.

28.4. Extract drying

28.4.1. Combine the extracts and pour through a funnel containing acidified sodium sulfate into a flask or bottle containing approximately 10 g acidified sodium sulfate. Rinse the funnel with a little extra diethyl ether.

28.4.2. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken. Proceed to section 11.5, concentration.

28.5. Concentration

28.5.1. Transfer the ether extract by decanting, or through a funnel plugged with acid washed glass wool, into a Turbovap concentrator tube or a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a stirring rod to crush the caked sodium sulfate during transfer. Rinse the flask or bottle with 20-30 mL ether to complete transfer.

28.5.2. Attach a three ball Snyder column to the K-D apparatus, prewet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 2 mL, remove from the water bath and allow to completely cool.

28.5.3. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

28.5.4. Add 0.1 mL of methanol.

28.5.5. The extract is now ready for esterification by either the diazomethane solution method (11.6) or the bubbler method (11.7)

28.6. Esterification (diazomethane solution method)

28.6.1. Preparation of Diazomethane solution

- **CAUTION: Diazomethane is potentially explosive.**
- **A temporary shield or the sash of the hood must protect the face and body of the analyst.**
- **Never heat solutions of diazomethane above 90°C, due to the explosive potential.**
- **Do not use glass stirring rods or any glassware with ground glass joints, as this can initiate violent reaction or explosion.**
- **All glassware must be scrupulously cleaned and free from scratches, to avoid potential initiation of violent reaction or explosion.**

28.6.1.1. Weigh out 10.0 g potassium hydroxide in a 125 mL beaker. Add 16 mL water and 20 mL ethanol. Mix well until the potassium hydroxide is dissolved and pour into the reaction vessel.

28.6.1.2. Attach a 100 mL receiving flask to the condenser and cool the receiver in an ice bath.

28.6.1.3. Fill the condenser with dry ice, then add acetone slowly until the cold finger is about one third full.

28.6.1.4. Mix 10.0 g diazald and 90 mL ether. Place in a separatory funnel over the reaction vessel.

28.6.1.5. Warm the reaction vessel on the water bath to 50-60°C or until the ether begins to reflux. CAUTION: Do not allow the temperature to exceed 70°C. Add diazald solution over a period of 40 minutes. The rate of distillation should approximate the rate of addition. Replenish the cold finger with dry ice as necessary.

28.6.1.6. When the diazald solution has been used up, slowly add 10 mL of ether and continue distillation until the distillate is colorless.

28.6.1.7. The diazomethane solution is documented with a lot number. It is stored in a freezer at -10 to -20°C and has an expiration date of six months.

28.6.2. Disposal of outdated diazomethane solutions

28.6.2.1. Add 20 mL of ether to 2 mL of glacial acetic acid in a large beaker in the hood.

28.6.2.2. Add the diazomethane solution slowly to the acetic acid. The yellow color of the diazomethane disappears as it reacts with the acetic acid. If the yellow color persists at any time during the addition, and does not disappear with gentle swirling of the beaker, add additional acetic acid in ether before continuing the diazomethane addition.

28.6.2.3. Dispose of the ether solution in the non-chlorinated wastes bottle.

28.6.3. Esterification (Diazomethane solution method)

28.6.3.1. Add approximately 2 mL of diazomethane solution and let sit for 10-15 minutes.

28.6.3.2. Add approximately 0.2 g of silicic acid to the extract. Allow to spontaneously evaporate to about 1.0 mL, then make up to 10 mL with hexane.

28.6.3.3. Extract is ready for analysis by gas chromatography.

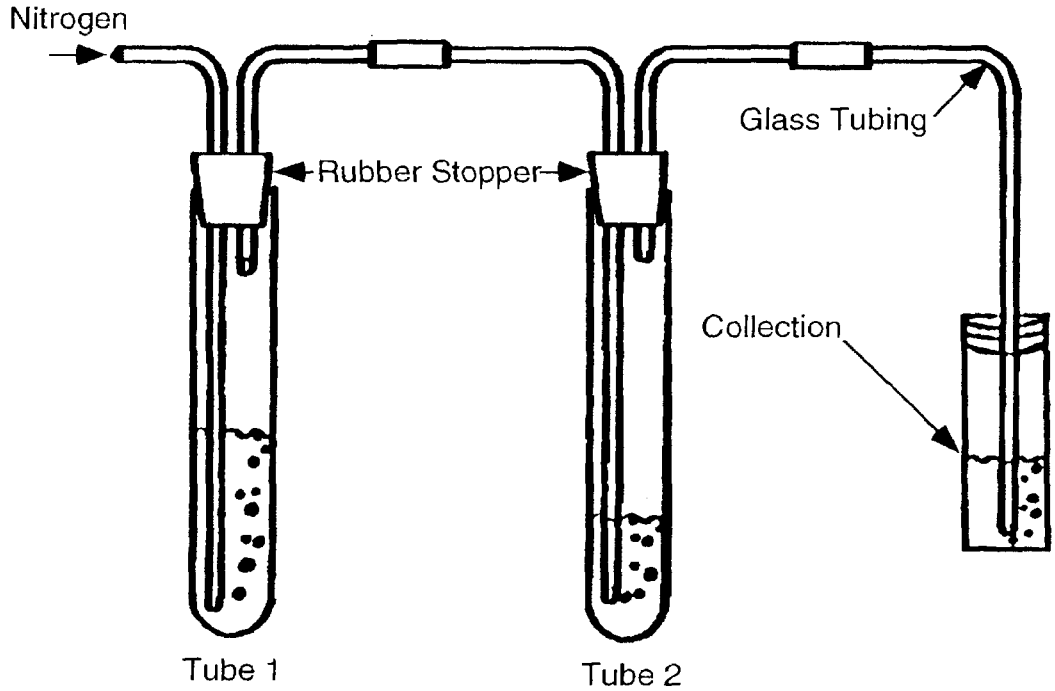
28.7. Esterification (Bubbler Method)

28.7.1. Assemble the diazomethane apparatus (see figure below) in a hood. Add 10 mL of diethyl ether to tube 1. Add 5 mL of 2% methanolic KOH, 3 mL of ether and 0.5-1 g of diazald to tube 2.

28.7.2. Place the tip of the disposable pipette into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 1 minute, or until the yellow color persists. Replace the disposable pipette and place the tip into the vial containing the second extract. Continue until the diazald is consumed. (An additional 0.1-0.5 g diazald may be added to extend the generation of diazomethane).

28.7.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silicic acid to each extract. Allow to stand for an additional 20 minutes.

28.7.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.



29. DATA ANALYSIS AND CALCULATIONS

Not applicable

30. METHOD PERFORMANCE

Refer to CORP-GC-0001 for details of method performance.

31. POLLUTION PREVENTION

Refer to section 14 of the main body of this SOP.

32. WASTE MANAGEMENT

Refer to section 15 of the main body of this SOP.

33. REFERENCES

33.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Chlorinated Herbicides, Method 8151A.

34. MISCELLANEOUS

34.1. Modifications from Reference Method

34.1.1. Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 11.1.2)

34.1.2. The bubbler esterification method uses methanolic KOH in place of the aqueous KOH / carbitol mixture recommended in method 8150B. This has been found to provide a more effective and reliable esterification.

34.2. Modifications from previous revisions

References have been updated

Tables

Table A1
Herbicide Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
Herbicides	Herbicides SS	1.0

Table A2
Herbicide Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
Herbicides	Herbicides MS	1.0

Table A3
Herbicide Surrogate Spike Components

Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides SS	2,4-DCAA	Methanol	10

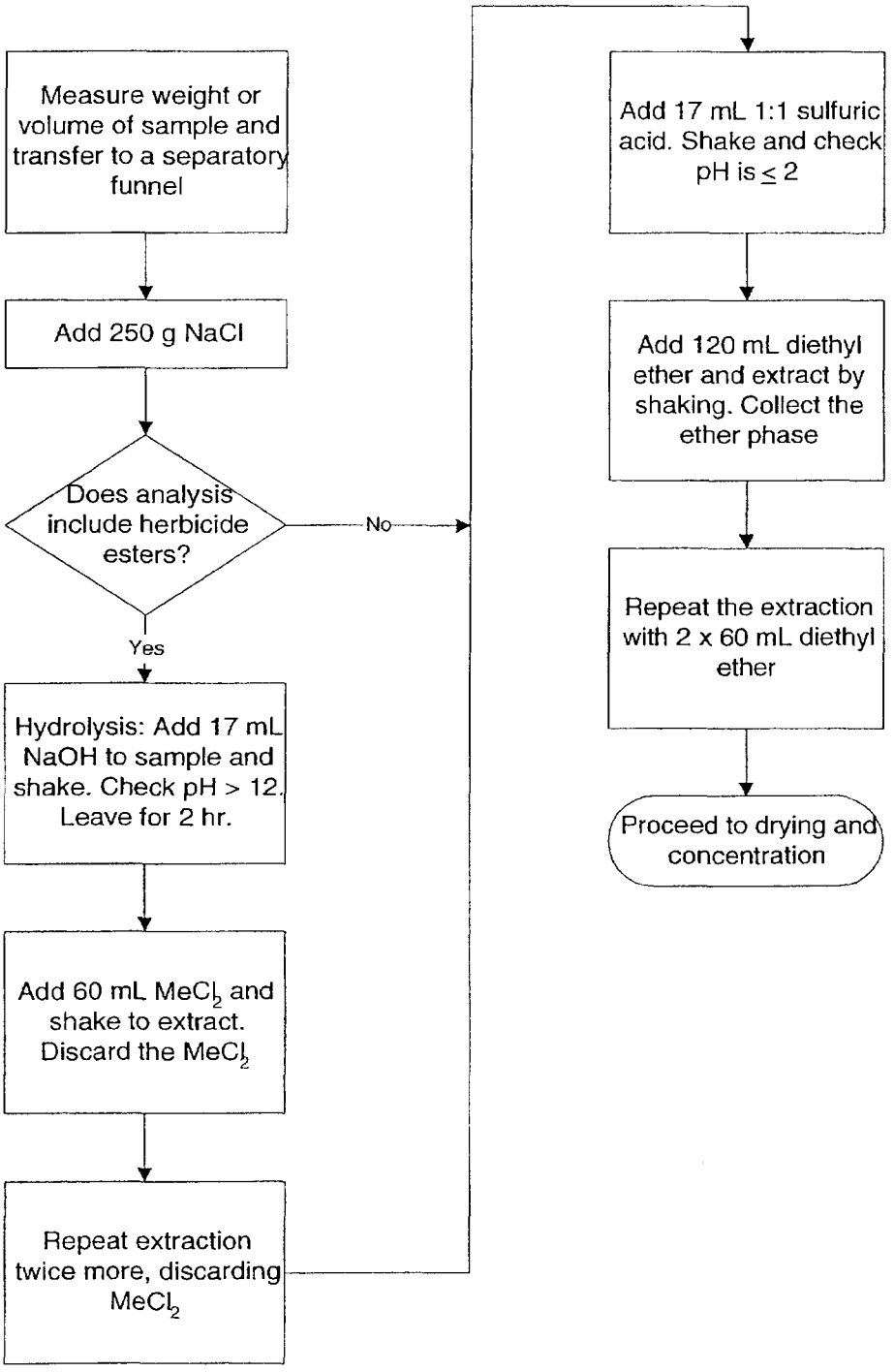
[1]The surrogate is spiked as the free acid

Table A4
Herbicide Matrix Spike Components

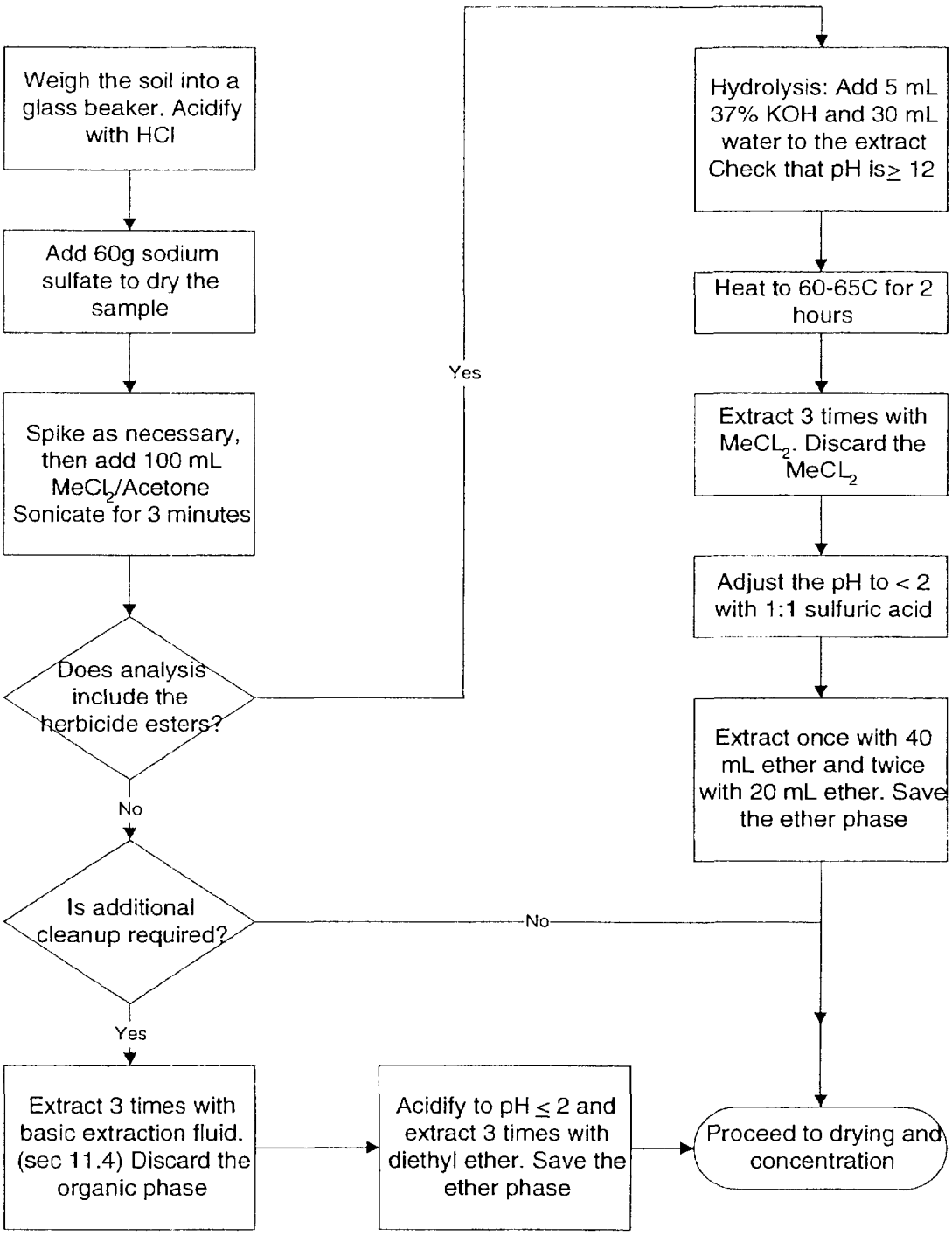
Type	Compounds[1]	Solvent	Conc. (ug/mL)	TCLP Conc. (ug/mL)
Herbicides MS	2,4-D	Methanol	16	6
	2,4-DB		16	--
	2,4,5-TP (Silvex)		4	6
	Dalapon		8	--
	2,4,5-T		4	6

[1]The herbicide spiking solution contains the herbicides as the free acids.

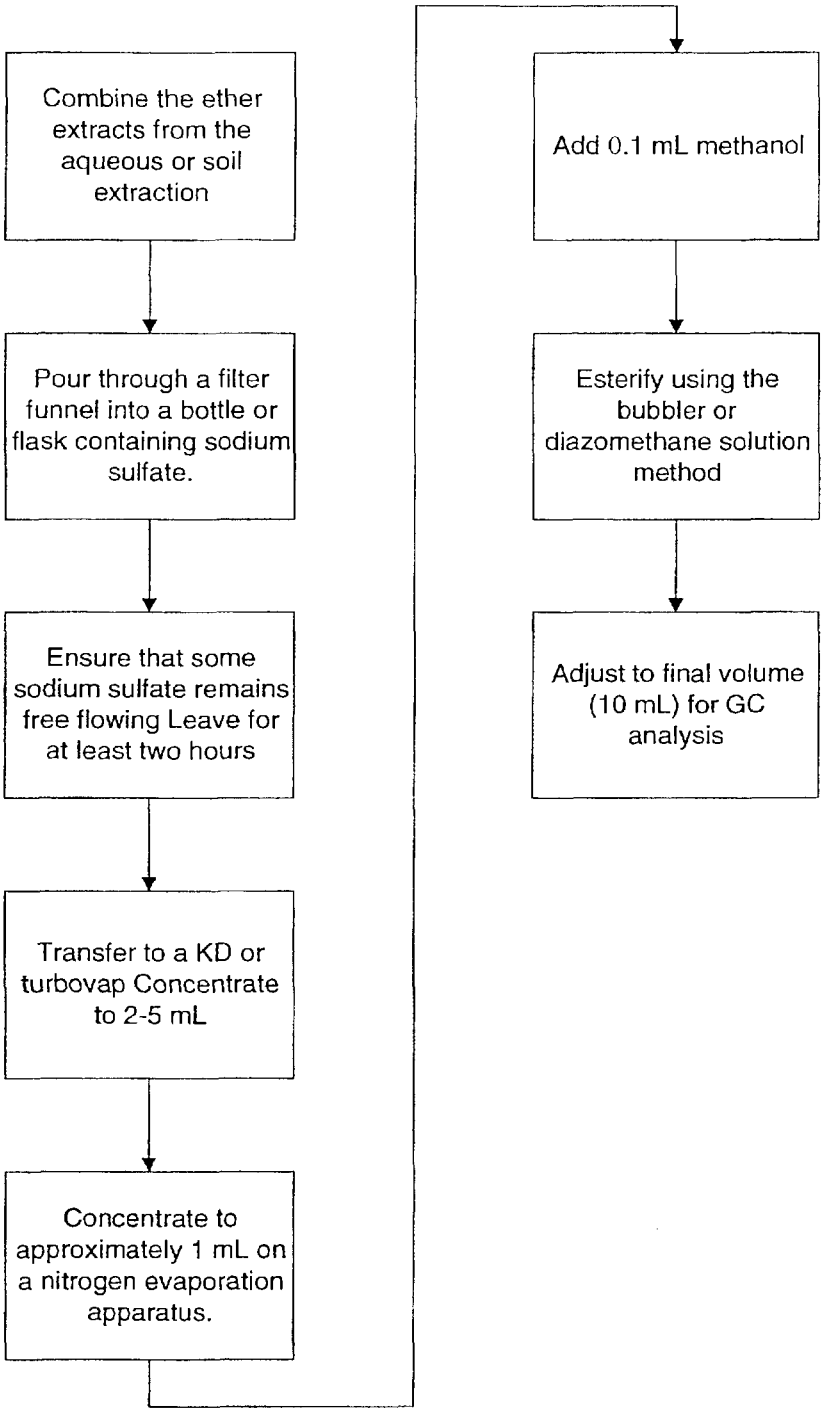
Extraction of Aqueous Samples



Extraction of Soils and Sediments



Drying, Concentration and Esterification



QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: GC/MS ANALYSIS BASED ON METHODS 8270C AND 625

(SUPERSEDES: Revision 1)

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TABLE A-1 Method 625 Reporting List and Limits

TABLE-A-2 Method 625 LCS and MS Compounds and Spike Concentrations

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 $\leq 6^{\circ}C$ when not in use. Refrigeration at $-10^{\circ}C$ to $-20^{\circ}C$ 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 $\leq 6^{\circ}C$.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Reference appropriate facility SOP for sample bottle preservation and storage.

8.2. Samples are stored at $4 \pm 2^{\circ}C$. 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 $1/\text{Concentration}^2$ 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 $4 \pm 2^{\circ}C$, 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 ≤ 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
Parathion[2]	56-38-2				X

Table 4

Reportable analytes for STL Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
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**

CAPE Technologies

High Performance Dioxin/Furan Immunoassay Kit

Application Note AN-007

Analysis of PCDD/Fs in soil at 500 ppt using rapid extraction and rapid one-step cleanup

Contents of this Application Note

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B. Summary of Procedure
C. Reagents Required
D. Equipment Required
E. Supplies Required
F. Detailed Sample Preparation Procedure
G. Data Reduction and Interpretation of Immunoassay Results
H. Additional Extract Cleanup by Carbon Mini-Column
I. Validation Data Supporting this Method

A. Introduction

This Application Note describes a rapid immunoassay specific extraction and rapid one step cleanup to prepare soil samples for screening analysis at 500 ppt (pg/g) using the CAPE Technologies High Performance Dioxin/Furan Immunoassay Kit. The method described here includes a much faster and simpler extraction and cleanup than typically required for GC-MS analysis. This procedure has been submitted to the US EPA for review as Method 4025. Using this method, one analyst can screen up to 20 samples per day in a facility as simple as a small mobile laboratory. This Application Note is intended to be used in conjunction with the DF1 Dioxin/Furan Immunoassay Kit and its insert (IN-DF1) and the SP1-12 and/or SP2-12 Sample Preparation Kits and their inserts (IN-SP1 and/or IN-SP2). Please read this Application Note carefully as part of planning your sample preparation and analysis. Important recommendations for quality assurance samples are noted at certain points in section F. The documents cited in this Application Note are available at the CAPE Technologies web site (www.cape-tech.com).

B. Summary of Procedure

1. Add sodium sulfate to soil sample and mix. Add dimethylformamide (DMF) and extract soil sample by shaking 2 hours. Remove the supernatant DMF extract.
2. Add hexane to an aliquot of the DMF extract, then shake 15 minutes with 15% SO_3 in conc. H_2SO_4.
3. Remove the supernatant hexane and evaporate to exchange sample into water-miscible keeper solution.
4. Perform the immunoassay procedure as described in the kit insert IN-DF1.
5. Interpret the immunoassay results as described in section G of this Application Note.

C. Reagents Required

1. Anhydrous sodium sulfate, approx. 20 g per sample; reagent grade
2. Dimethylformamide (DMF), approx. 15 mL per sample; HPLC grade or better
3. Solution of 15% SO_3 in conc. H_2SO_4, approx. 2 mL per sample (fuming sulfuric acid, CASRN 8014-95-7; can be purchased from Aldrich Chemical Company as 15% [catalog number 37,561-6]; NOTE- fuming sulfuric acid can not be shipped by air; inquire about time required for shipment and plan accordingly)

4. Hexane, approx. 6 mL per sample; HPLC grade or better of mixed isomer type (CASRN 73513-42-5; this is typically 85% n-hexane with remainder methylcyclopentane and other hexane isomers; do not use n-hexane; all development and validation work for this method is based on mixed isomer hexane)

Additional reagents needed for carbon column cleanup (see section H to determine if this is required):

5. Toluene, approx. 25 mL per sample; ultrapure or residue grade (such as Burdick & Jackson) or better
6. Increase hexane (C4) by approx. 25 mL per sample
7. Increase sodium sulfate (C1) by approx. 2 g per sample

D. Equipment Required

1. Equipment for performing the DF1 Immunoassay; summarized in section G of the kit insert (IN-DF1) and described in detail in Equipment List (EL-001)
2. Balance for weighing sample (0.1 g or better readability; see Equipment List EL-002)
3. Orbital platform shaker for mixing during extraction and oxidation (see Equipment List EL-002)
4. Centrifuge with capacity for holding 40 mL vials (28 mm outside diameter x 98 mm high, flat bottoms; see Equipment List EL-002)
5. Fume hood and solvent exchange system (refer to IN-DF1, section I3; also see Equipment List EL-002)
6. Computer with Microsoft Excel (for Win97 or later, or for Mac OS9 or later) for data analysis

E. Supplies Required

1. DF1 Immunoassay Kit and supplies specified in section G of the kit insert (IN-DF1)
2. Pipet bulbs and glass Pasteur pipets for transfer of oxidized extracts
3. Pipettors and glass pipets for items C2 to C7 above
4. Glass vials (2 to 12 mL) with Teflon lined caps for storage of sample extracts
5. Glass tubes (10-15 mL) for evaporation of oxidized extracts
6. SP1-12 or SP2-12 Sample Preparation Kit. The SP1 Kit is sufficient for most situations. The SP2 Kit may be required for cleanup of samples which are highly contaminated with oil. See section H below for more detailed discussion.

Additional supplies needed for carbon column cleanup (see section H to determine if this is required):

7. SP2-12 Sample Preparation Kit containing carbon mini-columns
8. SP2-ST Starter Sample Preparation Kit containing reusable hardware for manual execution of the column cleanup procedure described in steps H1-6 below
9. Rack for holding SP2-ST reservoirs (glass columns like 25 mL pipets; 16 mm dia. by 30 cm long)
10. Basin or other receptacle to catch waste from carbon mini-column procedure

F. Detailed Sample Preparation Procedure

Before beginning this procedure, please read section F carefully, especially step F9. This section has several references to the DF1 Kit Insert (IN-DF1), which has a detailed description of the EIA procedure in section J. Steps I1 and J1-2 of the EIA procedure should be performed before step F8 below. Steps J3-6 of the EIA procedure should be done at the end of step F8 below. Steps F1-3 below are the same with or without the additional carbon column cleanup. Before beginning step F4, please first read section H about the possible need for carbon column cleanup.

1. **Weigh sample**: Use CAPE Technologies Sample Preparation Kit (SP1-12 or SP2-12; see Section H below for discussion of choice). Using wooden spatula from Sample Preparation Kit, mix sample thoroughly and weigh 5 g into 40 mL extraction vial from Sample Preparation Kit. Quality assurance samples to verify method performance (unspiked and spiked method blanks and reference soils) should be included at this point.
2. **Extract sample**: Add 15-20 g anhydrous sodium sulfate to extraction vial and mix with wooden spatula until sample is free flowing. Add 3 steel mixing balls from the Sample Preparation Kit, then 15 mL DMF. Read and follow precautions and other instructions in Sample Preparation Kit insert (IN-SP1/2). Cap

vials tightly and extract by shaking 2 hours at 350 rpm on orbital platform shaker. Extraction vials should lie flat on their sides for maximum agitation.

3. **Spin extract and store**: Centrifuge extraction vial for 10-15 minutes at 1000 x g or less and remove a portion of the supernatant DMF extract to a clean vial with Teflon lined cap for storage. **Caution**: Exceeding this force during centrifugation can cause breakage of glass vials. The concentration of soil matrix in the extract will be 0.33 mg soil equivalent per µL. Extracts are stable for months at room temp. in tightly sealed vials.
4. **Remove aliquot of extract**: Place 180 µL of DMF extract (equivalent to 60 mg of sample) into an 8 mL oxidation vial from Sample Preparation Kit SP1 or SP2. This procedure allows analysis using single or duplicate EIA tubes at 20 mg of sample equivalent per EIA tube.
5. **Oxidize aliquot of extract**: Add 6 mL of hexane to the oxidation vial containing the 180 µL aliquot of extract. Using a glass pipet, slowly add 1.8 mL of 15% SO_3 in concentrated H_2SO_4. **Caution**: Fuming sulfuric acid is corrosive and hygroscopic. Carefully follow handling and storage instructions. Excessive exposure to ambient air will allow absorption of water, which will decrease the SO_3 concentration and may cause invalid results due to incomplete oxidation. Cap sample oxidation vial tightly and mix for 15 minutes at 350 rpm on orbital platform shaker. Oxidation vials should lie flat on their sides for maximum agitation. At end of oxidation vials should be slightly warm, but not hot. Centrifuge oxidation vials to separate phases completely (5 minutes at 1-2000 x g). **Important Note**: The acid phase should be dark reddish brown and should separate cleanly from the hexane. DMF extracts which are extremely dark may produce a black or dark gray acid phase during oxidation. Some oxidized DMF extracts also may not yield a clean phase separation after the specified centrifugation, showing flocculation or murkiness at the interface. If any of these problems are observed, oxidation should be considered incomplete and a second treatment of the hexane supernatant with fuming sulfuric acid is required (see for example section I2 below, Table 3, sample 46). EIA data from samples which are analyzed without complete oxidation should not be considered valid. Quality assurance samples (such as spiked vs. unspiked aliquots of one extract) to verify complete oxidation are strongly recommended. Other quality assurance samples to verify method performance (unspiked and spiked oxidation blanks and reference DMF extracts) should be included at this point. See for example section I2 below, Table 3.
6. **Recover supernatant**: Remove as much hexane supernatant as possible without disturbing the lower layer. **Caution**: Do not allow the lower phase to contaminate the hexane sample. Any oxidizer which contaminates the sample at this point will be carried through into the immunoassay, leading to invalid results. Greater than 95% volume recovery should be attainable without danger of contamination from oxidizer (95% is 5.7 mL recovered and only 300 µL remaining with oxidizer). Place the recovered hexane in a small round bottom glass tube, such as 13 x 100 mm. If contamination with oxidizer occurs, repeat separation and supernatant removal with clean pipet and evaporation tube.
7. **Add keeper**: Keeper solution (80:20 methanol:tetraethylene glycol [TEG] + 100 ppm Triton X-100) is made by adding methanol to a stock vial which is part of the DF1 kit. See the immunoassay kit insert IN-DF1 section I1 for instructions. Add 150 µL of keeper solution to each evaporation tube containing an oxidized sample in hexane.
8. **Evaporate solvent**: Evaporate the hexane at 40-50°C under a gentle stream of nitrogen as described in the immunoassay kit insert IN-DF1, section I3. When the hexane is gone, the 30 µL of TEG remaining (20% of 150 µL added in last step) should be visible as a clear viscous residue on the walls and bottom of the evaporation tube. When this point is reached, centrifuge the tube at 1-2000 x g for 2 minutes to concentrate all of the sample at the bottom.
9. **Dilute sample with methanol**: Before beginning this step you should have completed steps 1 through 6 described in section J of the DF1 Immunoassay Kit Insert (IN-DF1). Once these beginning EIA steps are completed, add 120 µL of methanol (setting 6 of Repeater Plus pipettor with 1.0 mL tip) to each evaporation tube and mix vigorously for 15 sec. Remove one or two 50 µL aliquots for EIA analysis in single or duplicate EIA tubes. Dilution and EIA loading should be done in batches of 4 samples or fewer to minimize concentration changes due to methanol evaporation before pipetting. Add the sample directly to the water in EIA tube, not above water or to side of EIA tube. Mix each tube individually as soon as sample is added. At this point, enough sample remains in the evaporation tube

for preparation of a small amount of 1/5 or 1/10 dilution (e.g. 20 µL into 80 µL keeper for 1/5). If such a dilution is made, it should be done immediately to avoid concentration changes due to evaporation. The diluted sample should then be loaded into the EIA immediately.

10. Run EIA: Perform remainder of EIA as described in section J of DF1 Immunoassay Kit Insert (IN-DF1).

G. Data Reduction and Interpretation of Immunoassay Results

1. Open Calculation Module C (Microsoft Excel workbook downloadable from CAPE Technologies web site [www.cape-tech.com] or available by email at cape-tech@ceemaine.org). Select "Introduction" worksheet and read the information on background and procedure, then select the "AN-007" worksheet. Install Excel "Solver" Add-In if it is not already done.
2. Enter optical density (OD) data for standards and samples into designated spaces.
3. Perform non-linear curve fitting procedure using Excel "Solver" function.
4. Verify sample load (20 mg sample equivalent per EIA tube) and decision level (500 ppt).
5. Modify calibration adjustment factor if necessary for specific sample group.
6. Read ppt values and/or positive/negative interpretation for each sample in designated row.

H. Additional Extract Cleanup by Carbon Mini-Column

Note on the need for carbon column cleanup:

The combination of cosolvents and detergent in the sample incubation of the EIA (IN-DF1, step J7) is designed to give a substantial capacity for solubilizing non-polar molecules. If this capacity is exceeded, the sample incubation mixture separates into a biphasic system, resulting in visible heterogeneity (cloudiness). Because the dioxin stays with the non-polar portion of the biphasic system, this condition leads to false negative results and requires additional extract cleanup before valid results can be obtained. Adequate quality assurance, including extract spikes (see section I2 below), is critical to overall method performance.

The use of DMF as an extraction solvent reduces the co-extraction of aliphatic oils from samples, while effectively extracting PCDD/Fs. Some samples which are heavily contaminated with aliphatic oils may still give DMF extracts with levels of oil beyond the capacity of the EIA to dissolve them. In such cases, the co-extracted oils are typically unaffected by fuming sulfuric acid and must be removed before EIA analysis. The simplest cleanup method is adsorption of the PCDD/Fs on activated carbon, followed by washing to remove the oils and elution to recover the PCDD/Fs. This can be done easily using the SP2-12 and SP2-ST Sample Preparation Kits, as described in steps H1-6 below.

The need for additional carbon column cleanup can be influenced by many factors, including age and weathering of the site, plus the original source material and vehicle for the PCDD/F contamination. For the first sample set described in Section I (Table 1), only 2 of 56 samples required this additional carbon column cleanup. In the second sample set of Section I (Table 2), no cloudiness was observed for any samples and no additional carbon column cleanup was required.

Detailed procedure for carbon column cleanup:

This additional cleanup requires both SP2-ST and SP2-12 kits as noted in section E above, plus a rack for holding reservoirs during the procedure. The sample should be in hexane after step F6 above. Running a column positive control to use for column recovery correction is strongly recommended. Additional quality assurance samples are also encouraged.

1. **Prepare column:** Read this entire step carefully before beginning. Place 25 mL glass reservoir from the SP2-ST Kit into rack. Put a small PTFE frit from SP2-12 Kit into the reservoir, making sure it fits as far as possible into the reservoir tip. Rinse the sides of the reservoir with 3-4 mL hexane, then immediately add approx. 2 g of sodium sulfate. To avoid air bubbles, the sodium sulfate should always be submerged in hexane. Immediately place a carbon mini-column from the SP2-12 Kit firmly onto tip of reservoir, square-cut end first (to avoid air bubbles, fill the top of the column with hexane first). Rinse sides of reservoir with approx. 5 mL of hexane to wash sodium sulfate down. Place stopper/stopcock assembly from SP2-ST Kit securely into top of reservoir. Pressurize column by placing syringe from SP2-ST Kit into open

stopcock and pushing 10-25 mL of air into the reservoir. Close stopcock and remove syringe. Add air as needed to maintain dropwise flow rate of 0.5 to 1.0 mL per minute. Open the stopcock to release the pressure as soon as the hexane level reaches the top of the sodium sulfate. Discard all solvent passed through column. **Important Note:** Avoid air bubbles in the sodium sulfate and in the carbon mini-column.

2. **Load sample**: Add oxidized sample (hexane supernatant from step F6 above) to reservoir. Replace stopper and pressurize as in step H1. Open the stopcock to release the pressure as soon as the hexane level reaches the top of the sodium sulfate. Discard all solvent passed through column.
3. **Wash 1**: Add 10 mL hexane to reservoir. Replace stopper and pressurize. Open the stopcock to release the pressure as soon as the hexane level reaches the top frit of the carbon mini-column. Discard all solvent passed through column.
4. **Wash 2:** Remove carbon mini-column from reservoir and place in same direction (square cut end first) on tip of clean reservoir. Add 7 mL of 1:1 toluene:hexane to reservoir and pressurize. Open the stopcock to release the pressure as soon as the solvent level reaches the top frit of the carbon mini-column. Discard all solvent passed through column.
5. **Elute column**: Remove carbon mini-column and replace on tip of same reservoir in reverse direction (slant cut end first). Add 12 mL of toluene to reservoir and pressurize until air passes through column. Capture eluate in a 16 x 125 mm or similar size glass tube.
6. **Evaporate toluene**: Add 150 µL of keeper solution as for step F7 above. Evaporate the toluene as for step F8 above, except for using 60-75°C. Continue from step F8 to complete sample preparation.

I. Validation Data Supporting this Method

1. Correlation between immunoassay screening analysis and TEQ as determined by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS): Two sets of soil samples from two separate sites were extracted, oxidized, and analyzed as described in Sections F and G above. Subsamples of each sample from both sites were analyzed separately by HRGC-HRMS. The TEQ values were calculated from individual congener concentrations and TEF values. Congener concentrations stated to be below the HRGC-HRMS detection limit were assumed to be 1/4 of that detection limit for calculation purposes.

Table 1. Correlation between immunoassay screening analysis and TEQ as determined by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) for 56 soil samples from Site 1. Samples were prepared and analyzed as described in Sections F and G above. An empirically determined calibration factor of 1.07 was applied to all quantitative EIA results before semiquantitative scoring. Results by category are 29 correct negative, 22 correct positive, and 5 false positive (91% correct, 9% FP). Two immunoassay samples which appeared heterogeneous or contained visible precipitate during the first EIA incubation were interpreted as giving invalid results. These samples were put through an additional carbon column cleanup for oil removal, were analyzed again by EIA, and the latter results reported (*).

Sample ID	ppt TEQ	EIA Result	Sample ID	ppt TEQ	EIA Result
1	94338	CP	29	13	CN
2	1528119	CP	30	14	CN
3	234492	CP	31	11	CN
4	822885	CP	32	579	CP
5	73750	CP	33	220	CN
6	4733	CP	34	13	CN
7	39	CN	35	1501	CP
8*	6278	CP	36	3702	CP
9	276	*FP*	37	248	CN
10	2390	CP	38	216	*FP*
11	2101	CP	39	1088	CP
12	30	CN	40	1210	CP
13	14	CN	41	13	CN
14	210	CN	42	451	CN
15	5860	CP	43	16	*FP*
16	2191	CP	44	105	CN
17	343	*FP*	45	16	CN
18	18	CN	46	10	CN
19	25	CN	47	211	*FP*
20	70	CN	48	1725	CP
21	599	CP	49	41	CN
22	217	CN	50	551	CP
23	27	CN	51	622	CP
24	43	CN	52*	26856	CP
25	18	CN	53	2122	CP
26	18	CN	54	24	CN
27	14	CN	55	31	CN
28	26	CN	56	31	CN

29 CN, 22 CP, 5 FP, 0 FN from 56 samples

Table 2. Correlation between immunoassay screening analysis and TEQ as determined by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) for 18 soil samples from Site 2. Samples were prepared and analyzed as described in Sections F and G above. No calibration adjustment factor was applied to EIA results before semiquantitative scoring. None of these samples required additional cleanup before EIA analysis. Several days later, aliquots of 13 of the 18 DMF extracts were oxidized and analyzed in a second EIA and the concentrations were calculated based on a new standard curve. The mean coefficient of variation for the 13 pairs of duplicate ppt values was 35%.

ppt by GC-MS	EIA run 1	EIA run 2
2730	CP	FN**
470	FP	FP
65	CN	CN
1400	CP	CP
70	CN	
4900	CP	CP
245	FP	
7300	CP	CP
365	CN	
360	CN	CN
140000	CP	CP
7000	CP	
33	CN	CN
990	CP	CP
4100	CP	CP
205	CN	
360	CN	CN
65	CN	CN

** actual calculated value with no calibration adjustment was 497 ppt (run 1 was 630 ppt)

8 CN, 7 CP, 2 FP, 1 FN (**) from 18 samples

2. Accuracy and Precision Data From EIA Analysis of Spiked Negative Soil Extracts: Fourteen extracts of the Site 1 soils presented in Table 1, ranging from 10 to 26 ppt by HRGC-HRMS, were spiked with 2378-TCDD at levels corresponding to 250 and 1000 ppt in the original sample. Extracts were oxidized and analyzed by EIA according to the method described in section F, steps 4-10. Four aliquots of each extract were spiked, two at each level. Each oxidation replicate was split for duplicate EIA analyses. All standards were unreplicated within runs. Results for each run were calculated as described in section G. Controls consisting of DMF spiked at both levels were processed with each of the 5 runs and the calculated ppt values were used to correct samples for spike recovery within each run. None of these 14 extracts required carbon column cleanup.

Table 3: False positive/false negative data for negative soil extracts spiked near the 500 ppt decision level. Samples were spiked and analyzed as described above. Individual EIA replicate ppt values were scored as positive if equal to or greater than 500 ppt and were scored as negative if less than 500 ppt. Each semiquantitative score below corresponds to one EIA tube. Sample 41A and 41B were field duplicates which appeared different based on gross color and particle size. Extract 46 was nearly black in color and totally opaque. Initial data for sample 46 (*) indicated false negatives at the high spike level (individual EIA replicates were 401, 366, 366, and 332 ppt). The sample 46 analysis was repeated using a second oxidation of the first hexane supernatant (plus a fresh aliquot of DMF). The individual EIA replicates of 1872 and 1318 ppt gave a correct positive interpretation (the corresponding twice oxidized DMF controls were 1068 and 846 ppt).

	Spike Level	250 ppt spike		1000 ppt spike	
		Oxidation Replicate		Oxidation Replicate	
Sample #	EIA Replicate	1	2	1	2
13	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
18	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
19	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
25	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
27	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
28	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
29	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
30	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
31	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
34	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
41A	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
41B	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
45	1	CN	CN	CP	CP
	2	CN	CN	CP	CP
46*	1	CN*	CN*	*FN**	*FN**
	2	CN*	CN*	*FN**	*FN**
46 (oxid. x 2)	1			CP	
	2			CP	

Summary of FN/FP results (based on repeat oxidation data for sample 46):

Correct Positives:	54	False Positives:	0
Correct Negatives:	52	False Negatives:	0

Table 4: Summary of quantitative accuracy and precision data from false positive/false negative experiment of Table 3. Data are based on four parameter curves and calculated ppt values for each of 5 runs on 5 separate days. The accuracy and precision shown in sections A and B support the semiquantitative screening method described here. These data also support quantitative use of the test in certain situations with sufficient quality assurance samples. It should be noted that the data of section B include variation among the 14 different soils, as well as the intrinsic variability of the method itself. The precision data shown in sections C and D support screening analysis based on unreplicated sample oxidation and unreplicated EIA tubes for both standards and samples.

A. Summary of quantitative ppt data from DMF controls

spike level	250 ppt spike	1000 ppt spike
number of runs (2 or 4 EIA replicates within each run)	4	5
mean±SD of within run means (ppt)	271±74	957±174
coefficient of variation of ppt	27%	18%

B. Summary of quantitative ppt data from spiked extracts (sample 46 data includes only 2x oxidation)

spike level	250 ppt spike	1000 ppt spike
number of individual EIA replicates	56	54
overall mean±SD (ppt)	266±61	984±356
coefficient of variation of ppt	23%	36%

C. Coefficients of variation for ppt within runs (all EIA replicates at each spike level for each run)

	spiked extracts	DMF controls
number of runs	9	9
mean of within run %cv values	18%	15%

D. Summary of EIA replicate precision (both spike levels combined)

	spiked extracts	DMF controls
number of pairs of EIA replicates	57	11
mean of all EIA replicate %cv values for ppt	10%	13%

CAPE Technologies

High Performance Dioxin/Furan Immunoassay Kit

DF1 Kit Insert (IN-DF1)

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A. Intended Use

The CAPE Technologies High Performance Dioxin/Furan Immunoassay Kit is an Enzyme ImmunoAssay (EIA) for analysis of PolyChlorinated DibenzoDioxins and PolyChlorinated DibenzoFurans (PCDD/Fs) in prepared sample extracts. Extracts of fly ash, soil, stack gas, tissue, sediment, food, water, or other samples which have been prepared by conventional extraction methods can be exchanged to a water miscible solvent system for EIA analysis. Samples can also be prepared by immunoassay specific methods for analysis by EIA. Please read this kit insert and other related CAPE Technologies literature carefully to gain maximum understanding of the capabilities and limitations of the test. Refer to Technical Notes and Application Notes available from the CAPE Technologies web site (http://www.cape-tech.com) for discussion of technical issues and for individual applications for different sample matrices. **Note:** Samples analyzed by EIA must contain either no mass-labeled internal standards or immunoassay compatible internal standards. For discussion of issues related to internal standards, consult CAPE Technologies Technical Note TN-001.

B. Background Information

PCDD/Fs are a family of compounds with the same general structure. There are 75 dibenzodioxin congeners and 135 dibenzofuran congeners, containing from 1 to 8 chlorine atoms on the dibenzodioxin or dibenzofuran nucleus. Only 7 of the 75 PCDD congeners and 10 of the 135 PCDF congeners contain the 2,3,7,8 chlorination pattern thought to be required for dioxin-like toxicity. Only these 17 of the 210 total PCDD/F congeners contribute to the Toxic Equivalency (TEQ) of a sample, which is generally the critical analytical target. Based on a variety of toxicity tests, these 17 congeners have been assigned Toxic Equivalency Factors (TEFs) of 1.0 to 0.0001 relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

The PCDD/F congener composition of samples can be highly variable. Because PCDD/Fs are formed unintentionally by a variety of chemical and combustion processes, samples usually contain a mixture of many different congeners. Samples from different sources often have very different mixtures of congeners which are consistent within the source. In most samples, the majority of the PCDD/F mass present does not contribute significantly to the total sample TEQ. Also, in most samples, only a few PCDD/F congeners are responsible for the majority of the TEQ. This immunoassay is designed to measure sample TEQ by responding to the toxic PCDD/F congeners in correlation with their TEFs. Variation in accuracy among samples may occur solely because of the variability of congener composition noted above. Best kit performance will be obtained when all samples are from a single group which shares as many properties as

possible (common source of contamination, similar congener composition, similar sample matrix, etc.). To maximize accuracy, the congener composition of the target sample population should be known.

Both screening and quantitative analysis are possible with this kit. Consult the appropriate CAPE Technologies Application Note for details. Please also consult CAPE Technologies Technical Note TN-004 for further discussion of quantitative use of the kit.

C. Test Principles

PCDD/Fs are typically extracted with organic solvents which are incompatible with the EIA. Before introduction of the sample into the EIA a solvent exchange is required. PCDD/Fs have very low volatility and are retained during this solvent exchange in a small volume of a keeper solution (Triton X-100 detergent in tetraethylene glycol [TEG]) after evaporation of the original solvent. Methanol is added to dilute this solution and the methanol-TEG-Triton mixture is added directly to the EIA tubes. It should be noted that the literature value for solubility of 2,3,7,8-TCDD in methanol is 10 ppm, which is 5000 times higher than the concentration of the highest standard recommended for this kit. Additionally, the solubility of PCDD/Fs in methanol is augmented significantly by the addition of TEG and Triton X-100. These factors assure the solubility of PCDD/Fs in the EIA system.

During the first EIA incubation, PCDD/Fs are specifically bound by the anti-dioxin antibodies, which have been immobilized on the EIA tube surface. After washing away the unbound material, the bound PCDD/Fs remain and a competitor-HorseRadish Peroxidase (HRP) conjugate is added. Bound PCDD/Fs occupy the dioxin binding sites of the antibodies in proportion to the PCDD/F content of the sample and prevent binding of the competitor-HRP conjugate. After a short incubation, unbound conjugate is removed and the test tubes are washed thoroughly. The amount of conjugate bound by the anti-dioxin antibody is inversely related to the amount of PCDD/Fs originally present in the sample.

Finally, a solution of chromogenic HRP substrate and hydrogen peroxide is added to the test tubes. Color development is directly proportional to enzyme concentration and inversely related to the PCDD/F concentration in the original sample. The test tubes are analyzed using a tube reader or spectrophotometer to measure the optical density (OD) at 450 nm. The OD values of unknown samples are compared to the OD values of standards to determine the level of PCDD/Fs in the samples.

D. Performance Characteristics

Sensitivity and Reproducibility

Standard curve data developed by CAPE Technologies for the High Performance Dioxin/Furan Immunoassay Kit are given in Table 1. Response values are expressed as a percentage of the negative control, which is 100 ppm Triton X-100 in 80-20 methanol-TEG. The detection limit of the kit is approximately 4 pg 2,3,7,8-TCDD per EIA tube. Results for samples which are compared to the standards shown in Table 1 must be related to the original sample concentration by back calculation using the proper dilution and volume factors. Matrix detection limits will vary according to matrix, sample size, and dilution factor. Consult the appropriate CAPE Technologies Application Note for further information. The data in Table 1 can be used to determine if kit performance is acceptable. If your results for the standards in Table 1 are not consistently within the percent of negative control ranges given, contact CAPE Technologies for assistance.

Table 1: Sensitivity and Reproducibility of the EIA Standard Curve. Data are accumulated responses for 2,3,7,8-TCDD standards in methanol/Triton over ten months. No sample matrix was present. A total of 41 tests were run in four different labs. The detection limit, which is approximated by the I_{85} or the concentration giving 85% of the negative control OD, was 3.9±1.4 pg/tube (mean±SD). The midpoint of the curve, defined as the I_{50} or the concentration giving 50% of the negative control OD, was 21.9±7.4 pg/tube (mean±SD).

Standard Number	1	2	3	4
ng/mL 2378-TCDD in standard (50 µL per EIA tube)	0.064	0.2	0.64	2
pg 2378-TCDD per EIA tube	3.2	10	32	100
mean percent of negative control (%NC)	87	66	41	29
standard deviation (SD)	6	7	7	6
range of mean±2SD	74-99	51-80	27-55	17-40

Specificity

The anti-dioxin antibody in this kit binds to different PCDD/F congeners with different affinities. The specificity of the test is predominantly for PCDD/Fs which contain 3 to 6 chlorines, with a strong preference for the 2,3,7,8 chlorinated congeners. Test specificity roughly parallels the TEF values of the individual PCDD/F congeners. Crossreactivity data given in the following table are reactivities relative to 2,3,7,8-TCDD.

Table 2: Specificity of the EIA. Response curves were prepared for each congener as noted. The percent crossreactivity = (((congener I_{50}) ÷ (2,3,7,8-TCDD I_{50})) x 100). Values are typically based on 2 to 4 independent curves, each containing at least 4 concentrations.

Compound Toxic Dioxin Congeners	Percent Crossreactivity
2,3,7,8-TCDD	100
1,2,3,7,8-PeCDD	105
1,2,3,4,7,8-HxCDD	1.6
1,2,3,6,7,8-HxCDD	7.9
1,2,3,7,8,9-HxCDD	39
1,2,3,4,6,7,8-HpCDD	0.7
OCDD	<0.001
Toxic Furan Congeners	
2,3,7,8-TCDF	20
1,2,3,7,8-PeCDF	4.6
2,3,4,7,8-PeCDF	17
1,2,3,4,7,8-HxCDF	0.4
1,2,3,6,7,8-HxCDF	1.0
1,2,3,7,8,9-HxCDF	3.3
2,3,4,6,7,8-HxCDF	4.9
1,2,3,4,6,7,8-HpCDF	0.02
1,2,3,4,7,8,9-HpCDF	0.9
OCDF	<0.001

Compound Other PCDD/F Congeners	Percent Crossreactivity
2,3-dichlorodibenzo-*p*-dioxin	0.13
2,7-dichlorodibenzo-*p*-dioxin	0.003
2,3-dichlorodibenzofuran	0.02
2,7-dichlorodibenzofuran	<0.002
2,3,7-trichlorodibenzo-*p*-dioxin	24
2,3,8-trichlorodibenzofuran	0.26
1,2,3,4-TCDD	<0.001
1,2,3,4-TCDF	<0.001
1,3,6,8-TCDD	0.05
1,3,6,8-TCDF	0.007
PolyChlorinated Biphenyls	
3,3',4,4' (PCB 77)	0.4
3,3',4,4',5 (PCB 126)	0.5
2,2',4,4',5 (PCB 153)	<0.1
3,3',4,4',5,5' (PCB 169)	<0.1
Aroclor 1254	<0.1

E. Precautions

- **Important: Please read the following precautions carefully.**
- **Follow precautions and instructions in this insert to achieve the best results.**

Safety:

- This kit should only be used by properly trained personnel in an appropriate laboratory environment.
- Treat PCDD/Fs, solutions that contain PCDD/Fs, and potentially contaminated samples as hazardous materials.
- Use gloves, proper protective clothing, and means to contain and handle hazardous material where appropriate.
- Obtain (if appropriate) permits pertaining to the handling, analysis and transport of dioxin-containing materials.
- **Stop solution is 1N hydrochloric acid. Handle carefully.**

Storage and Use of Kit:

- **Do not freeze test kit components or expose them to temperatures greater than 37°C (99°F).**
- **If desiccant in tube bag is not blue, do not use kit; contact CAPE Technologies.**
- **Do not expose substrate to direct sunlight.**
- If substrate is blue before adding to EIA tubes, do not use; contact CAPE Technologies.

- Store all test kit components at 2°C to 6°C (36 °F to 43°F) when not in use.
- Storage at ambient temperature (20°C to 27°C or 68°F to 81°F) on the day of use or overnight before the day of use is acceptable. Do not store at ambient temperature for extended periods.
- ***Allow all reagents to reach ambient temperature (20°C to 27°C or 68°F to 81°F) before beginning the test. This typically requires at least 60 minutes at ambient temperature to warm from recommended storage conditions. Warming will occur faster if bottles and tube bags are removed from the kit box.***
- Do not use test kit after the expiration date.
- Do not use components from one test kit with components from a different test kit.

Sample Preparation:

- ***Because this EIA recognizes many of the congeners in mass labeled internal standard mixtures designed for GC-MS methods, EIA samples must contain either immunoassay compatible internal standards or no internal standards.*** For specific recommendations regarding mass labeled internal standards, consult CAPE Technologies Technical Note TN-001.
- ***Water immiscible solvents in sample extracts must be evaporated completely before diluting in methanol for the EIA.*** Residual solvents or excessive oil may cause precipitation when the sample is added to the EIA tubes. If this occurs, the test result may be invalid and the cause should be corrected before repeating the analysis. Quality assurance methods such as comparison of spiked and unspiked sample extracts are essential for determining the validity of such results. Contact CAPE Technologies for assistance with selection of appropriate quality assurance methods.

EIA Protocol:

- ***When adding standards and samples to the EIA tubes, the methanol solutions must be dispensed directly into the liquid and not above the liquid surface or onto the side of the tube. Each EIA tube must be mixed briefly as soon as the sample or standard is added, until the tube contents appear uniform.***

Interpretation of Results:

- Consult the appropriate CAPE Technologies Application Note for proper interpretation of results.
- Proper quality assurance is the responsibility of the analyst and is strongly encouraged. Your quality assurance plan should include GC-MS confirmation of some fraction of both positive and negative results.
- Distribution of PCDD/Fs in samples may vary greatly. The analyst is responsible for adequate frequency, distribution, and homogenization of samples.

F. Materials Provided

The contents of this kit are described in a separate **Materials List** (ML-DF1-12 or ML-DF1-60).

G. Materials Supplied by the User

- Sample preparation supplies and equipment (the SP1 and SP2 Sample Preparation Kits contain vials and other supplies for rapid preparation of soil, food, or other samples). You must consult the relevant Application Note for equipment, reagents, and supplies required for your application. Visit the CAPE Technologies web site (www.cape-tech.com) or contact CAPE Technologies if additional technical assistance is required.
- The remainder of this list gives only those materials needed for a generic solvent exchange and the EIA portion of the analysis.
- HPLC or analytical grade methanol for solvent exchange
- Sample evaporation system for solvent exchange (nitrogen or other gas source)
- Glass tubes or vials for solvent exchange
- Glass vials (1-2 mL) with Teflon lined caps for storage of standards after opening ampoules

- 1 variable volume glass capillary positive displacement pipettor for dispensing 50 to 100 µL of standards, samples, and keeper (Drummond 275 or equivalent)*
- 1 Eppendorf Repeater or Repeater Plus Pipettor and minimum of 6 tips (one 0.5 or 1 mL, four 10 or 12.5 mL, and one 50 mL), for pipetting 50 µL to 1.0 mL volumes (or equivalent repeating pipettor)*
- Artel Differential Photometer or other means for measuring OD of finished immunoassay tubes at 450 nm (alternatives include conventional spectrophotometers, other tube readers, or microplate readers)*
- Marking pen
- Watch or timer
- Reagent grade or bottled distilled water for sample dilution and tube washing
- Basin or other system for capture and disposal of wash water and other waste liquids.

  * see Recommended Equipment List (EL-001) for more information

H. Suggestions for Pipettor Use

- ***Please read these suggestions carefully before performing your first EIA.***
- Use empty tubes and extra tips to practice your pipettor technique before analyzing samples. For the glass capillary positive displacement pipettor, use methanol; for the Repeater pipettor, use water.
- Use a different tip for each reagent dispensed with the Eppendorf Repeater Plus Pipettor to avoid reagent cross-contamination, especially between conjugate and substrate. Label four 10 or 12.5 mL tips "water", "Conjugate", "Substrate", and "Stop".
- Draw the desired reagent volume into the Repeater pipettor and dispense at least one portion of reagent back into the container to properly engage the ratchet mechanism. If this is not done, the first volume delivered will be inaccurate.
- When adding reagents to the EIA tubes using the Repeater pipettor, direct the liquid stream down the side of the tube just below the rim to avoid splashback.
- ***When using the glass capillary positive displacement pipettor for adding samples or standards to EIA tubes, the solution must be dispensed directly into the water in the tube, not above the liquid level or onto the side of the tube. The tubes must be individually mixed immediately after the addition of methanol-TEG-Triton solutions to distribute the analyte evenly and to avoid locally high or low concentrations at the antibody coated surface of the tube.***
- When using the glass capillary positive displacement pipettor for standards and samples, the following approach (as for a GC autosampler) has proven effective. After each pipetting operation, repeatedly rinse both inside and outside of the capillary by pipetting several methanol aliquots to a waste container. When changing capillaries, rinse the plunger to minimize carryover. ***If capillaries are not changed after each standard, water on the outside of the capillary must be removed to avoid contamination of the standard with water.***

I. Preparation of PCDD/F Sample Extracts for EIA by Solvent Exchange

1. **Prepare keeper working solution from stock**: Locate the 8 mL vial labeled "TEG-Triton X-100 keeper" and stand upright for several minutes (or centrifuge briefly) to allow TEG-Triton mixture to drain away from lid. Make working solution of keeper by adding 6.0 mL of analytical grade methanol to the vial and mixing thoroughly. This solution of 100 ppm Triton X-100 in 80/20 methanol/TEG will be used for adding keeper to extracts prior to solvent exchange.

2. **Select sample size and keeper volume for solvent exchange**: The following is a generic extract preparation procedure which is appropriate for samples which have gone through the full cleanup procedure prior to GC/MS analysis (using immunoassay compatible internal standards or no internal standards). **For other samples, consult the appropriate Application Note.** Use of this EIA for screening analysis depends upon the same amount of each sample being introduced into the EIA. This quantity (the sample load in "mg Sample Equivalent Delivered to EIA Tube") is dictated by your target

level and must be determined in advance. Consult Table 3 below (or your Application Note) to determine the appropriate sample load.

Table 3: Sample Load Selection Guide:

(Correspondence among EIA standards, sample TEQ levels, and amount of sample used in the EIA)

How to use Table 3: Locate your target concentration in the body of the table, then read the "mg Sample Equivalent Delivered to EIA Tube" at the top of that column. This is the amount of sample you must load into each EIA tube. If your decision level occurs in more than one table column, use the one farthest to the left (corresponding to lower standards). This will allow less sample to be used, giving less potential for matrix interferences. This process of estimating the amount of sample needed is illustrated by the examples below. Note that these values are the amount of sample actually delivered to the EIA tube and do not account for replication or the extra volume required to assure that a given volume can be comfortably recovered from the evaporation tube. Read the paragraph immediately below Table 3 and/or consult the appropriate Application Note for selection of keeper volume.

Important Note: Table 3 is for guidance only because it assumes 100% recovery through the sample preparation procedure, including sample extraction efficiency and extract cleanup. Guidance on data interpretation is given in Section K below.

Example 1: When using 10 mg sample equivalent per EIA tube, a nominal sample concentration of 1 ppb would be approximately equivalent to Standard 2 (.2 ppb or 10 pg/EIA tube 2,3,7,8-TCDD).

Example 2: To make a nominal sample concentration of 10 ppt (0.01 ppb) approximately equivalent to Standard 2 (10 pg/EIA tube), use 1000 mg sample equivalent per EIA tube.

Example 3: When using 1000 mg sample equivalent per EIA tube, a nominal sample concentration of 0.1 ppb would be approximately equivalent to Standard 4 (2.0 ppb 2,3,7,8-TCDD).

	2378-TCDD Standards (50 µL per EIA tube)		mg Sample Equivalent Delivered to EIA Tube					
	stock ppb	pg/tube	0.1 mg	1 mg	10 mg	100 mg	1000 mg	10,000 mg
Standard 2	0.2	**10**	100 ppb TEQ	10	1	0.1	0.01	0.001
Standard 3	0.64	**32**	320	32	3.2	0.32	0.032	0.0032
Standard 4	2.0	**100**	1000	100	10	1	0.1	0.01
			Target Concentration in Original Sample (ppb TEQ)					

Selection of keeper volume: It is best to exchange only enough sample for immediate analysis, plus an extra amount to cover waste in pipetting. Leave the rest of the sample in toluene or other low volatility solvent. **For analysis at high pg/g levels**, where only a small fraction of the sample may be used in the EIA, evaporate the sample from 150 µL of keeper. After evaporation, add 120 µL of methanol to reconstitute the sample to 150 µL, allowing recovery of one or two 50 µL aliquots for single or duplicate EIA analysis. In this case, the total amount of sample exchanged is 3x the amount delivered to each EIA tube. **For analysis at low pg/g levels**, where maximum sample recovery is critical, evaporate the sample from 62.5 µL of keeper. After evaporation, add 50 µL of methanol to reconstitute the sample to 62.5 µL, allowing recovery of one 50 µL aliquot, representing 80% of the original sample, for single tube EIA analysis. In this case, the total amount of sample exchanged is 1.25x the amount delivered to the EIA tube. For example, 5 g of sample equivalent would be exchanged so that 4 g of sample equivalent could be added to the EIA tube.

3. **Perform solvent exchange**: Use a clean glass tube or conical vial for evaporating each sample to be analyzed. Add the amount of methanol-TEG-Triton keeper solution (determined in the preceding section) to each evaporation tube or vial. Add sample in volatile solvent such as toluene, hexane, isooctane, or acetone. Solvents with boiling points higher than toluene (111°C) should be avoided if possible. Evaporate solvent completely under dry gas stream such as nitrogen. After removing the original solvent, rinse the sides of the tube once with 2 mL of dichloromethane and evaporate again. Recovery will not be adversely affected if the sample remains under the gas stream for a few minutes after complete evaporation of the solvent. **The original solvent must be completely gone- there should be no solvent odor.** Application of gentle heat (50°C) is acceptable. During solvent exchange the TEG and Triton X-

100 function as a "keeper", similar to the conventional use of dodecane or tetradecane. When the original solvent is completely evaporated, the PCDD/Fs stay in solution in the TEG-Triton and are easily diluted with methanol.

4. **Reconstitute sample**: Centrifuge the evaporation tubes for 2 minutes at 1-2000 x g to collect the residual TEG-Triton in the bottom of the tube. Add a volume of methanol to each tube equal to 80% of the original keeper volume used (replacing the evaporated methanol). Mix vigorously for 15 seconds to dissolve the keeper and sample completely. Sonication or longer mixing times are not necessary. Pipet the redissolved sample into the EIA tube which has been prepared, then mix immediately (as noted in Section J below). **Perform this sample dilution and EIA loading procedure in batches of 4 or fewer samples. This will minimize changes in sample concentration due to evaporation of the methanol.**

J. EIA Analysis of Standards and Prepared Samples

Prepare samples according to the directions above in "Preparation of PCDD/F Sample Extracts by Solvent Exchange" or in the appropriate Application Note. The following steps explain how to analyze your prepared samples using the CAPE Technologies High Performance Dioxin/Furan Immunoassay Kit. For quick reference, a summary of this protocol is provided on a separate sheet (PS-DF1). The number of tubes per run should be limited by the amount of time it takes to add **Competitor-HRP Conjugate** in step 9 below, and is typically 20 or fewer. This is the largest batch size that can be done on one filling of the 10 mL tip of the Eppendorf Repeater Plus pipettor. Follow precautions in Section E above. **Do not expose Substrate to direct sunlight.**

1. **Warm reagents**: Bring all reagents to ambient temperature as described in Section E (Precautions, Storage and Use of Kit).
2. **Prepare wash 1**: Locate the vial labeled "0.5 mL neat Triton X-100". Make a wash solution of 100 ppm (0.01% v/v) Triton in reagent grade or bottled distilled water by adding 10 µL of Triton X-100 to 100 mL of water and mixing thoroughly (this will typically take several minutes on a magnetic stirrer). This amount is sufficient for 20 tubes (20 tubes x 4 washes per tube x 1 mL/wash/tube = 80 mL nominal). This wash can be prepared in larger volumes and stored at room temperature.
3. **Prepare tubes**: Place the anti-Dioxin **antibody coated tubes** in the rack and label them. Put the standard tubes first, from low to high concentration, then the sample tubes.
4. **Prerinse tubes**: **Rinse** tubes once by filling each tube with reagent grade or bottled distilled **water.** Dump water out and tap inverted tubes on absorbent material to remove excess water.
5. **Add water for sample incubation**: Insert the 10 or 12.5 mL pipet tip labeled "water" into the Repeater pipettor and set volume to 500 µL. Dispense one **500 µL** aliquot of reagent grade or bottled distilled **water** into each tube.
6. **Add standards**: Using a glass capillary positive displacement pipettor, pipet **50 µL** of **standard** solution into each EIA standard tube. ***The solutions must be dispensed directly into the liquid and not above the liquid surface or onto the side of the tube.*** **Immediately after addition, mix each tube briefly until appearance is homogeneous**. The mixing should be vigorous enough to visibly swirl the liquid around the bottom of the tubes.
7. **Add samples**: Using a glass capillary positive displacement pipettor, pipet **50 µL** of **prepared sample** into each EIA sample tube. ***The solutions must be dispensed directly into the liquid and not above the liquid surface or onto the side of the tube.*** **Immediately after addition, mix each tube briefly until appearance is homogeneous**. Mix the rack of tubes by shaking for 10 seconds after adding the last sample. The mixing should be vigorous enough to visibly swirl the liquid around the bottom of the tubes. Incubate at room temperature for 2 to 24 hours. For longer incubation times, cover the rack of tubes or place in a closed plastic bag or other airtight container with limited headspace. The amount of time taken for addition of negative control, standard and sample has little effect on the results because of the long sample incubation. (It is preferred to incubate overnight at this point rather than 2 hours because of the slight improvement in sensitivity [up to two-fold] with the longer incubation). Also, results may be affected by proportionally higher variations in incubation time among samples, due to the sample addition process.
8. **Wash 1**: Dump or aspirate the EIA tube contents into a suitable waste container. Tap inverted tubes on absorbent material to remove excess liquid. Insert a 50 mL pipet tip into the Repeater pipettor and

set volume to 1.0 mL. Dispense one **1 mL** aliquot of **100 ppm Triton X-100 in water** (made in step J2 above) into each tube. Dump or aspirate the EIA tube contents into a suitable waste container. **Repeat** this wash step three more times for a **total of 4 washes**. Be certain to shake or tap out as much wash solution as possible on each wash, especially the last one.

9. **Add conjugate**: Insert the 10 or 12.5 mL pipet tip labeled "conjugate" into the Repeater pipettor and set volume to 500 µL. Dispense one **500 µL** aliquot of "**Competitor-HRP Conjugate**" into each tube. Incubate tubes at room temperature for 15 minutes. Timing for this step is the most important of the EIA steps. Rapid and accurate addition of conjugate and consistent incubation times are necessary to maintain equal treatment within and among runs.

10. **Wash 2**: **Repeat** the **wash** procedure described in step 6 above *except use reagent grade or bottled distilled water with no detergent added*.

11. **Add substrate**: Insert the 10 or 12.5 mL pipet tip labeled "substrate" into the Repeater pipettor and set volume to 500 µL. Dispense one **500 µL** aliquot of "**HRP Substrate Solution**" into each tube. Incubate at room temperature for 30 minutes.

WARNING: Stop solution is 1N hydrochloric acid. Handle carefully.

12. **Add stop solution**: Insert the 10 or 12.5 mL pipet tip labeled "stop" into the Repeater pipettor and set volume to 500 µL. Dispense one **500 µL** aliquot of "**Stop Solution**" into each tube. The Stop Solution converts the developed color to yellow. If Stop Solution is not added, all tubes will eventually turn dark blue. **Read** the tubes as soon as possible after stopping; the yellow color is stable for only 30 minutes.

13. **Read OD values**: To use the Artel Differential Photometer, add at least 1 mL of reagent grade or bottled distilled water to a blank test tube and insert the tube into the left well of the photometer. Dry the outside of each EIA tube, insert tube into the right well of the photometer, and record the absorbance (optical density [OD]) of each tube. Alternatively, read the absorbance of each sample at 450 nm using a tube reader, conventional spectrophotometer, or microplate reader. Consult the Recommended Equipment List (EL-001) for information on how to contact Artel.

K. Interpretation of the Results

1. After each EIA run, calculate for each standard and sample the %NC value (OD as a percent of the negative control OD). The %NC values for standards should be compared to Table 1 to determine if the EIA has been performed properly. Refer to Table 3 and/or the appropriate Application Note for instructions on interpretation of sample results. Contact CAPE Technologies if additional assistance is required regarding interpretation of results.

2. The CAPE Technologies High Performance Dioxin/Furan Immunoassay Kit is designed primarily for screening decisions. Quantitative interpretation of data may be possible in certain situations. Consult the appropriate Application Note and Technical Note TN-004 for discussion of this topic. Quantitative interpretation can be performed using **Module C** from the CAPE Technologies web site (**www.cape-tech.com**). This Microsoft Excel workbook file contains background information and operating instructions. The file utilizes a four parameter equation designed specifically for immunoassays and used in most commercial immunoassay software. Module C plots the actual data and the calculated four parameter solution, and determines sample concentrations based on the calculated curve fitting solution. It is necessary to use all the standards listed in Table 1 to produce an acceptable curve fit. Contact CAPE Technologies if additional assistance is required regarding interpretation of results.

L. Limitations of the Procedure

The CAPE Technologies High Performance Dioxin/Furan Immunoassay Kit is designed for screening of samples according to their TEQ by responding to the toxic PCDD/F congeners in approximate correlation with their TEFs. Quantitative interpretation of data may be possible in certain situations. Consult the appropriate Application Note and Technical Note TN-004 for discussion of this topic. Confirmation of positive samples and a portion of the negative samples by GC-MS analysis is strongly recommended. Other quality assurance methods and samples should be used at all stages of sample preparation and analysis.

Samples which appear heterogeneous during the first incubation (step J7 above) may be invalid due to phase separation. Adequate sample cleanup based on the protocol in the chosen Application Note must be assured by the analyst. Contact CAPE Technologies if this is a recurrent problem.

Samples analyzed by EIA must contain either immunoassay compatible internal standards or no internal standards. Consult Technical Note TN-001 and Calculation Module D for discussion and other assistance.

The distribution of PCDD/Fs can be extremely heterogeneous. Adequate sample number, distribution, and homogeneity are the responsibility of the analyst.

To ensure accurate and reliable results, every effort should be made to perform the CAPE Technologies High Performance Dioxin/Furan Immunoassay Kit at temperatures between 20°C (68°F) and 27°C (81°F).

M. Storage

- Store all test kit components at 2°C to 6°C (36 °F to 43°F) when not in use.
- Do not expose test kit components to temperatures greater than 37°C (99°F). Storage at ambient temperature (20°C to 27°C or 68°F to 81°F) on the day of use is acceptable. Prolonged exposure (many days) or repeated exposure to ambient temperatures may cause a loss of reagent (especially conjugate) activity, resulting in decreased OD values for all tubes.
- **Do not freeze test kit components. Kits which have been frozen must not be used.**
- **If desiccant in tube bag is not blue, do not use kit; contact CAPE Technologies.**
- Do not use test kit components after the expiration date printed on the kit box label.

N. Quality Assurance

- Samples which appear milky during the first EIA incubation may contain more oil than can be tolerated by the test. These samples should be diluted or cleaned more, then analyzed again by EIA.
- Response values for 2,3,7,8-TCDD standards typically should be in the ranges given in Table 1.
- If a blue color does not develop in the negative control test tube within 15 minutes after adding the substrate solution, the test is invalid and must be repeated. If the problem persists, contact CAPE Technologies.
- ***The antibody used in this immunoassay recognizes PCDD/F congeners based on structure, not mass. Therefore, conventional stable isotope labeled internal standards are detected as native material. Typical levels of conventional stable isotope labeled internal standards can not be used with this EIA***. Please consult Technical Note TN-001 for recommendations on the use of immunoassay compatible mass labeled internal standards. Contact CAPE Technologies if additional assistance is required regarding these issues. Immunoassay compatible internal standards are available from Wellington Laboratories (Guelph, Ontario, Canada).
- Replication, check samples, standard reference materials, and other QA samples and methods can and should be used with this kit, with the exception of conventional stable isotope labeled internal standards (as noted in the above paragraph). The Starter Kit DF1-ST includes two toluene check samples which should be used to determine if the solvent exchange portion of the sample preparation has been performed properly. Consult Wellington Laboratories to obtain additional QA materials.

O. References

All of the documents cited in this and other CAPE Technologies literature are available from the CAPE Technologies web site at "**www.cape-tech.com**". **Application Notes** describe procedures for analysis of a variety of matrices, TEQ levels, and sample preparation methods. **Technical Notes** provide discussion and recommendations pertaining to important technical issues. **Technical References** are papers from technical journals or other sources which provide extensive background information about selected topics relevant to immunochemical analysis of PCDD/Fs. Additional questions can be directed to CAPE Technologies using the contact information from the web site.

P. General Limited Warranty

CAPE Technologies, LLC ("CAPE Technologies") warrants the products manufactured by it against defects in materials and workmanship when used in accordance with the applicable instructions for a period not to extend beyond the expiration date printed on the product. **CAPE Technologies MAKES NO OTHER WARRANTY, EXPRESSED OR IMPLIED. THERE IS NO WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE.** The warranty provided herein and the data, specifications and descriptions of CAPE Technologies products appearing in CAPE Technologies' published catalogues and product literature may not be altered except by express written agreement signed by an officer of CAPE Technologies. Representations, oral or written, which are inconsistent with this warranty or such publications are not authorized and if given, should not be relied upon.

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CAPE Technologies

High Performance Immunoassay Kits

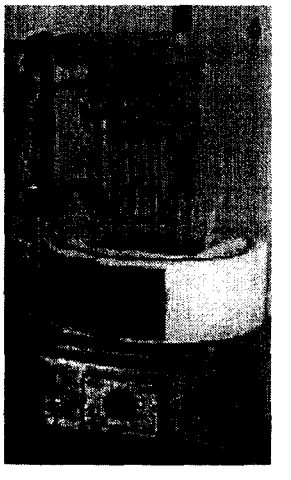
Sample Preparation Equipment List (EL-002)

This list contains equipment that may be required for sample preparation and must be provided by the user. No cost estimates or manufacturer information are given here. To understand the following comments completely, read the kit insert IN-DF1 first. For a list of the equipment actually required for preparation of your samples prior to the immunoassay analysis, consult the appropriate Application Note.

1. Chemical fume hood

A solvent exchange step is required to go from non-aqueous systems used in sample preparation to a methanol-based system for the immunoassay procedure. For health and safety reasons, this step should be performed in a chemical fume hood. In addition, CAPE Technologies sample preparation protocols often use materials that require a fume hood for safe use.

This item is essential to all applications.



2. Sample evaporation system

The solvent exchange step noted above can be done easily with both a heat source and clean gas supply. For health and safety reasons, this step should be performed in a chemical fume hood. In addition, CAPE Technologies sample preparation protocols often use solvents and other materials that require a fume hood for safe use. The temperatures specified in CAPE Technologies Application Notes range up to 75°C. for evaporating toluene. Heat can be applied to the samples by either water bath or dry block heater. Nitrogen is generally used, but clean compressed air has been used successfully by some customers. It is critical that the gas source be oil free to avoid contamination of the sample.

This item is essential to all applications.

3. Benchtop centrifuge

Centrifugation is required after solvent exchange to concentrate the non-volatile portion of the keeper residue in the bottom of the sample evaporation tube. This is required for complete and consistent recovery of the sample. Because this viscous residue must be dissolved in 120 µL or less of methanol, it is impractical to accomplish this by rinsing the tube with volatile solvents. In addition, some sample preparation protocols require separation after either extraction or liquid phase oxidative cleanup. The centrifuge buckets should be able to hold vials 97 x 28 mm for extraction, vials 68 x 20 mm or smaller for oxidation, and tubes 16 x 125 mm or smaller for solvent exchange. The maximum force required is 1-2000 x g. A timer is helpful, but not required.

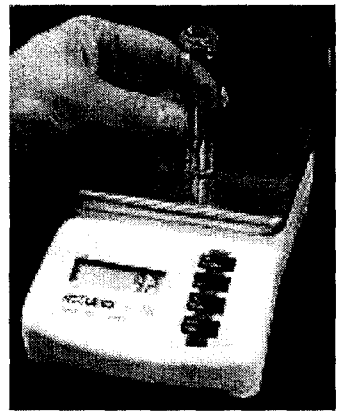
This item is essential to all applications.

4. Vortex mixer

The final sample preparation step for all applications is the addition of methanol to the keeper residue in the solvent exchange tube. It is crucial to mix vigorously for several seconds to dissolve all of the viscous keeper residue in the added methanol. Any mixer similar to the one at right will be adequate for this task.

This item is essential to all applications.

5. Top loading balance, 0.1 g



Soils and other solid samples are generally weighed to the nearest 0.1 g. Any balance is acceptable, but top loaders are most convenient. A removable pan is helpful for cleanup. The far right balance is battery powered, inexpensive, and has been used successfully for several years by analysts performing environmental immunoassay tests.

This item is not needed for every application.

6. Orbital Platform Shaker

Extractions of solid samples and liquid phase oxidative cleanup steps require this type of shaker. Because mixing times may be 1 hour or more, shaking by hand is not a practical substitute. Vials of many different sizes can be packed in a box padded tightly with soft foam and held down by elastic cords. When agitation by platform shaker is specified, it is generally vigorous, such as 350 revolutions per minute, and requires vials to lay flat on their sides. A stable location on a skid-proof surface is essential. A platform of 25 x 30 cm (approx. size of shaker at right) is more than adequate in size.

This item is not needed for every application.