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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 initial 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 μ L 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/ μ L 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 $\text{pH} \leq 2$ 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 ($< 50 \mu\text{g}/\text{kg}$ 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 $<10^{\circ}\text{C}$ 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

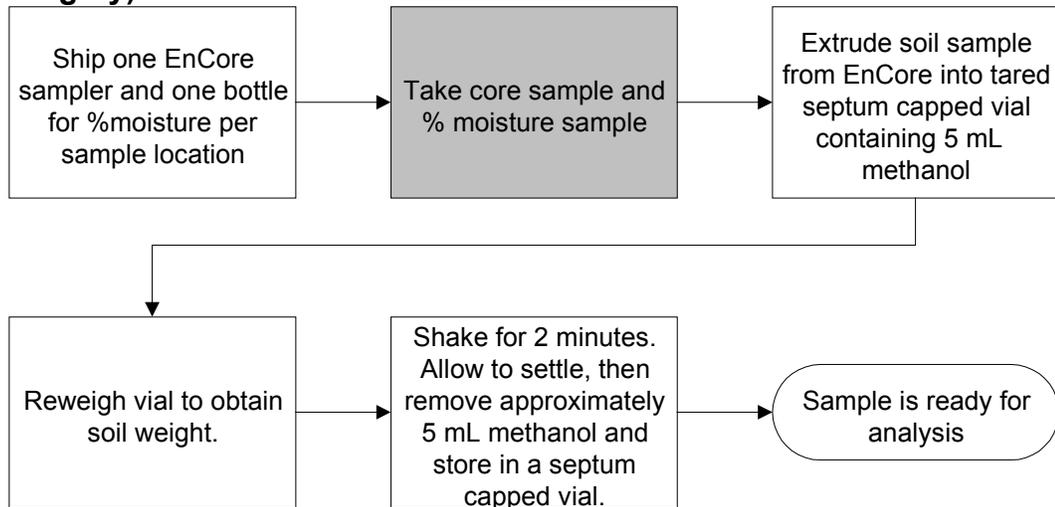
- 8.8.1 *At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A. It is no longer included and is likely to generate results that are biased low, possibly by more than an order of magnitude.*

8.9 Aqueous samples are stored in glass containers with Teflon lined septa at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$, with minimum headspace.

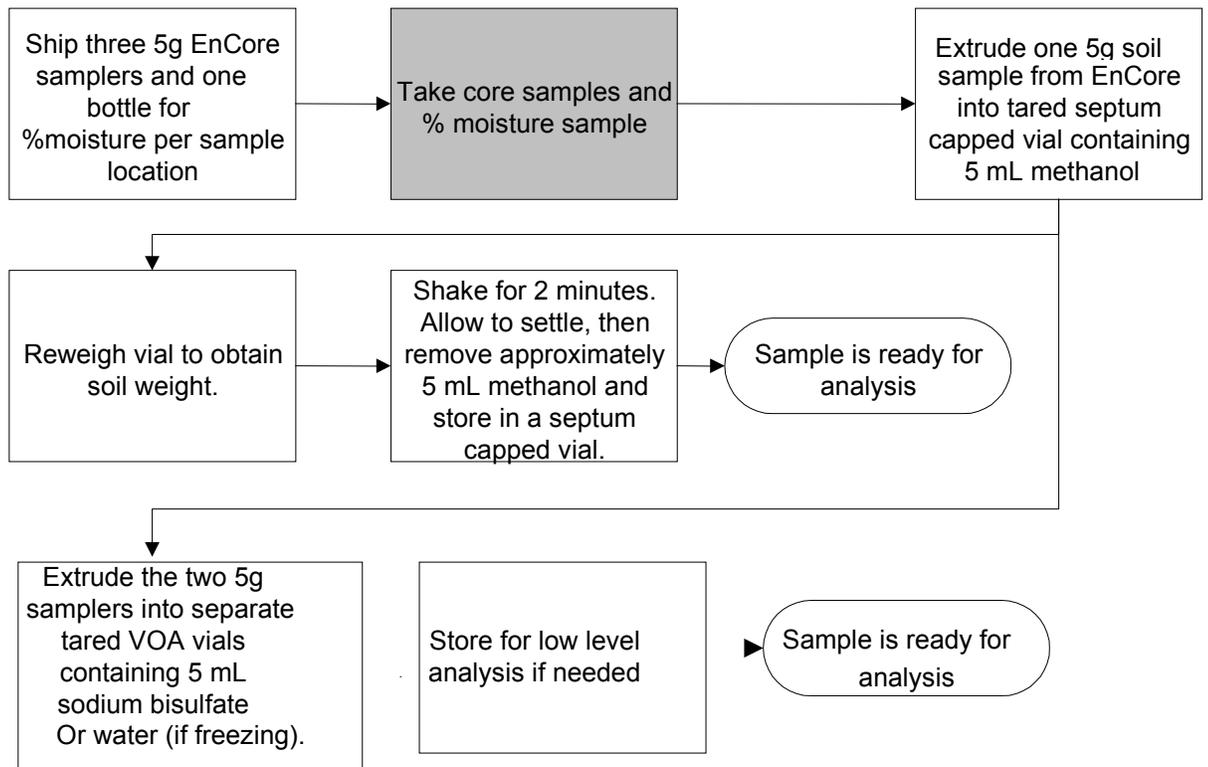
8.10 Medium level solid extracts are aliquoted into 2 mL glass vials with Teflon lined caps and stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The extracts are stored with minimum headspace.

- 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.

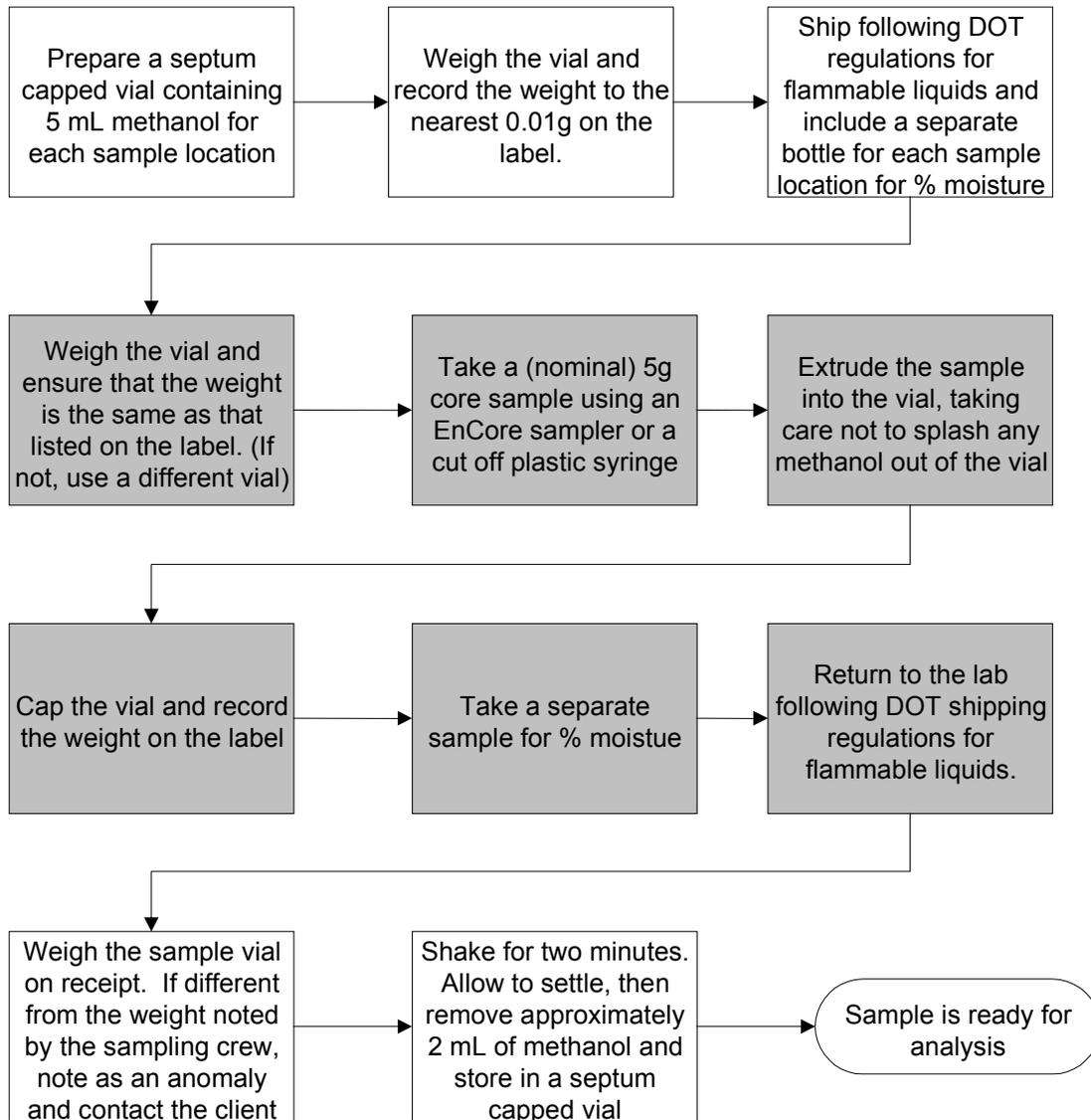
EnCore procedure when low level is not required (field steps in gray)



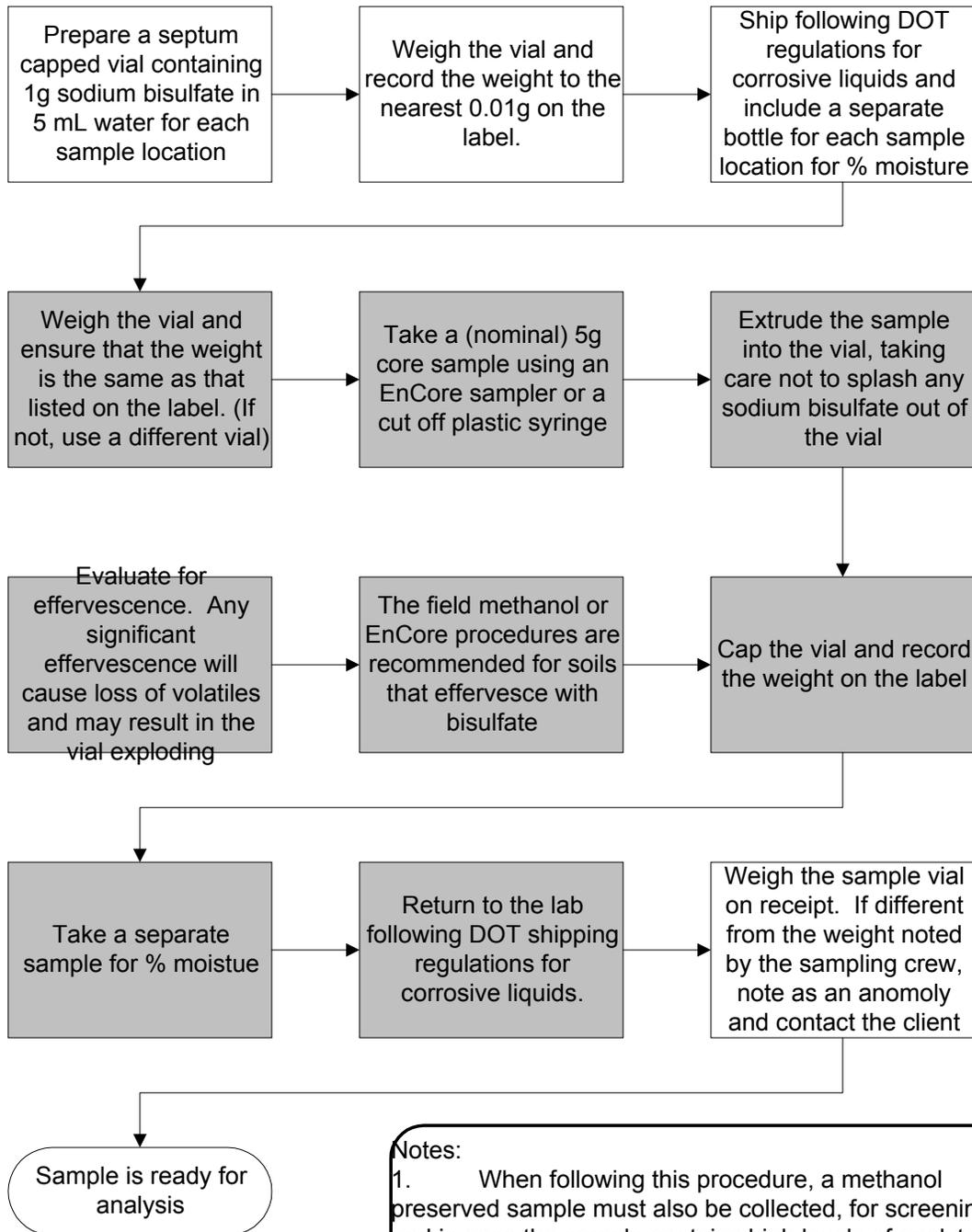
EnCore procedure when low level is required



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 reparation 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 re-preparation 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-Bromofluorobenzene (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
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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
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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 or 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 calibration. Target 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 ≥ 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 ≥ 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. $1/\text{Concentration}^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

- 10.7.8 If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.
- 10.7.9 A separate five point calibration must be prepared for analysis of low level soils. Low level soils analysis requires the use of a closed vial autosampler such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1 g sodium bisulfate, if using sodium bisulfate preservation or 5ml of water if freezing. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging. Medium soil extracts should be analyzed using the water (unheated) calibration curve.
- 10.7.10 Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation. However, if the analyte is not detected, the non-detect may be reported and no further action is necessary.
- 10.7.11 All ICALs will be verified by a second source standard, as per QA Directive 99-1, before being used.
- 10.8 Continuing Calibration: The initial calibration must be verified every twelve hours.
- 10.8.1 Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 3 calibration standard is used as the continuing calibration.
- 10.8.2 The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in equation 4, Section 12.3.4.
- 10.8.3 The % drift or % deviation of the CCCs must be $\leq 20\%$ for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 11. In addition, the % drift or % deviation of all analytes must be $\leq 50\%$ with allowance for up to six target analytes to have % drift or % deviation $> 50\%$.
- 10.8.3.1 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.
- 10.8.3.2 Cyclohexanone, one of the components of the Appendix IX standard, is unstable in the calibration solution, forming 1,1-dimethoxycyclohexane.

No calibration criteria are applied to cyclohexanone and quantitation is tentative. Cyclohexanone is included on the Universal Treatment Standard and FO-39 regulatory lists (but not on Appendix IX).

- 10.8.4 If the CCCs and or the SPCCs do not meet the criteria in Sections 10.5.3 and 10.5.4, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action such as a different type of column will require a new initial calibration.
- 10.8.5 Once the above criteria have been met, sample analysis may begin. **Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs.** Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 12 hours after the BFB is acceptable.)

11 PROCEDURE

11.4 Procedural Variations

- 11.4.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation shall be completely documented using a Nonconformance Memo and approved by a Supervisor or group leader and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.
- 11.4.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.5 Preliminary Evaluation

- 11.5.1 Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.
- 11.5.2 Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in volumetric flasks or in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 1 μL of sample then serial dilutions must be made in volumetric flasks.

11.5.2.1 The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.6 Sample Analysis Procedure

11.6.1 All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.6.2 All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, a LCS, and a method blank.

11.6.2.1 If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next tune period. However, if any re-tuning of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For medium level soils the batch is defined at the sample preparation stage.

11.6.2.2 Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

11.6.2.3 It is not necessary to reanalyze batch QC with reanalyses of samples. However, any reruns must be as part of a valid batch.

11.7 Water Samples

11.7.1 All samples and standard solutions must be at ambient temperature before analysis.

11.7.2 Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq 5 \mu\text{L}$. 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 $\mu\text{g}/\text{mL}$ 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 $\mu\text{g}/\text{L}$ solution for a 5 mL sample, and a 10 $\mu\text{g}/\text{L}$ 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 $\mu\text{g}/\text{mL}$ spiking solution. (Note that TCLP

reporting limits will be 10 times higher than the corresponding aqueous limits).

11.7.4 Purge the sample for eleven minutes (the trap must be $\leq 35^{\circ}\text{C}$).

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 5 μL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5 μL 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 5 μL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5 μL 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 be 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 $\pm 30\%$ 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

$$SD = \sqrt{\frac{\sum_{i=1}^N (X_i - X)^2}{N - 1}}$$

X_i = Value of X at i through N

N = Number of points

X = Average value of X_i

12.3.3 Percent relative standard deviation (%RSD):

Equation 3

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

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

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

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

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

12.3.6.2 Calculation of concentration using Linear fit

Equation 7

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

12.3.6.3 Calculation of concentration using Quadratic fit

Equation 8

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

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:

A_x = Area in the total ion chromatogram for the compound being measured

A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference

$RF = 1$

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

$$\text{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result

SR = Sample result

SA = Spike added

12.3.8 Relative % Difference calculation for the MS/MSD

Equation 13

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

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

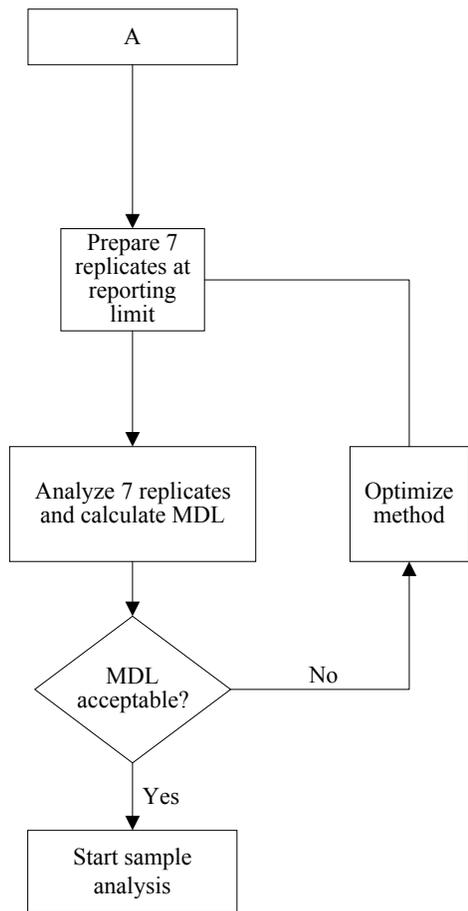
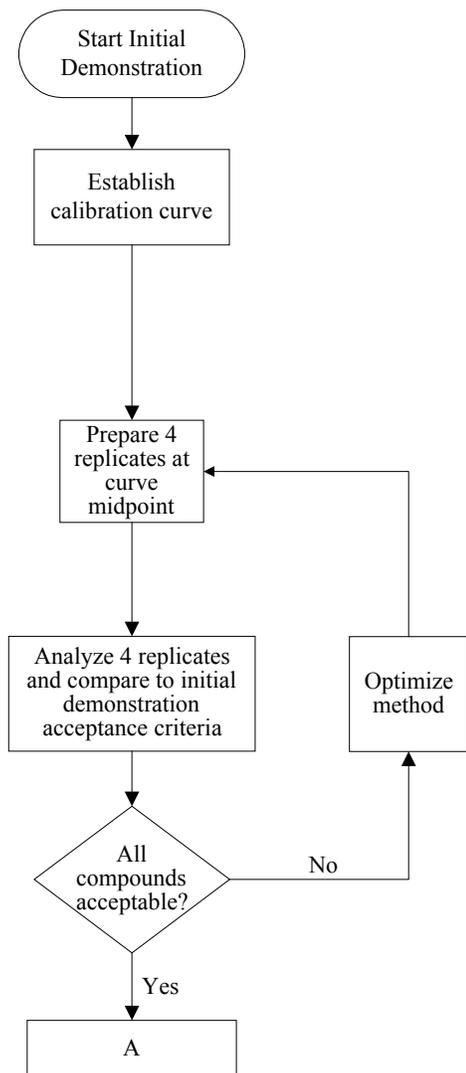


Table 1
STL Primary Standard and Reporting Limits

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	5	1	5	250
Chloromethane	74-87-3	5	1	5	250
Bromomethane	74-83-9	5	1	5	250
Vinyl chloride	75-01-4	5	1	5	250
Chloroethane	75-00-3	5	1	5	250
Trichlorofluoromethane	75-69-4	5	1	5	250
Acetone	67-64-1	20	10	20	1000
Trichlorotrifluoroethane	76-13-1	5	1	5	250
Iodomethane	74-88-4	5	1	5	250
Carbon disulfide	75-15-0	5	1	5	250
Methylene chloride	75-09-2	5	1	5	250
1,1-Dichloroethene	75-35-4	5	1	5	250
1,1-Dichloroethane	75-34-3	5	1	5	250
trans-1,2-Dichloroethene	156-60-5	5	1	5	250
Methyl <i>tert</i> -butyl ether (MTBE)	1634-04-4	20	5	20	1000
cis-1,2-Dichloroethene	156-59-2	5	1	5	250
1,2-Dichloroethene (Total)	540-59-0	5	1	5	250
Chloroform	67-66-3	5	1	5	250
1,2-Dichloroethane	107-06-2	5	1	5	250
Dibromomethane	74-95-3	5	1	5	250
2-Butanone	78-93-3	20	5	20	1000
1,1,1-Trichloroethane	71-55-6	5	1	5	250
Carbon tetrachloride	56-23-5	5	1	5	250
Bromodichloromethane	75-27-4	5	1	5	250
1,2-Dichloropropane	78-87-5	5	1	5	250
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250
Trichloroethene	79-01-6	5	1	5	250
Dibromochloromethane	124-48-1	5	1	5	250
1,2-Dibromoethane	106-93-4	5	1	5	250
1,2,3-Trichloropropane	96-18-4	5	1	5	250
1,1,2-Trichloroethane	79-00-5	5	1	5	250
Benzene	71-43-2	5	1	5	250
trans-1,3-Dichloropropene	10061-02-6	5	1	5	250
Bromoform	75-25-2	5	1	5	250
4-Methyl-2-pentanone	108-10-1	20	5	20	1000

Table 1
STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits ¹			
		5 mL Water µg/L	Low Levelwater µg/L	Low soil µg/kg	Med. Soil µg/kg
2-Hexanone	591-78-6	20	5	20	1000
Tetrachloroethene	127-18-4	5	1	5	250
Toluene	108-88-3	5	1	5	250
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250
1,1,1,2-Tetrachloroethane	630-20-6	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	5	1	5	250
Chlorobenzene	108-90-7	5	1	5	250
Ethylbenzene	100-41-4	5	1	5	250
Styrene	100-42-5	5	1	5	250
m and p Xylenes		10	2	10	500
o-xylene	95-47-6	5	1	5	250
Total xylenes	1330-20-7	15	3	15	750
1,3-Dichlorobenzene	541-73-1	5	1	5	250
1,4-Dichlorobenzene	106-46-7	5	1	5	250
1,2-Dichlorobenzene	95-50-1	5	1	5	250

¹ Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

Table 2
STL Primary Standard Calibration Levels, 5 mL purge¹

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 <i>tert</i> -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 purge¹

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 <i>tert</i> -butyl ether (MTBE)	1634-04-4					
cis-1,2-Dichloroethene	156-59-2	X		X		
Chloroform	67-66-3	X	X	X	X	X
1,2-Dichloroethane	107-06-2	X	X	X	X	X
Dibromomethane	74-95-3				X	X
2-Butanone	78-93-3	X	X	X	X	X
1,4-Dioxane	123-91-1				X	X
1,1,1-Trichloroethane	71-55-6	X		X	X	X
Carbon tetrachloride	56-23-5	X	X	X	X	X
Bromodichloromethane	75-27-4	X		X	X	X
1,2-Dichloropropane	78-87-5	X		X	X	X
cis-1,3-Dichloropropene	10061-01-5	X		X	X	X
Trichloroethene	79-01-6	X	X	X	X	X
Dibromochloromethane	124-48-1	X		X	X	X
1,2-Dibromoethane	106-93-4				X	X
1,2,3-Trichloropropane	96-18-4				X	X
1,1,2-Trichloroethane	79-00-5	X		X	X	X
Benzene	71-43-2	X	X	X	X	X

Table 5

Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Ethylmethacrylate	97-63-2				X	X
trans-1,3-Dichloropropene	10061-02-6	X		X	X	X
Bromoform	75-25-2	X		X	X	X
4-Methyl-2-pentanone	108-10-1	X		X	X	X
2-Hexanone	591-78-6	X		X	X	
Tetrachloroethene	127-18-4	X	X	X	X	X
Toluene	108-88-3	X		X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	X		X	X	X
2-Chloroethyl vinyl ether	110-75-8					
Vinyl acetate	108-05-4				X	
Chlorobenzene	108-90-7	X	X	X	X	X
Ethylbenzene	100-41-4	X		X	X	X
Styrene	100-42-5	X		X	X	
t-1,4-Dichloro-2-butene	110-57-6				X	
m and p Xylenes		X		X	X	X
o-xylene	95-47-6	X		X	X	X
Total xylenes	1330-20-7	X		X	X	X
1,3-Dichlorobenzene	541-73-1					
1,4-Dichlorobenzene	106-46-7					
1,2-Dichlorobenzene	95-50-1					

Table 6

Reportable Analytes for STL Standard Tests, Appendix IX standard

Compound	Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Allyl Chloride	107-05-1				X	
Acetonitrile	75-05-8				X	X
Chloroprene	126-99-8				X	
Propionitrile	107-12-0				X	
Methacrylonitrile	126-98-7				X	X
Isobutanol	78-83-1				X	X
Methyl methacrylate	80-62-6				X	X
1,1,1,2-Tetrachloroethane	630-20-6				X	X
1,2-Dibromo-3-chloropropane	96-12-8				X	X
Ethyl Acetate	141-78-6					X
Isopropylbenzene	98-82-8					

Table 7
Internal Standards

	Standard Concentration µg/mL	Quantitation ion (5 mL purge)	Quantitation ion (25 mL purge)
Fluorobenzene	25	96	96
Chlorobenzene-d5	25	119	119
1,4-Dichlorobenzene-d4	25	152	152

Notes:

- 1) 10 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L for a 5 mL purge or 10 µg/L for low level waters, Method 624 and Method 524.2.
- 2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 8
Surrogate Standards

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d ₄	25
Dibromofluoromethane	25
Toluene-d ₈	25
4-Bromofluorobenzene	25

Notes:

- 1) 10 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L for a 5 mL purge and 10 µg/L for low level SW846, Method 624 and Method 524.2.
- 2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.
- 3) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 9

Matrix Spike / LCS Compounds

Compound	Standard Concentration µg /mL
1,1-Dichloroethene	25
Trichloroethene	25
Toluene	25
Benzene	25
Chlorobenzene	25

Notes:

- 1) 10 µL of the standard is added to the LCS or matrix spiked sample. This results in a concentration of each spike analyte in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a low level SW846, Method 624 and 524.2.
- 2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by the QA department.

Table 10

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 11
SPCC Compounds and Minimum Response Factors

Compound	8260B Min. RF
Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	>0.100
1,1,2,2-Tetrachloroethane	0.300
Chlorobenzene	0.300

Table 12
CCC compounds

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	≤30.0	≤20.0
1,1-Dichloroethene	≤30.0	≤20.0
Chloroform	≤30.0	≤20.0
1,2-Dichloropropane	≤30.0	≤20.0
Toluene	≤30.0	≤20.0
Ethylbenzene	≤30.0	≤20.0

Table 13
Characteristic ions

Compound	Primary*	Secondary	Tertiary
1,2-Dichloroethane-d ₄ (Surrogate)	65	102	
Dichlorodifluoromethane	85	87	50, 101, 103
Chloromethane	50	52	49
Vinyl chloride	62	64	61
Bromomethane	94	96	79
Chloroethane	64	66	49
Trichlorofluoromethane	101	103	66
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141

Table 13
Characteristic ions

Compound	Primary*	Secondary	Tertiary
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Ethanol	45	46	
Acetone	43	58	
Methylene chloride	84	49	51, 86
tert-Butyl alcohol	59	74	
trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl tert butyl ether	73		
Hexane	57	43	
1,1-Dichloroethane	63	65	83
cis-1,2-Dichloroethene	96	61	98
2-Butanone	43	72**	
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121
Benzene	78	52	77
Trichloroethene	130	95	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d ₈ (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone	43	58	57, 100
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114

Table 13
Characteristic ions

Compound	Primary*	Secondary	Tertiary
2-Hexanone	43	58	57, 100
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133
Allyl Chloride	76	41	78
Acetonitrile	40	41	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52
Isobutanol	41	43	74
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo-3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	

* The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.

** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

18 SUMMARY

This appendix lists modifications to the main body of the SOP that are necessary for analysis of drinking water by method 524.2.

18.1 A target analyte list based on the list in method 524.2 is frequently requested for analysis by method 8260B. STL's standard analyte list for this test, and the internal and surrogate standards used, are listed in Tables A-1 to A-2 below. In all other respects the method is as described in the main body of this SOP.

19 MODIFICATIONS REQUIRED FOR DRINKING WATER ANALYSIS BY METHOD 524.2

19.1 This method can be applied to surface water, ground water and drinking water.

19.2 Sample concentrations are calculated using initial calibration curve.

19.3 Three internal standards (see SW846) are used for this method.

19.4 A maximum of 25 ng of BFB is used for tuning for method 524.2

19.5 BFB tuning criteria for mass 75 are 30-80% of mass 95.

19.6 The recovery limits for the initial demonstration of capability are 80-120% with %RSD less than 20%.

19.7 Initial calibration curve requirements:

19.7.1 The number of calibration standards depends on the calibration range used. For a range of up to a factor of 20 (e.g. 1µg/L - 20µg/L) a minimum of three standards are necessary. For a factor of up to 50 four standards are necessary, and for a factor of up to 100 five standards are necessary.

19.7.2 All target compounds must have $RSD \leq 20\%$.

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 $\%D \leq 30\%$.

- 19.8.2 The internal standards in each CCV must be over 70% of the abundance found in the CCV analysis immediately preceding it *and* over 50% of the calibration point in the initial calibration curve whose concentration matches that of the CCV.
- 19.8.3 The same analysis run may be used to satisfy the requirements for an LCS (also known as a laboratory fortified blank, LFB) and a continuing calibration verification. The LCS/CCV does not need to be a second source standard.
- 19.9 Method clarifications, modifications and additions
- 19.9.1 Section 7.1 requires that the trap packing materials be Tenax GC, Methyl silicone, silica gel and coconut charcoal. STL routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.
- 19.9.2 Section 7.8.2 of the source method requires that each calibration standard be prepared by diluting the appropriate volume of the working standard with organic-free water adjusted to pH < 2 in a volumetric flask. STL prepares calibration standards by diluting the the appropriate volume of the working standard with organic-free water in the gas-tight syringe that will be used to inject the sample into the purge and trap device.
- 19.9.3 Sections 9.8 and 9.9 of the source method require that duplicate spiked blanks and a second-source initial calibration verification standard be analyzed at least quarterly. Since some STL laboratories do not normally analyze drinking waters samples, these QC samples will be analyzed only during the conduct of projects that require this method.
- 19.9.4 If drinking water samples are to be analyzed, a 0.5 ppb standard will be run that day to confirm that this level can be seen by the instrument.

Table A-1

STL 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limit ²	Reporting Limits ¹			
			5 mL water µg/L	Low level water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	1	5	1	5	500
Chloromethane	74-87-3	1	5	1	5	500
Bromomethane	74-83-9	1	5	1	5	500
Vinyl chloride	75-01-4	1	5	1	5	500
Chloroethane	75-00-3	1	5	1	5	500
Trichlorofluoromethane	75-69-4	1	5	1	5	500
Acetone ¹	67-64-1	10	20	10	20	1000
Methylene chloride	75-09-2	1	5	2	5	250
1,1-Dichloroethene	75-35-4	1	5	1	5	250
1,1-Dichloroethane	75-34-3	1	5	1	5	250
trans-1,2-Dichloroethene	156-60-5	1	5	1	5	250
Methyl <i>tert</i> -butyl ether (MTBE) ¹	1634-04-4	1	20	5	20	250
2,2-Dichloropropane	590-20-7	1	5	1	5	250
cis-1,2-Dichloroethene	156-59-2	1	5	1	5	250
1,2-Dichloroethene (Total)	540-59-0	1	5	1	5	250
Chloroform	67-66-3	1	5	1	5	250
Bromochloromethane	74-97-5	1	5	1	5	250
1,2-Dichloroethane	107-06-2	1	5	1	5	250
Dibromomethane	74-95-3	1	5	1	5	250
2-Butanone ¹	78-93-3	5	20	5	20	1000
1,1,1-Trichloroethane	71-55-6	1	5	1	5	250
Carbon tetrachloride	56-23-5	1	5	1	5	250
1,1-Dichloropropene	563-58-6	1	5	1	5	250
Bromodichloromethane	75-27-4	1	5	1	5	250
1,2-Dichloropropane	78-87-5	1	5	1	5	250
1,3-Dichloropropane	142-28-9	1	5	1	5	250
cis-1,3-Dichloropropene	10061-01-5	1	5	1	5	250
Trichloroethene	79-01-6	1	5	1	5	250
Dibromochloromethane	124-48-1	1	5	1	5	250
1,2-Dibromoethane	106-93-4	1	5	1	5	250
1,2,3-Trichloropropane	96-18-4	1	5	1	5	250
1,1,2-Trichloroethane	79-00-5	1	5	1	5	250
Benzene	71-43-2	1	5	1	5	250
trans-1,3-Dichloropropene	10061-02-6	1	5	1	5	250
Bromoform	75-25-2	1	5	1	5	250

Table A-1

STL 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limit ²	Reporting Limits ¹			
			5 mL water µg/L	Low level water µg/L	Low soil µg/kg	Med. Soil µg/kg
4-Methyl-2-pentanone ¹	108-10-1	5	20	5	20	1000
2-Hexanone ¹	591-78-6	5	20	5	20	1000
Tetrachloroethene	127-18-4	1	5	1	5	250
Toluene	108-88-3	1	5	1	5	250
1,1,2,2-Tetrachloroethane	79-34-5	1	5	1	5	250
Chlorobenzene	108-90-7	1	5	1	5	250
1,1,1,2-Tetrachloroethane	630-20-6	1	5	1	5	250
Ethylbenzene	100-41-4	1	5	1	5	250
Styrene	100-42-5	1	5	1	5	250
m and p Xylenes		2	10	2	10	500
o-xylene	95-47-6	1	5	1	5	250
Total xylenes	1330-20-7	3	15	3	15	750
Isopropylbenzene	98-82-8	1	5	1	5	250
Bromobenzene	108-86-1	1	5	1	5	250
n-Propylbenzene	103-65-1	1	5	1	5	250
2-Chlorotoluene	95-49-8	1	5	1	5	250
4-Chlorotoluene	106-43-4	1	5	1	5	250
1,3,5-Trimethylbenzene	108-67-8	1	5	1	5	250
tert-Butylbenzene	98-06-6	1	5	1	5	250
1,2,4-Trimethylbenzene	95-63-6	1	5	1	5	250
sec-butylbenzene	135-98-8	1	5	1	5	250
1,3-Dichlorobenzene	541-73-1	1	5	1	5	250
1,4-Dichlorobenzene	106-46-7	1	5	1	5	250
1,2-Dichlorobenzene	95-50-1	1	5	1	5	250
4-Isopropyltoluene	99-87-6	1	5	1	5	250
n-Butylbenzene	104-51-8	1	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	1	5	1	5	250
1,2,4-Trichlorobenzene	120-82-1	1	5	1	5	250
Napthalene	91-20-3	1	5	1	5	250
Hexachlorobutadiene	87-68-3	1	5	1	5	250
1,2,3-Trichlorobenzene	87-61-6	1	5	1	5	250

1 Not included on the method 524.2 analyte list, but included in the calibration standard as an add on frequently requested by method 8260B. These Reporting Limits are for Method 8260B.

2 These Reporting Limits are for Method 524.2.

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 \leq 35%.
- 20.7.2 If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.
- 20.7.3 For compounds not listed in Method 624, the average response factor will be used.
- 20.8 Continuing calibration verification requirements:
- 20.8.1 The continuing calibration standard is from a different source than the initial calibration standard. The acceptance criteria are listed in Table B-2.
- 20.9 MS/MSD and LCS requirements
- 20.9.1 The LCS, MS and MSD will be 10ppb for all compounds except, 2CEVE (20ppb), Acrolein (30ppb) and Acrylonitrile (30ppb). . The recovery limits for MS/MSD and LCS recovery are listed in Table B-2.

20.10 Method clarifications, modifications and additions

20.10.1 Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. STL routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

20.10.2 Section 5.3.2 of the source method describes a packed analytical column. STL routinely employs capillary columns when performing this method.

20.10.3 The source method provides a suggested list of compounds for internal and surrogate standards. STL uses the same internals and surrogates found in SW846 Method 8260B (See Tables 7 and 8).

Table B-1.
Method 624 Analytes and Reporting Limits

Analytes	µg/L
Benzene	1
Bromodichloromethane	1
Bromoform	1
Bromomethane	1
Carbon tetrachloride	1
Chlorobenzene	1
Chloroethane	1
2-Chloroethyl vinyl ether	2
Chloroform	1
Chloromethane	1
Dibromochloromethane	1
1,2-Dichlorobenzene	1
1,3-Dichlorobenzene	1
1,4-Dichlorobenzene	1
1,1-Dichloroethane	1
1,2-Dichloroethane	1
1,1-Dichloroethene	1
trans-1,2-Dichloroethene	1
1,2-Dichloropropane	1
cis-1,3-Dichloropropene	1
trans-1,3-Dichloropropene	1
Ethylbenzene	1
Methylene chloride	1
1,1,2,2-Tetrachloroethane	1
Tetrachloroethene	1
Toluene	1
1,1,1-Trichloroethane	1
1,1,2-Trichloroethane	1
Trichloroethene	1
Trichlorofluoromethane	1
Vinyl chloride	1

Table B-2.
Method 624 QC Acceptance Criteria

Analytes	Daily QC Chk acceptance criteria %Recovery	Mean recovery, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Standard deviation, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Matrix spike acceptance criteria (% Recovery)
Benzene	64-136	15.2-26.0	6.9	37-151
Bromodichloromethane	65-135	10.1-28.0	6.4	35-155
Bromoform	71-129	11.4-31.1	5.4	45-169
Bromomethane	14-186	D-41.2	17.9	D-242
Carbon tetrachloride	73-127	17.2-23.5	5.2	70-140
Chlorobenzene	66-134	16.4-27.4	6.3	37-160
Chloroethane	38-162	8.4-40.4	11.4	14-230
2-Chloroethyl vinyl ether	0-224	D-50.4	25.9	D-305
Chloroform	67-133	13.7-24.2	6.1	51-138
Chloromethane	0-204	D-45.9	19.8	D-273
Dibromochloromethane	67-133	13.8-26.6	6.1	53-149
1,2-Dichlorobenzene	63-137	11.8-34.7	7.1	18-190
1,3-Dichlorobenzene	73-127	17.0-28.8	5.5	59-156
1,4-Dichlorobenzene	63-137	11.8-34.7	7.1	18-190
1,1-Dichloroethane	72-128	14.2-28.5	5.1	59-155
1,2-Dichloroethane	68-132	14.3-27.4	6.0	49-155
1,1-Dichloroethene	50-150	3.7-42.3	9.1	D-234
trans-1,2-Dichloroethene	69-131	13.6-28.5	5.7	54-156
1,2-Dichloropropane	34-166	3.8-36.2	13.8	D-210
cis-1,3-Dichloropropene	24-176	1.0-39.0	15.8	D-227
trans-1,3-Dichloropropene	50-150	7.6-32.4	10.4	17-183
Ethylbenzene	59-141	17.4-26.7	7.5	37-162
Methylene chloride	60-140	D-41.0	7.4	D-221
1,1,2,2-Tetrachloroethane	60-140	13.5-27.2	7.4	46-157
Tetrachloroethene	73-127	17.0-26.6	5.0	64-148
Toluene	74-126	16.6-26.7	4.8	47-150
1,1,1-Trichloroethane	75-125	13.7-30.1	4.6	52-162
1,1,2-Trichloroethane	71-129	14.3-27.1	5.5	52-150
Trichloroethene	66-134	18.6-27.6	6.6	71-157
Trichlorofluoromethane	48-152	8.9-31.5	10.0	17-181
Vinyl chloride	4-196	D-43.5	20.0	D-251