VOLATILE ORGANIC ANALYSIS IN WATER BY GC/MS
(EPA/SW-846 Method 8000B and 8260B)

CONTENTS

CONTENTS (cont)

* These sections affected by Revision 2.0

SUPERCEDES: SOP #1806; Revision 1.0; 09/08/05; U.S. EPA Contract EP-W-09-031.

VOLATILE ORGANIC ANALYSIS IN WATER BY GC/MS
(EPA/SW-846 Method 8000B and 8260B)

1.0 SCOPE AND APPLICATION

The objective of this Standard Operating Procedure (SOP) is to provide the requirements for the routine gas chromatographic/mass spectrometric (GC/MS) analysis of volatile organic compounds (VOCs) in water samples from environmental sites. This method is based on Environmental Protection Agency (EPA) Methods SW846/8000B and 8260B and those requirements set forth in the latest approved version of the National Environmental Laboratory Accreditation Committee (NELAC) Quality Systems section. A list of target compounds routinely analyzed by the Scientific, Engineering Response and Analytical Services (SERAS) Laboratory and the corresponding reporting limits (RLs) are provided in Table 1, Appendix A.

This method can be used to identify and quantify most VOCs with boiling points below 200 degrees Centigrade (^{o}C) and are insoluble or slightly soluble in water. Such compounds include low molecular weight halogenated hydrocarbons, aromatic compounds, ketones, ethers, and carbon disulfide.

This method may not be changed without the expressed approval of the Organic Group Leader, the Analytical Section Leader and the Quality Assurance Officer (QAO). Only those versions issued through the SERAS document control system may be used. Modifications made to the procedure due to interferences in the samples or for any other reason must be documented in the case narrative.

2.0 METHOD SUMMARY

VOCs, surrogates, and internal standards with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through a 5-milliliter (mL) sample in a sparging tube that is connected to a concentrator. The inert gas bubbling through the solution at ambient temperature effectively transfers the purgeable VOCs from the aqueous phase to the vapor phase. The vapor is then swept through a three sorbent bed trap where the VOCs are trapped. When purging is complete, the sorbent trap is heated and back flushed with helium to desorb the trapped target analytes onto a GC capillary column interfaced to a MS. The GC column is temperature programmed to separate the target analytes, which are detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a database. Reference spectra and retention times for analytes are obtained from the measurement of calibration standards under the same GC/MS operating conditions used for water samples. The concentration of each identified analyte is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound used as an internal standard. Surrogate compounds, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

3.1 Sample Storage

Samples must be collected in 40-mL Teflon-lined septum vials. The samples must be protected from light and refrigerated at 4°C (± 2°C) from the date and time of collection until analysis. VOC samples must be kept separate from standards to reduce any potential contamination in a dedicated refrigerator. All samples must be kept refrigerated for the periods specified by the SERAS Task Leader (TL) or ERT Work Assignment Manager (WAM).

3.2 Holding Times

The analysis of water samples for VOCs at SERAS must be completed within seven days of sample collection since hydrochloric acid (HCl) is not used by SERAS personnel to preserve VOC samples. If samples are received with 1+1 HCl added to reduce the pH to less than (<) 2, the holding time may be extended to 14 days from date of collection before any qualifiers are applied to the data.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be contaminant free by analyzing laboratory blanks. The use of non-Teflon tubing, non-Teflon thread sealants or flow controllers with rubber components in the purging device is not allowed.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons, acetone, and methylene chloride) through the septum seal into the sample during storage and handling. A field blank prepared from commercially available water suitable for VOC analysis and carried through sample collection, shipment, and storage serves as a check on such contamination.

Carryover contamination may occur when samples containing high levels of target and non-target compounds are analyzed. This contamination can be reduced by rinsing the autosampler syringe, the concentrator sparger and sampling lines with hot water. If an unusually concentrated sample is analyzed, the sorbent trap may be baked for approximately 10 minutes and water blanks are analyzed. If contamination still persists, manufacturer purge and trap concentrator and/or GC/MS system bakeout suggestions are implemented.

The laboratory where VOC analysis is performed should be completely free of solvents. Any solvents, or solvent waste containers, used or stored in the laboratory during the analysis must be kept in a vented hood or vented storage area.

5.0 EQUIPMENT/APPARATUS

- Micro syringes, 10-microliter (µL) and larger, 0.006 inch inner diameter (ID) needle

- Syringes, 5, 10, and 25-mL, gas tight with Luer end

- Glassware
  - Vials - 40-mL, screw cap, with Teflon- lined septum
  - Volumetric flasks - Class A with ground-glass stopper
  - Vials - 2-mL with screw caps with Teflon-lined septum
  - Inserts - 15-mL glass with O-ring for 40-mL vial

- Purge and trap device, consisting of Tekmar 3000 Concentrator and ARCHON autosampler system, or equivalent. Both units are commercially available and meet required specifications.

- VOCARB 3000 adsorbent trap, Supelco Catalog Number (No.) 2-4920 -U or equivalent, used in the Tekmar 3000 Concentrator system containing three 60/80 mesh adsorbent beds [Carbopack B (10-centimeter [cm] granular graphitized carbon), Carboxen-1000 (6-cm spherical porous carbon) and Carboxen-1001 (1-cm spherical porous carbon)]. For initial conditioning, bake trap at 260 to 270°C for one hour prior to use.

- Hewlett-Packard (HP) 6890 GC/5973 MS, interfaced with a HP CHEM STATION data system or equivalent

- Restek Rtx-Volatiles capillary column, 30 meters (m) long, 0.25 millimeter (mm) ID, and 3.0 micron (µm) film thickness or equivalent

6.0 REAGENTS

- Purge water, commercially available, suitable for VOC analysis

- Methanol, purge and trap quality

- Calibration Stock VOC Standard Solution, 250 micrograms per milliliter (µg/mL), available commercially (Accustandard Product S-4821or equivalent), consisting of 64 individual compounds (Table 1, Appendix A).

  Alternatively, the stock standard solution may be prepared from standard mixtures and individual compounds, which are commercially available. All mixtures are combined based on their concentrations to give a final concentration of 250 µg/mL.

- Surrogate/Internal Standard Solution, commercially available (Accustandard QCLP-PIPS-0.1X or equivalent), consisting of three internal standard (Bromochloromethane, Chlorobenzene-d_5, and 1,4-Difluorobenzene) and three surrogate (1,2-Dichloroethane-d_4, Toluene-d_8, and 4-

Bromofluorobenzene) compounds each at 250 µg/mL in methanol.

- Matrix Spike (MS) Stock Solution, commercially available (Supelco No. 4-8399 or equivalent), consisting of the following compounds each at 2500 µg/mL in methanol:

1,1-Dichloroethene	Toluene
Trichloroethene	Benzene
Chlorobenzene	

This solution must be a different source from that used for calibration.

- MS Intermediate Solution, 250 µg/mL - Prepare a 1:10 dilution in methanol.

- MS Working Solution, 25 µg/mL - the 250 µg/mL intermediate solution, prepare a 10-fold dilution in methanol. If stock or intermediate solutions of different concentration levels are used, appropriate dilutions must be made to give a final working solution of 25 µg/mL in methanol.

- 4-Bromofluorobenzene (BFB) Standard, 250 µg/mL, commercially available in methanol and must be diluted to the level of 50 µg/mL. Alternatively, the 250 µg/mL surrogate and internal standard, which contains 4-BFB, can be used.

- Laboratory Control Sample (LCS) - With each batch of twenty samples, prepare a LCS at a concentration of 50 micrograms per liter (µg/L) using the second source MS stock standard. On a quarterly basis, prepare a LCS from a second source stock standard containing all of the target compounds at a concentration of 50 µg/L.

- Helium, ultra high purity (99.999%)

- Defoamer solution, commercial antifoam solution

NOTE: All of the above mentioned standard solutions must be stored at -4°C to -10°C (freezer section of the standards refrigerator) in tightly capped vials with Teflon liners. Commercially prepared standard solutions that are received in sealed ampoules may be stored in the shelf section of the standards refrigerator. Fresh mixtures should be prepared when the percent drift of the gases and/or any other compounds (e.g., ketones) in the working standard mixture change by more than 20 percent (%) or at least every six months.

NOTE: Premixed certified standards will be stored according to the manufacturer's documented storage requirements. These standards may be kept in storage up to the manufacturer's stated expiration date. Once the standard vials are opened, the standards will be stored with minimal headspace in the freezer for a period not to exceed six months or the manufacturer's expiration

date, whichever is less.

NOTE: All calibration standards, surrogates, internal standards, and spiking solutions will be prepared and documented in accordance with SERAS SOP #1012, *Preparation of Standard Solutions and Reagents.*

7.0 PROCEDURE

7.1 GC/MS Operating Conditions

The following GC/MS operating conditions are recommended:

Mass Spectrometer/Data System, HP 5973 MS, equipped with a HP CHEM STATION data system. The conditions of the Electron Impact Ionization mass spectrometer are:

Electron Energy:	70 volts (nominal)
Mass Range:	35 - 350 atomic mass units (amu)
Scan Time:	To give at least 5 scans per peak and not to exceed 3 seconds per can.

Gas Chromatograph/Capillary GC column, HP 6890 GC equipped with a 30 m x 0.25 mm ID, Rtx-Volatiles (Restek Corp.) capillary column with 3.0-µm film thickness using helium carrier gas at a flow rate of 1.0 mL/minute (min). The column temperature is isothermal at 40 °C for 4 minutes, then programmed to ramp at 9°C per minute to 165°C and held for 2 minutes, then ramped at 12°C per minute to 220°C and held for 7 minutes. Inlet temperature is 150°C. Source temperature is set according to manufacturer's specifications (230 °C). Total run time is approximately 31 minutes.

GC/MS Interface, capillary direct with 1 mL/min helium carrier gas at 250 °C.

Purge and Trap Unit, Tekmar 3000 concentrator equipped with an ARCHON Autosampler. The purge and trap conditions are:

Purge - 10 min at 35°C	Dry Purge - 2 min at ambient
Desorb - 4 min at 250°C	Desorb preheat at 245 °C
Purge Flow Rate - 40 mL/min	Bake - 10 min at 260°C

7.2 Bromofluorobenzene Tune

The autosampler adds 1 µL of the BFB solution to a 5-mL aliquot of reagent water. This mixture (50 ng BFB) is purged and analyzed. The ion abundance criteria can be found in Table 2, Appendix A. The tune is acquired using either the apex or ± one scan. Background subtraction is required and must be accomplished using a single scan no more than 20 scans

prior to the elution of the BFB. The BFB tune criteria must be met every 12 hours during sample analysis. If the software does not indicate what scan was subtracted, the analyst will document the scan number directly on the tune report.

7.3 Initial Calibration

1. Add 1 µL, 4 µL, 10 µL, 20 µL, 30 µL, and 40 µL of the 250 µg/mL calibration intermediate standard solution into 50-mL aliquots of commercially available water respectively, to prepare the initial calibration standards. This will result in a calibration curve of 5, 20, 50, 100, 150, and 200 µg/L. Add a sufficient volume of methanol to bring the total volume in each of the standards up to 40 µL.

2. The autosampler adds 1 µL of the surrogate/internal standard mixture (250 µg/mL) to each 5-mL aliquot of the calibration standards, resulting in a final concentration of 50 µg/L for each surrogate and internal standard. Purge and analyze each of the initial calibration standards using an ambient purge.

3. Calculate and tabulate the relative response factor (RRF) against the concentration for each compound, including the surrogates, by using the equation below. The primary ion from the specific internal standard must be used for quantitation. The average RRF and percent relative standard deviation (%RSD) must also be calculated and tabulated.

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

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 internal standard (µg/L)
C_x = Concentration of the compound to be measured (µg/L)

$$RRF = \frac{\sum_{i=} RF_i}{n}$$

where:

RRF_i = relative response factor for each initial calibration level
N = total number of initial calibration levels

$$\%RSD = \frac{SD}{\bar{X}} x\ 100$$

$$SD = \sqrt{\frac{\sum_{i=} \quad - \quad ^{2}}{N - \ '}}$$

where:

N = 6 (number of calibration standards used)
X = average RRF
X = individual RRF
SD = standard deviation

The criteria for the average RRF and %RSD for each target analyte are found in Section 9.2.

7.4 Continuing Calibration

A check of the initial calibration curve must be performed every 12 hours after an acceptable BFB analysis. Sample analysis may begin only after a successful BFB tune and a continuing calibration check have been acquired..

1. Add 10 µL of the 250 µg/mL calibration stock standard solution into a 50-mL aliquot of reagent water to prepare the continuing calibration standard.

2. The autosampler adds 1 µL of the surrogate/internal standard mixture (250 µg/mL) into a 5-mL aliquot of the continuing calibration standard. Purge and analyze the continuing calibration standard using an ambient purge.

3. Calculate and tabulate the continuing calibration RRF for each compound.

4. Calculate the percent difference (%D) for the continuing calibration RRF compared to the average RRF from the initial calibration curve.

$$\%D = \frac{RRF_{Continuing} - RRF_{Average}}{RRF_{Average}} x\ 100$$

The criteria for the continuing RRF and %D are found in Section 9.3.

5. The extracted ion current profile (EICP) area for each internal standard in the continuing calibration must be compared to the internal standard area in the mid-point

standard of the current initial calibration. The criterion for comparison is found in section 9.3.

7.5 Sample Analysis

Prior to the analysis of calibration standards, blanks, and/or samples, it is necessary to verify that the GC/MS:

- Met the BFB ion abundance criteria listed in Table 2, Appendix A and in Section 9.1. The BFB tune criteria must be demonstrated every 12 hours by analyzing 50 ng of BFB.

- Successfully passed an initial six-point calibration and/or continuing calibration check. The continuing calibration check must be demonstrated every 12 hours during sample analysis by analyzing a 50 µg/L VOC standard.

Sample foaming check - All samples should be tested for foaming before loading into the autosampler. This is done to avoid foaming problems during the purging sequence. Pour approximately 5-10 mL of sample into an empty 40-mL vial and shake vigorously. Check for foaming. If no foaming exists, analyze a aliquot from a full vial. If foaming persists, add several drops of defoamer solution to the sample aliquot and shake again. Repeat addition of defoamer solution (up to 10 drops total) until no foaming is observed after shaking. To prepare a sample that foams for analysis, add the appropriate amount of defoamer to a 15-mL VOA vial insert and fill with sample. Seal the vial and continue with the analysis sequence below.

The method blanks, LCS, MS/matrix spike duplicate (MSD) and samples must be analyzed with the same instrument conditions used for the calibration standards. Load all samples into the ARCHON autosampler and use the water autosampler method (ambient purge). The analyses are carried out in the following sequence:

1. Method Blank(s) - Fill a 40-mL vial with commercially available water and seal. Check the vial for air bubbles by inverting the vial. If air bubbles are present, refill the vial and check again.

2. Undiluted Sample - Load the 40-mL sample vial or vial with 15-mL insert into the autosampler.

3. Diluted Sample - If the analyst has reason (e.g., history or screening result) to believe that diluting the sample will be necessary, an undiluted run may not be required. If a target analyte exceeds the linear calibration range, use the appropriate dilution factor needed to bring the concentration within range. Ideally, the concentration of the analyte should fall between midrange and the upper range of the curve after dilution. Dilutions may be done using the autosampler dilution function or manually.

4. MS/MSD Samples - Spike 30 µL of the working MS solution (25 µg/mL) to 15 mL of a selected sample in duplicate for MS/MSD analysis. For water samples that require dilution, use appropriate diluted sample aliquots for the MS/MSD. Alternatively, spike 10 µL of MS intermediate solution (250 µg/mL) to 50 mL of sample.

5. LCS - Spike 30 µL of the matrix spike working solution (25 µg/mL) to 15 mL of commercially available water for the LCS analysis using a 15-mL insert vial. Alternatively, spike 10 µL of MS intermediate solution (250 µg/mL) to 50 mL of commercially available water and transfer to a 40-mL vial.

7.6 Identification of Target Compounds

Target compound identification will be made by comparison of the sample mass spectrum to the mass spectrum of a standard of the target compound. Two criteria must be satisfied to verify the identification:

- Elution of the sample component at the same GC relative retention time as the standard component
- Correspondence of the sample component and standard component mass spectra

1. For establishing correspondence of the GC relative retention times (RRTs), the sample component RRTs must compare within ± 0.06 RRTs units of the RRTs of the standard component. For reference, the calibration standard must be analyzed within the same 12-hour time period as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRTs from the total ion chromatogram, the RRTs should be assigned by using extracted ion current profiles for ions unique to the component of interest.

2. For comparison of standard and sample component mass spectra, reference mass spectra must be obtained from the analysis of the 50 µg/L calibration standard. These standard spectra may be obtained from the calibration run used to obtain reference RRTs and daily relative response factors.

3. The requirements for qualitative verification by comparison of mass spectra are as follows:

   a. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. Characteristic ions from reference mass spectra are the two or three ions of greatest intensity.

b. The relative intensities of ions specified in (a) must agree within ± 20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70%).

c. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the reporting limits, report the actual value followed by "J", e.g., "3J".

4. If a compound cannot be verified by all of the criteria in Step 3, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the analyst shall report that identification and proceed with calculation in Section 8.0. The analyst should report in the case narrative that technical judgment was utilized.

7.7 Library Search

A library search will be performed for non-target compounds present in the method blank and the samples for the purpose of tentative identification. The 1998 release of the NIST/EPA/NIH Mass Spectral Library (NIST98.L) containing more than 100,000 spectra will be used.

1. Any non-surrogate organic compounds not listed in Table 1, Appendix A shall be tentatively identified via a forward search of the NIST/EPA/NIH mass spectral library. Substances with responses less than 10% of the nearest internal standard are not required to be searched. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

NOTE: Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

2. Guidelines for making tentative identification:

- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

- The relative intensities of the major ions should agree within ± 20% between the standard and sample spectra. For example, if an ion has an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30

and 70%.

- Molecular ions present in reference spectrum should be present in sample spectrum.

- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of chelating compounds.

- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co eluting compounds.

NOTE: Data system library reduction programs can sometimes create these discrepancies.

3. If all the above conditions for a compound are met and if the Q value of the search is ≥80%, that compound will be reported as a tentatively identified compound (TIC). If the Q value is <80% or the mass spectral interpretation specialist indicates that no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid, and unknown chlorinated compound). If probable molecular weights can be distinguished, include them on the TIC report. Report only one type of unknown compound per retention time (RT). Do not report carbon dioxide (CO_2), target compounds, internal standards or surrogates as a TIC.

8.0 CALCULATIONS

8.1 Target Compounds

Identified target analytes must be quantitated by the internal standard method. The internal standard used must be the one nearest the retention time to that of a given analyte listed in Table 3, Appendix A. The extracted ion current profile (EICP) area of the characteristic ion of each target analyte listed in Table 4, Appendix A is used for quantitation.

Use the following equation to calculate the concentration of the identified analytes using the average relative response factor (RRF) obtained from the initial calibration as described in Section 7.3.

A compound concentration will be calculated using the formula:

$$Concentration\ (\mu g/L) = \frac{(A_C)(I_{IS})(DF)}{(A_{IS})(RRF_{avg})(V_O)}$$

where:

C_c = Compound concentration in µg/L
A_c = Area of the characteristic ion for the compound
I_{is} = Amount of internal standard in nanograms (ng)
DF = Dilution factor
A_{is} = Area of the characteristic ion for the internal standard
RRF_{avg} = Average Relative Response Factor from the water (ambient) purge
V_0 = Volume of water purged in milliliters (mL)

The following EPA-defined flags will be used in the lab to qualify data:

U: This flag indicates that the compound was analyzed for but not detected

J: This flag indicates an estimated value under the sample RL. Any concentration less than 25% of the RL will not be reported

B: This flag is used when the analyte is found in the associated method blank as well as in the sample

E: This flag identifies compounds whose concentrations exceed the upper calibration range of the instrument

All target concentrations are reported to three significant figures. For any concentrations reported from diluted runs, be sure to report the corresponding RL. For example, if a compound is run at a 10x dilution to bring the concentration within linear range, the RL must be reported at 50 µg/L instead of 5 µg/L.

8.2 Tentatively Identified Compounds

An estimated concentration for tentatively identified compounds (TICs) must be calculated by the internal standard method. The nearest preceding internal standard free of interferences must be used. The equation for calculating the concentration is the same as in Section 8.1, except that area count or peak height of the TICs and their assigned internal standards from the total ion chromatogram is used for calculation. The RRF of both is assumed to be 1.0. All non-target concentrations are reported to one significant figure for concentrations less than 10 and two significant figures for all concentrations greater than or equal to 10.

8.3 Surrogate Spike Recoveries

Calculate surrogate standard recovery on all samples, blanks, and spikes by the following equation:

$$Percent\ Recovery\ (\%R) = \frac{Q_D}{Q_A}\ x\ 100$$

where:

Q_D = Quantity determined by analysis
Q_A = Quantity added to sample

8.4 Matrix Spike Recoveries

Accuracy is calculated from the recovery of the MS/MSDs. Precision is calculated from the relative percent difference (RPD) of the recoveries measured for the MS/MSD pair. Matrix spike recoveries and RPD will be calculated by the following equations:

$$Matrix\ Spike Recovery (\%R) = \frac{SSR - SR}{SA}\ x\ 100$$

where:

SSR = Concentration of target analyte in spike sample (spiked)
SR = Concentration of target analyte in sample (unspiked)
SA = Concentration of spike added

and

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

where:

RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

Note: RPD is always expressed as a positive value.

8.5 Laboratory Control Sample Recoveries

The recoveries of each of the compounds in the LCS solution will be calculated using the following equation:

$$Laboratory\ Control\ Sample\ Recovery\ (\%R) = \left(\frac{LCSR - B}{SA} \right) x\ 100$$

where:

LCSR = Concentration of target analyte in LCS
B = Concentration of target analyte in blank
SA = Concentration of spike added

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 GC/MS Tuning and Performance Criteria

The GC/MS must be tuned with BFB and the ion abundance criteria listed in Table 2, Appendix A must be met prior to any standard, blank or sample analysis. In addition, the criteria must be achieved during every 12-hour period during which standards, blanks, and samples are analyzed. The 12-hour time period for GC/MS tuning begins at the time of injection of the BFB analysis that the laboratory submits as documentation of a compliant tune.

9.2 GC/MS Initial Calibration

A minimum mean response factor for the following volatile system performance check compounds (SPCCs) must be met:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

All other compounds must meet a minimum mean RF of 0.05.

The %RSD should be less than or equal to 15% for each target analyte with the exception of the calibration check compounds (CCCs). The %RSD for the CCCs must be equal to or less than 30% for the following compounds:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

Corrective action must be taken if any of the CCCs or SPCCs do not meet criteria. Once these criteria have been met, blanks and samples may be analyzed. Any deviations must be documented in the case narrative.

If the RSDs exceed criteria, then linearity through the origin cannot be assumed. A linear regression analysis plot not forced through "zero" may be used to calculate concentrations using area counts on the "y" axis as the dependent variable versus concentrations on the "X" axis as the independent variable. At the SERAS Laboratory, Chemstation EnviroQuant software is used . The coefficient of determination (r^2) must be greater than 0.98.

NOTE: All initial calibration standards must be analyzed prior to the analysis of any method blanks, QC samples or environmental samples.

9.3 GC/MS Continuing Calibration

After 12 hours of sample acquisition have passed, the GC/MS must be re-tuned using BFB, and the initial calibration curve verified by the mid-level calibration standard.

1. The BFB tune must pass the criteria in Table 2, Appendix A.

2. The 50 µg/L calibration standard must be used for the continuing calibration.

3. The %D should be less than or equal to 20% for each target analyte with the exception of the CCCs that must be equal to or less than 20% for the following compounds:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

4. A minimum response factor for the following volatile SPCCs must be met:

Chloromethane	0.10	Chlorobenzene	0.30
1,1-Dichloroethane	0.10	1,1,2,2-Tetrachloroethane	0.30
Bromoform	0.10		

All other compounds must meet a minimum mean RF of 0.05.

For any target compounds present in the sample at a concentration greater than the RL, those analytes in the continuing calibration must meet the minimum RRF of 0.05 and the %D criteria of ≤20%.

5. The EICP area for each internal standard in the continuing calibration must be between 50% and 200% of the respective internal standard EICP area in the mid-point standard of the current initial calibration. If this criterion is not met, re-analysis is required.

6. A maximum of two continuing calibrations may be run to meet the requirements in item 3 above. A new calibration curve must be reanalyzed if both continuing calibrations are unacceptable.

   If the instrument is set up on an overnight run with two continuing calibrations back to back and the first continuing calibration passes but the second one fails, refer to Section 9.14, System Troubleshooting. It is not acceptable to use the first continuing calibration if the second continuing calibration is out.

7. If any of the requirements listed in Step 3 are not met, notify the Organic Group Leader and/or Analytical Section Leader.

9.4 Method Blank

A method blank is a volume of commercially available water and internal standard/surrogate mix carried through the entire analytical scheme. The method blank volume must be approximately equal to the sample volume.

1. A method blank analysis must be performed every 12 hours and must be analyzed immediately after calibration and prior to the analysis of any samples.

2. The method blank must contain less than the RL of all volatile target compounds, and less than five times the RLs of acetone, 2-butanone and methylene chloride. A maximum of two method blanks may be run. If both method blanks fail, the source of the contamination must be investigated prior to re-tuning the instrument.

   NOTE: If the instrument is set up on an overnight run with two method blanks back to back and the first method blank passes but the second one fails, the source of the contamination must be investigated prior to re-tuning the instrument. It is not acceptable to use the first method blank if the second method blank is out. The source of the contamination must be investigated and corrective action implemented.

9.5 System Blank

A system blank may be run after any samples or dilutions that contain a level of target analyte exceeding the initial calibration range to ensure that there is no carryover from a previous sample. If samples are run after a system blank, the system blank must be free of the contaminants which are being quantitated in the subsequent samples.

9.6 Surrogate Spike Analysis

1. Each sample, LCS, MS, MSD and blank are spiked with surrogate compounds prior to purging at a concentration of 50 µg/L. Deviations from the spiking protocol are not permitted.

2. The surrogate compound upper and lower percent recovery limits are listed below. If the sample surrogate recoveries do not meet the criteria, the affected sample must be reanalyzed to establish whether the non-conformance was due to the sample matrix or to a laboratory problem.

   If upon re-analysis of the sample, the surrogate recoveries fall within the QC limits, the problem was within the laboratory's control. Submit only the data from the analysis with the surrogate recoveries within the QC limits. This shall be considered the initial analysis and reported in the data package. If the analysis is outside the holding time, both sets of data will be submitted. Sample results will be evaluated based on the surrogate and the associated target compounds.

   If upon re-analysis, the surrogates still fall outside QC limits, submit both sets of data. Distinguish between the initial and re-analysis in the data package.

   The client-specified surrogate recovery limits are taken from the Contract Laboratory Program (CLP) Statement of Work (revision 5/99) and are as follows:

	% Recoveries
1,2-Dichloroethane-d_4	76 - 114
Toluene-d_8	88 - 110
p-Bromofluorobenzene	86 - 115

3. If blank surrogate recoveries do not meet criteria, re-analysis of all affected samples is required.

9.7 Matrix Spike/Matrix Spike Duplicate

1. A MS/MSD must be analyzed every 10 samples or per project. The MS/MSD must be associated with a method blank that meets the criteria in section 9.4, a calibration in sections 9.2 and 9.3 and a tune in section 9.1. The MS/MSD must be run on the same instrument that the sample was analyzed on at the lowest dilution reported for the sample. The MS/MSDs should be run on the same 12-hour shift as the sample.

2. The client-specified MS recovery limits are taken from the Contract Laboratory Program (CLP) Statement of Work (revision 5/99) and are as follows:

	% Recovery	RPD
1,1-Dichloroethene	61-145	14
Trichloroethene	71-120	14
Benzene	76-127	11
Toluene	76-125	13
Chlorobenzene	75-130	13

State in case narrative if recoveries are outside criteria. If more than half of the spiked compounds are out, the MS/MSD should be reanalyzed. A matrix effect is indicated if the LCS data are within limits but the MS/MSD are not. A similar pattern must be observed for both the MS and MSD.

If the lab fails to meet the QC recovery limits and/or the RPD on a routine basis, the Organics Group Leader must investigate the cause and take corrective action. The MS/MSD must be prepared at the same dilution as the least diluted analysis from which sample results will be reported.

9.8 Internal Standard Area Evaluation

1. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate.

2. If samples, blanks, LCS or MS/MSDs are analyzed immediately following an initial calibration but before another BFB tune and a continuing calibration, evaluation will be conducted on the basis of the internal standard areas of the 50 µg/L initial calibration standard.

3. If samples, blanks, LCS or MS/MSDs are analyzed immediately following a BFB tune and a continuing calibration, evaluation will be conducted on the basis of the internal standard areas in the continuing calibration standard.

4. The EICP area for each internal standard in all samples, blanks, and matrix spike/matrix spike duplicates must be between 50% and 200% of the respective internal standard EICP area in the appropriate calibration standard. In addition, the retention time of each internal standard must be within ±0.50 minutes (30 seconds) of its retention time in the continuing calibration standard.

5. If one or more internal standard EICP areas do not meet criteria, the GC/MS system

must be inspected for malfunctions and corrections made as appropriate. When corrections are made, re-analysis of all affected samples is required.

6. If after re-analysis, the EICP areas for all internal standards meet criteria (between 50% and 200%), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only data from the analysis with EICPs within the limits are required to be submitted. If re-analysis confirms matrix effects, submit both sets of data but report the initial run.

9.9 Manual Integrations

Manual integration of all target analytes, surrogates, and internal standards will be submitted for review. The manual integration results will be flagged with a "M" and will be initialed and dated by the analyst and group leader indicating that the integration was performed properly. Documentation of the manual integration of quantitation ion peaks must be included in the data package. Refer to SERAS SOP #1001, *Chromatographic Peak Integration Procedures*.

9.10 Laboratory Control Sample

1. A LCS must be analyzed every 20 samples or per batch. The LCS must be prepared at 50 µg/L from the second source. The LCS must be associated with a method blank that meets the criteria in section 9.4, a calibration in sections 9.2 and 9.3 and a tune in section 9.1.

2. The QC limits for the LCS recoveries are listed below.

	% Recovery
1,1-Dichloroethene	70-130
Trichloroethene	70-130
Benzene	70-130
Toluene	70-130
Chlorobenzene	70-130

State in case narrative if recoveries are outside criteria. On a quarterly basis, a LCS will be prepared and run that contains all of the target analytes. The above limits will be used until the first 20 points are available to prepare a control chart. At that point, control and warning limits will be calculated every 10 to 20 points and updated at least quarterly.

If the lab fails to meet the QC recovery limits on a routine basis, the Organics Group Leader and/or Analytical Section Leader must investigate the cause and take corrective action.

9.11 Initial Demonstration of Capability

Initial proficiency in VOC analysis must be demonstrated by each analyst initially and each time significant changes are made in the procedure or for instrumentation. Each analyst will generate precision and accuracy data using a reference standard other than the source used for calibration. Four replicates of a well-mixed reference standard is analyzed using the procedures outlined in this SOP. Calculate the average mean in µg/L and the standard deviation (s) in µg/L. The QAO will tabulate the results from all of the analysts per matrix per parameter, and calculate control limits.

9.12 Method Detection Limit Studies

Method detection limit (MDL) studies will be run on an annual basis for each VOC instrument for the water matrix to verify the minimum concentration that can be measured and reported with 99% confidence. A minimum of seven replicates will be used for the study (EPA 1984).

9.13 Nonconformance Memo

A nonconformance memo will be generated any time an employee notices a deficiency suspected of being a nonconformance. This nonconformance memo will be forwarded to the Quality Assurance Officer for verification of corrective action.

9.14 System Troubleshooting

Re-calibration must take place when performance changes are to the point when that the calibration verification criteria cannot be achieved. The following examples of maintenance do not require automatic re-calibration of the instrument with an initial calibration: changing compressed gas cylinders or syringes; baking the trap, transfer line or column; or flushing the system with multiple system blanks. If these types of maintenance rectify the problem, the instrument may be re-tuned and a continuing calibration run. If the continuing calibration fails, then a new initial calibration must be run.

Maintenance activities that require automatic re-calibration of the instrument using an initial calibration include: changing, replacing or reversing the column; replacing the trap on a purge-and-trap; changing the entrance lens, draw out lens, or repeller; changing the electron multiplier and ion source chamber.

All maintenance activities must be documented in the instrument-specific preventive maintenance log.

10.0 DATA VALIDATION

Data will be assessed for usability in accordance with the guidelines set forth in the most current version of SERAS SOP #1015, *Data Validation Procedures for Routine Volatile Organic Analysis.* However, data is considered satisfactory for submission when *all* the requirements mentioned in Section 9.0 are met.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, refer to EPA, Occupational Safety and Health Administration (OSHA) and corporate health and safety practices. More specifically, refer to SERAS SOP #3013, *SERAS Laboratory Safety Program* and SERAS SOP #1501, *Hazardous Waste Management*.

12.0 REFERENCES

National Environmental Laboratory Accreditation Committee (NELAC), *Quality Systems*, current approved version.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste*, SW-846, 3rd ed., Method 8000B.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste*, SW-846, 3rd ed., Method 8260B.

U.S. Environmental Protection Agency. 1999. *Statement of Work for Organic Analysis,* Document Number OLM04.2, Contract Laboratory Program.

U.S. Environmental Protection Agency. 1984. Federal Register, 40 Code of Federal Regulations (CFR) Part 136, Appendix B, *Definition and Procedure of the Determination of the Method Detection Limit - Revision 1.11*, October 26, 1984.

13.0 APPENDICES

A - Tables

APPENDIX A
Tables
SOP #1806
January 2006

VOLATILE ORGANIC ANALYSIS IN WATER BY GC/MS
(EPA/SW-846 Method 8000B and 8260B)

TABLE 1. Target Compound List (TCL)

COMPOUND	RL (µg/L)
Dichlorodifluoromethane	5.00
Chloromethane	5.00
Vinyl Chloride	5.00
Bromomethane	5.00
Chloroethane	5.00
Trichlorofluoromethane	5.00
Acetone	20.0
1,1-Dichloroethene	5.00
Methylene Chloride	5.00
Carbon Disulfide	5.00
Methyl-tert-butyl Ether	5.00
trans-1,2-Dichloroethene	5.00
1,1-Dichloroethane	5.00
2-Butanone	5.00
2,2-Dichloropropane	5.00
cis-1,2-Dichloroethene	5.00
Chloroform	5.00
1,1-Dichloropropene	5.00
1,2-Dichloroethane	5.00
1,1,1-Trichloroethane	5.00
Carbon Tetrachloride	5.00
Benzene	5.00
Trichloroethene	5.00
1,2-Dichloropropane	5.00
Bromodichloromethane	5.00
Dibromomethane	5.00
cis-1,3-Dichloropropene	5.00
trans-1,3-Dichloropropene	5.00
1,1,2-Trichloroethane	5.00
1,3-Dichloropropane	5.00
Dibromochloromethane	5.00
1,2-Dibromoethane	5.00
Bromoform	5.00
4-Methyl-2-Pentanone	5.00
Toluene	5.00

TABLE 1. Target Compound List (TCL) (cont'd)

COMPOUND	RL (µg/L)
2-Hexanone	5.00
Tetrachloroethene	5.00
Chlorobenzene	5.00
1,1,1,2-Tetrachloroethane	5.00
Ethylbenzene	5.00
p & m-Xylene	10.0
o-Xylene	5.00
Styrene	5.00
Isopropylbenzene	.00
1,1,2,2-Tetrachloroethane	5.00
1,2,3-Trichloropropane	5.00
n-Propylbenzene	5.00
Bromobenzene	5.00
1,3,5-Trimethylbenzene	5.00
2-Chlorotoluene	5.00
4-Chlorotoluene	5.00
tert-Butylbenzene	5.00
1,2,4-Trimethylbenzene	5.00
sec-Butylbenzene	5.00
p-Isoproyltoluene	5.00
1,3-Dichlorobenzene	5.00
1,4-Dichlorobenzene	5.00
n-Butylbenzene	5.00
1,2-Dichlorobenzene	5.00
1,2-Dibromo-3-Chloropropane	5.00
1,2,4-Trichlorobenzene	5.00
Hexachlorobutadiene	5.00
Naphthalene	5.00
1,2,3-Trichlorobenzene	5.00

TABLE 2. GC/MS Performance Standard

Bromofluorobenzene (BFB)

m/z	Ion Abundance Criteria
50	8.0 - 40% of mass 95
75	30 - 66% of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of mass 95
173	Less than 2.0% of mass 174
174	50.0 - 120% of mass 95
175	4.0 - 9.0% of mass 174
176	93 - 101% of mass 174
177	5.0 -9.0% of mass 176

TABLE 3. List of Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

Bromochloromethane	Difluorobenzene	Chlorobenzene-d_5
Dichlorodifluoromethane	1,1,1-Trichloroethane	4-Methyl-2-Pentanone
Chloromethane	Carbon Tetrachloride	Toluene-d8 (surr.)
Vinyl Chloride	Benzene	Toluene
Bromomethane	Trichloroethene	2-Hexanone
Chloroethane	1,2-Dichloropropane	Tetrachloroethene
Trichlorofluoromethane	Bromodichloromethane	Chlorobenzene
Acetone	Dibromomethane	1,1,1,2-Tetrachloroethane
1,1-Dichloroethene	cis-1,3-Dichloropropene	Ethylbenzene
Methylene Chloride	trans-1,3-Dichloropropene	p & m-Xylene
Carbon Disulfide	1,1,2-Trichloroethane	o-Xylene
Methyl-tert-butyl Ether	1,3-Dichloropropane	Styrene
trans-1,2-Dichloroethene	Dibromochloromethane	Isopropylbenzene
1,1-Dichloroethane	1,2-Dibromoethane	1,1,2,2-Tetrachloroethane
2-Butanone	Bromoform	p-Bromofluorobenzene (surr.)
2,2-Dichloropropane		1,2,3-Trichloropropane
cis-1,2-Dichloroethene		n-Propylbenzene
Chloroform		Bromobenzene
1,1-Dichloropropene		1,3,5-Trimethylbenzene
1,2-Dichloroethane		2-Chlorotoluene
1,2-Dichloroethane-d4 (surr.)		4-Chlorotoluene
		tert-Butylbenzene
		1,2,4-Trimethylbenzene
		sec-Butylbenzene
		p-Isopropyltoluene
		1,3-Dichlorobenzene
		1,4-Dichlorobenzene
		n-Butylbenzene
		1,2-Dichlorobenzene
		1,2-Dibromo-3-Chloropropane
		1,2,4-Trichlorobenzene
		Hexachlorobutadiene
		Naphthalene
		1,2,3-Trichlorobenzene

TABLE 4. List of Characteristic Ions for Target, Internal Standard and Surrogate Compounds

COMPOUND	PRIMARY ION	SECONDARY ION(S)
Bromochloromethane (I)	128	49, 130
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl Chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
Acetone	43	58
1,1-Dichloroethene	96	61, 98
Methylene Chloride	84	49, 86
Carbon Disulfide	76	78
Methyl tert-Butyl Ether	73	57, 41
trans-1,2-Dichloroethene	61	96, 98
1,1-Dichloroethane	63	65
2-Butanone	43	72
2,2-Dichloropropane	77	97
cis-1,2-Dichloroethene	96	98
Chloroform	83	85
1,1-Dichloropropene	75	77, 110
1,2-Dichloroethane	62	64
1,2-Dichloroethane-d_4 (S)	65	102
1,4-Difluorobenzene (I)	114	88
1,1,1-Trichloroethane	97	99, 61
Carbon Tetrachloride	117	119
Benzene	78	51
Trichloroethene	130	132, 95
1,2-Dichloropropane	63	62, 76
Bromodichloromethane	83	85
Dibromomethane	174	176, 172
cis-1,3-Dichloropropene	75	77, 110
trans-1,3-Dichloropropene	75	77, 110
1,1,2-Trichloroethane	97	83, 99
1,3-Dichloropropane	76	78
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109

(I) - Internal Standard (S) – Surrogate

TABLE 4. List of Characteristic Ions for Target, Internal Standard and Surrogate Compounds (cont'd)

Compound	Primary Ion	Secondary Ion(s)
Bromoform	173	175
Chlorobenzene-d_5 (I)	82	52
4-Methyl-2-Pentanone	43	58
Toluene-d_8 (S)	98	100
Toluene	91	92
2-Hexanone	43	58, 100
Tetrachloroethene	166	164, 129
Chlorobenzene	112	114
1,1,1,2-Tetrachloroethane	133	131, 95
Ethylbenzene	91	106
p & m-Xylene	91	106
o-Xylene	91	106
Styrene	104	78
Isopropylbenzene	105	120
1,1,2,2-Tetrachloroethane	83	85, 131
p-Bromofluorobenzene (S)	174	176
1,2,3-Trichloropropane	110	112, 97
n-Propylbenzene	91	120
Bromobenzene	77	56, 158
1,3,5-Trimethylbenzene	105	120
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
tert-Butylbenzene	119	91, 134
1,2,4-Trimethylbenzene	105	120
sec-Butylbenzene	105	134
p-Isopropyltoluene	119	91, 134
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
n-Butylbenzene	91	92, 134
1,2-Dichlorobenzene	146	148, 111
1,2-Dibromo-3-Chloropropane	157	155
1,2,4-Trichlorobenzene	180	182, 145
Hexachlorobutadiene	225	223, 227
Naphthalene	128	127, 129
1,2,3-Trichlorobenzene	180	182, 145

(I) - Internal Standard (S) - Surrogate