



Preparation of Gas Phase Standards for Ambient Air Analysis

Application Note

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Introduction

Understanding gas phase standard preparation for ambient air methods is paramount to successful analyses. Standard preparation using EPA water, wastewater, and soil methods is routine. The analyst purchases stock methanolic standards and dilutes them into the working range of the instrument. Unlike conventional methods, air standard preparation is significantly more time consuming and technique intensive. Stock standards in compressed gas cylinders are available for specific method analytes, such as Compendium Method TO14¹ compounds. These, however, can be cost prohibitive and do not always address the needs of every customer. Custom blends are available in compressed gas cylinders, but are also costly and usually require four to eight weeks for preparation and stabilization.

This paper addresses several approaches to preparing gas phase standards for air toxics analysis. Included are techniques and calculations for making multi-component neat mixtures which can be diluted into static dilution bottles and ultimately into canisters for system calibration and performance checks. These techniques can be used to help alleviate cost when specific, non-routine analyses are requested. They can also be utilized by laboratories not receiving sufficient requests for air toxics analyses to justify the purchase of a compressed gas standard.

Also discussed are techniques for using compressed gas standards alone and combined with static dilution bottle standards to produce working standards in canisters. Some canister cleaning techniques are specified along with the importance of humidifying canisters for cleaning and standard preparation. Throughout the paper, good laboratory practices are described as these are essential to accurate and reproducible standard preparation.

Preparing Primary Stock Mixtures from Neat Liquids

A static dilution bottle (SDB) is a glass round bottom flask of known volume equipped with a septum-containing (Mininert) valve. It is used to vaporize and dilute small volumes of neat liquids to the gas phase, producing an intermediate standard. To prepare a gas phase standard in an SDB, a calculated amount of neat compound is injected into the flask. When preparing a multi-component standard, it is generally easier and more efficient to prepare an equimolar primary stock mixture of compatible neat compounds and make a single injection of the mixture into the SDB. This equimolar mixture is commonly referred to as a soup.

Before preparing the soup, the desired analytes are identified and categorized according to reactivity. An effective way to accomplish this is to group the compounds based on functionality, i.e., hydrocarbons, halocarbons, aromatics, alcohols, aldehydes, ketones, etc. If there are only a few compounds in each subset, decide if any subsets can be combined, such as alcohols, aldehydes, and ketones into a polar soup. The ratio of the molecular weight to the density provides the volume required for one mole of each component. This ratio is multiplied by the desired number of millimoles to adjust the volume per component injected. The number of millimoles injected per component is determined by the cost and availability of neat compounds, and the total volume of soup required. Soups are commonly prepared in 2 ml amber vials; therefore an appropriate total soup volume is 500 µl to 1500 µl.

$$\frac{\text{(Molecular weight (mg/mmol))}}{\text{Density (mg/}\mu\text{l)}} \text{ (Desired mmol (mmol/cmp))} = \text{Volume}(\mu\text{l})/\text{mmole component}$$

The total volume for the soup is determined by summing the individual component volumes, and adjusting the number of moles injected if the total volume is greater or less than the desired range. To establish the approximate molar concentration of an individual soup component, the following calculation is applied:

$$\frac{\text{Number of mmoles injected (mmol)}}{\text{Total soup volume (ul)}} = \text{Molar Concentration (mmol/ul)}$$

When sealed with a septum-containing screw cap or Mininert valve and stored in the freezer, a compatible primary stock soup is stable for approximately six months.

Meticulous cleaning of syringes by flushing with methanol and vacuum drying with a syringe cleaner will minimize contamination of the primary standard and the source neat compound. Ideally, a single syringe should be used for each neat compound. If this is not possible, carefully clean and dry the syringe between injections, and flush the syringe several times with a small volume of neat solution prior to final measurement and injection.

Preparing Gas Phase Intermediate Standards from Primary Stock Mixtures

Primary neat stock mixtures are diluted and vaporized in an SDB producing a gas phase intermediate standard. The SDB must first be cleaned and dried. The SDB is opened in a hood to allow existing contents to exhaust, and is then filled with water to force the remaining components out of the bottle. If the SDB is new, these first two steps can be eliminated. Next, the SDB is washed with laboratory detergent and warm water. The bottle is rinsed until no more soap is evident and lastly, several rinses are made with organic free water. The SDB is dried in a 100°C oven, removed, and allowed to cool. The SDB can be placed in a 300°C muffle furnace to char any remaining organics; however, high temperatures will change the shape and ultimately the volume of the container. As a general rule, the actual SDB volume should be determined upon initial purchase, and after baking at temperatures in excess of 100°C. Several clean glass beads are placed in the SDB, and the bottle is flushed with nitrogen gas. The SDB is capped immediately with a clean Mininert valve containing a new septum, and is now ready for standard preparation.

The desired SDB concentration is established and the actual SDB volume is recorded. From the ideal gas law, the molar volume of an ideal gas is determined ($V=nRT/P$). The volume of soup required for a given final concentration in the SDB is calculated by the following equation:

$$\frac{(\text{Conc}_{\text{SDB}}(\text{ug/L})) (V_{\text{SDB}}(\text{L}))}{(\text{Molar Conc}(\text{umol/ul})) (nRT/P)(\text{ul/umol})} = V_{\text{soup added to SDB}}(\text{ul})$$

The calculated volume of soup is added to the SDB through the septum port of the Mininert™ valve. The bottle is swirled, stirring the glass beads to enhance vaporization and the standard is allowed to equilibrate several hours. Heating the SDB to 65°C may be required for intermediate standards containing components with low vapor pressures similar to trichlorobenzenes and hexachlorobutadiene to ensure complete vaporization².

Concentration units for air analysis are commonly expressed as a volume to volume ratio. That is, an SDB containing analytes at a concentration of 200ppm v/v contains 200 microliters of analyte per liter of air. Conventional water and soil methodologies express concentration units in terms of mass of analyte per volume of water (ug/L) or mass of analyte per mass of soil (mg/kg)^{3,4}. Volume to volume measurements are easily converted to the more familiar mass to volume measurements by using the molar volume and molecular weight in a conversion equation. For example, an SDB containing acetone at a concentration 10ppm v/v yields 23.9ug/L of acetone:

$$\frac{(\text{SDB concentration}(\text{ul/L}))}{(\text{Molar volume of an ideal gas}(\text{ul/umol}))} (\text{MW of acetone}(\text{ug/umol})) = \text{Concentration of acetone (ug/L)}$$

$$\frac{10\text{ul/L}}{24.45\text{ul/umol}} (58.08 \text{ ug/umol}) = 23.9\text{ug/L}$$

Preparing Working Standards from SDB's

Canister Cleaning

The final step in ambient air standard preparation is diluting the SDB into a working range canister standard. Care must be taken to ensure the canister is clean. Many questions exist regarding parameters for canister cleaning, including the necessity of heat and humidity, the use of nitrogen or compressed air, the number of fill/evacuate cycles, the duration of final evacuation and the final evacuation pressure. The procedure outlined here performs well for cleaning canisters containing a modified TO14 standard up to 200ppbv, 100% relative humidity, and 5% carbon dioxide. Cleanliness specifications are less than 0.2ppbv per target analyte. Modifications to this procedure may be necessary depending on the source of the samples.

The canister is placed in an oven with the canister valve exposed to ambient air, and is heated to 140°C. A cold finger is placed in line before the vacuum pump to trap impurities which may diffuse from the vacuum pump oil. The canister is initially evacuated to ~25in vacuum, followed by pressurization to ~30psig, with humidified zero air. The cycles are repeated seven to ten times. The humidity chamber is then taken off line, and seven to ten fill/evacuate cycles are repeated with dry zero air. The final evacuation is held for 30-60 minutes. The canister valve is closed and the canister is now ready for standard preparation or sampling. Per EPA methodologies, all canisters must be tested for cleanliness until the cleaning system is verified, after which, a smaller percentage of canisters is tested. Canisters must also be pressure tested over a 24 hour period to ensure that the container is leak free⁵.

Standard Preparation

Prior to injecting standard into the cleaned, evacuated canister, the canister is humidified with purified water. Humidification further passivates the interior surface, reducing activity and facilitating the removal of compounds, and creates an environment that more accurately represents the actual sample matrix. Preparing canister standards at 50% relative humidity provides sufficient moisture to reduce canister surface activity. It is standard practice to base relative humidity on the canister volume at ambient pressure, not the final pressurized volume.

From a relative humidity table⁶, the mass of water contained in a cubic meter of saturated air at a specific temperature can be obtained. This value is used to calculate the volume of water required for a specific relative humidity. For example, at 25°C, 23.05g of water saturates a cubic meter of air. To calculate the volume of water required to provide 100% relative humidity in a six liter canister, apply the following relationship:

$$(23.05\text{g/m}^3) (\text{m}^3/1000\text{L}) (6\text{L}) = 0.1383\text{g H}_2\text{O in 6L canister}$$

$$\frac{(0.1383\text{g})}{1\text{g/ml}} (1000\text{ul/ml}) = 138.3\text{ul H}_2\text{O in 6L canister}$$

Injecting 138.3ul of water into a six liter canister will provide 100% relative humidity. Reducing the volume injected to 69ul will result in 50% relative humidity.

Relative humidity is strongly dependent on temperature. A drop of only 5°C in room temperature creates a 25% difference in the mass of water required to saturate a cubic meter of air. Therefore, for greatest accuracy, room temperature should be monitored and humidity tables utilized to determine the correct value for specific laboratory conditions.

Once the canister is humidified, the gas phase intermediate standard can be injected. To determine the volume of SDB intermediate standard to inject, the desired canister concentration, SDB concentration, and final canister volume must be known. The following relationship is used to calculate the volume required.

$$\frac{(\text{Desired canister concentration (ul/L)}) (\text{Final canister volume (L)})}{\text{Concentration}_{\text{SDB}} (\text{ul/L})} = \text{Volume}_{\text{from SDB}} (\text{L})$$

A six liter canister at atmospheric pressure has a volume of six liters. From this, the final canister volume can be calculated from the final canister pressure. The following conversion factors between atmospheric pressure units are valuable for making this determination.

$$1\text{atm} = 14.7\text{psia} = 0\text{psig} = 29.9\text{in Hg} = 760\text{mm Hg} = 760\text{Torr}$$

To accurately transfer a volume of gas from the SDB to the canister, a gas tight syringe must be used. Insert the syringe through the Mininert™ valve and draw an aliquot of standard. Flush the contents of the syringe into a hood and repeat. Once flushed, insert the syringe through the Mininert™ valve and pump several times, filling the syringe and releasing the contents back into the SDB. Finally, slowly draw standard into the syringe past desired final volume; allow several seconds for equilibration, then adjust to the correct volume. Remove the syringe from the SDB and immediately inject the contents into the humidified canister. The canister can now be pressurized to the final dilution volume.

Every time standard is removed from the SDB, the concentration changes. To increase the useful lifetime of an SDB standard, remove volumes of 25ml or less. The volume removed can be manipulated by increasing the SDB concentration or adjusting the canister final volume/pressure. Depending upon the volume removed, an SDB intermediate standard is usable for approximately two months.

Compressed gas standards are often used in conjunction with SDB standards to increase the number of compounds per analysis. Metering the cylinder standard through an electronic mass flow controller (MFC) is an accurate, effective and relatively inexpensive method for delivering the standard to a canister. The standard is allowed to flow through the MFC for approximately 15min to ensure that the contents are homogeneous. The outlet to the MFC is then connected to the canister and the standard transfer is timed to obtain the desired volume. Alternately, gas blending or permeation tube systems can be utilized to create working range standards. Although these techniques automate the standards preparation process, they are costly.

Conclusion

Standard preparation for air toxics analysis requires analyst skill and is time intensive. Understanding the basic calculations and close attention to good laboratory practices will greatly simplify the process. To eliminate repeated tedious calculations, the equations outlined can be incorporated into a spreadsheet program. Once established, spreadsheets are easily customized to reflect any analyte mixture.

Acknowledgment

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Preparation of Standards Using a “Cocktail” or “Soup”.

The Teldyne Application Note above is included for reference for technique. The actual procedures used by the lab are as follows:

The Summa can stock standard is prepared by spiking a small amount of a neat chemical cocktail and pressurizing with humid zero air in accordance with procedures below:

Cocktail Preparation Equi-mass “soup” (contains compounds in equal mass amounts) or cocktail prepared from the neat compounds:

Step 1: This cocktail is prepared by combining 25mg of each neat compound into a small glass vial. Use a microliter syringe to transfer each compound, cleaning with solvents in between. Put the vial in the freezer between aliquots to minimize volatilization. Take the density of each compound into account to determine the **actual amount of each compound to spike into the cocktail**:

$$S = \frac{A}{D}$$

Where:

S Actual spike amount (μL)

A Desired amount for each compound (mg)

D Density ($\text{mg}/\mu\text{L}$), refer to Table 3 for the density

Example: The actual amount of acrolein to add to the cocktail is calculated by the following.

$$S(\text{Acrolein}) = \frac{25\text{mg}}{\left(0.840 \frac{\text{mg}}{\mu\text{l}}\right)} = 29.8\mu\text{L}$$

Step 2: The concentration of each compound in the cocktail:

$$C = \frac{A}{V} \left(1000 \frac{\mu\text{g}}{\text{mg}} \right)$$

Where:

- C Concentration of cocktail ($\mu\text{g}/\mu\text{L}$)
- A Amount of each compound (mg)
- V Final volume of cocktail (added spike amounts of each compound) (μL)

Example:

$$C = \frac{25\text{mg}}{631.8\mu\text{L}} \left(1000 \frac{\mu\text{g}}{\text{mg}} \right) = 39.569\mu\text{g}/\mu\text{L}$$

Intermediate Standard - Prepare the intermediate standard by spiking a small aliquot of the soup into a certified clean, evacuated Summa canister in order to achieve a final nominal concentration of 1000ng/L. Attach a teflon line with a stainless steel tee to the fill station. Attach the empty canister to the tee. Put a septum in the remaining tee fitting. Open the canister valve for a few seconds, and then close it. Check the vacuum gauge for fifteen seconds to make sure there is no leak. Then open the valve again and spike in the neat cocktail. Start air flow into the can and slowly pressurize to 58.8 psig. Then allow the contents to equilibrate for approximately 24 hours before using the spike amount is determined by using the following equation.

$$S = \frac{C_1 V}{C_2 * 1000\text{ng} / \mu\text{g}}$$

Where:

- S Spike amount required in order to obtain the desired concentration (μL)
- C_1 Desired concentration (ng/L)
- C_2 Concentration of cocktail ($\mu\text{g}/\mu\text{L}$)
- V Final volume of Summa canister (L) – as calculated above

Example: Determine the spike amount of the cocktail required to achieve the desired intermediate standard concentration.

$$S = \frac{\left(1000 \frac{\text{ng}}{\text{L}} \right) (30\text{L})}{1000 \frac{\text{ng}}{\mu\text{g}} * 27.81 \frac{\mu\text{g}}{\mu\text{L}}} = 1.08\mu\text{L}$$

STANDARD OPERATING PROCEDURE
VOLATILE ORGANIC COMPOUNDS BY GC/MS

VOC-8260B

Revision 8

August 22, 2006

Approved By: _____
Supervisor _____ Date _____

_____ Date _____
QA Coordinator _____

_____ Date _____
Laboratory Manager _____

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Rochester, New York 14609

Annual review of this SOP has been performed
and the SOP still reflects current practice.

Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL

NUMBER: _____

Initials: _____ Date: _____

*See DOD Summary Attachment for DOD Specific Criteria

1. SCOPE AND APPLICATION

This SOP is used to determine the concentration of volatile organic compounds (VOCs) in water and soil, sediment and sludge using USEPA methods 8260B, 5030B, and 5035A. Method 5035A is discussed in a separate SOP (VOC-5035A). The use of this method for low concentrations by SIM Mode is discussed in Attachment I. This method may also be applicable to various types of aqueous and nonaqueous waste samples. Appendix C of the Quality Assurance Manual (QAM) lists the compounds that are routinely determined by this method with the associated Method Reporting Limits (MRLs) and Quality Control Limits for water and soil matrices. The reported compound list and MRLs may be adjusted if required for specific project requirements and supported by a current Method Detection Limit (MDL) study. The method can quantitate most volatile organic compounds with a boiling point <200°C.

2. METHOD SUMMARY

- 2.1. This method gives gas chromatographic/mass spectrometric (GC/MS) conditions for the detection of parts per billion (ppb) levels of volatile organic compounds. A sample aliquot is injected into the gas chromatograph (GC) by the purge and trap method. The compounds are separated on a small bore fused silica capillary column. The compounds are detected by a mass selective detector (MSD), which gives both qualitative as well as quantitative information.
- 2.2. Lower MRLs can be achieved by purging a volume larger than the standard 5 mL discussed herein. With a larger purge volume (10 or 25 mL), all reporting limits listed in Appendix C of the QAM would become half or one-fifth the listed value, respectively. All internal, surrogate, and matrix spike solutions are prepared in the same manner discussed herein, but when spiked into a larger sample volume the actual concentrations are diluted by a factor of two or five, respectively. Since the initial and continuing calibration standards would also require a larger purge, the range of calibration is decreased by the appropriate factor.
- 2.3. In the purge and trap process an inert gas, helium, is bubbled through the sample aliquot, at room temperature. This gas stream sweeps the volatile organic compounds out of the aqueous phase and into the gas stream - it purges the compounds out of the sample. The gas stream then passes through a sorbent column which selectively adsorbs (traps) these compounds out of the helium. After the purging sequence is done, the sorbent column (the trap) is heated and backflushed onto the GC column. The GC column separates the compounds and passes then onto the MSD for identification and quantification.
- 2.4. Method Summary for SIM mode is discussed in Attachment I.

3. DEFINITIONS

- 3.1. **Analysis Window** - Samples are analyzed in a set referred to as "a window". The window begins with the injection of the tune verification standard. Standards, required QC samples and samples may be run for 12-hours in this window. A new window must be opened to continue analysis.
- 3.2. **Initial Calibration Curve** – analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the detector to the target compounds.
- 3.3. **Laboratory Control Sample (LCS) or Reference Standard** – An aliquot of analyte-free water or other blank matrix to which known quantities of analytes of interest from a second source are added in the laboratory. The LCS is analyzed the same as a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate measurements. The LCS contains a full list of compounds. The LCS is evaluated for all client targets in the batch, however only a subset of compounds designated to represent the targets is typically reported.
- 3.4. **Matrix Spike/ Matrix Spike Duplicate Analysis (MS/MSD)** – An aliquot of a sample to which known amounts of compounds of interest from a second source are added in the laboratory prior to analysis. The MS/MSD are analyzed the same as a sample. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the compounds determined by the analysis. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision. The concentration of the spike should be at 5-10 times the MRL or at levels specified by a project analysis plan. The LCS is evaluated for all of the targets for which the system is calibrated. Corrective action is taken if acceptance criteria is not met for targets in the client's target list.
- 3.5. **Method Blank (MB)** - A volume of analyte-free water treated and analyzed exactly the same as a sample. The purpose of the blank is to determine if any of the analytes of interest or other interferences are present in the analytical system, particularly in regards to carry-over of analytes from highly contaminated samples into other analyses.
- 3.6. **Percent Drift or Percent Difference (%D)** - Used to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference).
- 3.7. **% Relative Standard Deviation (%RSD)**: statistical measure of variation. Used in this method to measure the relative variation of initial calibration

standards. Calculated by dividing the standard deviation of the individual response factors by the average response factor and multiplying by 100 to express as a percentage.

- 3.8. **Relative Percent Difference (RPD)** – The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.
- 3.9. **Surrogate** - Surrogates are organic compounds which are similar to the analytes of interest in chemical composition, and chromatography, but which are not normally found in environmental samples. The purpose of the surrogates is to help determine matrix effects and to evaluate the preparation and analysis of samples. These compounds were spiked into all blanks, standards, and samples prior to analysis. Percent recovery is calculated for each surrogate.
- 3.10. **Internal Standards** - Internal standards are organic compounds which are similar to the analytes of interest but which are not found in the samples. The chosen internal standards are used to calibrate the instrument's response.
- 3.11. **Batch** – group of samples (not to exceed 20) of the same matrix analyzed together within sequence. See ADM-BATCH for further discussion.
- 3.12. **Independent Calibration Verification (ICV)** - Verification of the ratio of instrument response to analyte amount. ICV solutions (also referred to as laboratory control samples or reference samples) are made from a stock solution which is different from the stock used to prepare calibration standards (Second Source).
- 3.13. **Continuing Calibration Verification Standard (CCV)** - A standard injected into the instrument at specified intervals and is used to verify the initial calibration. The source of this standard is the same as that used for calibration purposes.
- 3.14. **4-Bromofluorobenzene (BFB) Tune Standard** – 50 ng (on-column) of BFB (a solution in methanol) is analyzed to open an analysis window
- 3.15. **Method Detection Limit (MDL)**: a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero
- 3.16. **Method Reporting Limit (MRL)**: The minimum amount of a target analyte that can be measured and reported quantitatively. The MRL is equivalent to Practical Quantitation Level (PQL) and Estimated Quantitation Level (EQL). Typically, the MRL is calculated as five times the MDL (although this is a rule of thumb and not intended to be a strict policy of establishing the MRL for a compound).

3.17. **Target Analyte** – a compound of interest for which the method is capable of measuring.

4. **INTERFERENCES**

Interferences include but are not limited to impurities in the inert purge gas, dirty plumbing/purge vessels, cross contamination of highly contaminated samples, in transport and storage, and carry over from one analysis to subsequent ones.

Avoid using non-PTFE thread sealants, plastic tubing, and rubber components, since such materials out-gas organic compounds, which will concentrate in the trap during purge operation.

If a sample containing low concentration of VOCs is analyzed immediately after a sample containing high concentration of VOCs, a blank may be analyzed between samples to rinse the system and avoid carry-over. If samples are being injected using a syringe, the syringe should also be rinsed with sufficient volumes of methanol or DI between samples. Screening samples using the PID or Hnu may also be used to avoid injecting sample with high VOC concentration.

Storage blanks (cooler blanks) are placed in the coolers containing samples to be tested for VOCs. These blanks are prepared, held/sampled, and analyzed according to VOC-BLANK.

Trip blanks are collected with aqueous samples and carried through the sampling, handling, and storage to check for contamination of volatile compounds capable of diffusion such as methylene chloride and fluorocarbons.

5. **SAFETY**

Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. Sources of flammable gases (e.g., pressurized hydrogen) should be clearly labeled.

Refer to the Safety Manual for further discussion of general safety procedures and information.

6. **SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE**

*See DOD Summary Attachment for DOD Specific Criteria

6.1. All sample containers for VOC analysis are purchased precleaned and certified from major lab equipment suppliers. All containers should be of glass or amber glass and equipped with a screw top cap and PFTE (Teflon) lined septa and capable of containing a minimum of 40 mL of aqueous sample or 2-4 oz. of soil sample. New lots of vials are routinely checked for cleanliness and target compound contamination.

6.2. Aqueous Samples

6.2.1. Aqueous Samples should be collected (received) in 40 ml VOA vials with zero headspace. Samples should be preserved to pH <2 with hydrochloric acid (Because 2-chloroethylvinyl ether degrades in the presence of acid, it is recommended that samples are not preserved if this is compound of concern). Ideally, three VOA vials will be received for each sample. Samples will be refrigerated to 0-6°C upon sample login.

6.2.2. Aqueous sample bottles are slowly filled to just overflowing taking care not to flush out the preservative or to trap air bubbles in the samples. The bottles are sealed with PFTE lined septa toward the sample and inverted to check for air bubbles.

6.3. Soil Samples

Soil samples are collected per individual state, agency, or QAP requirements. See State Summary spreadsheet in VOA lab office for details. The following options are available:

6.3.1 Option 1:

Soil jars with PFTE lined septa are used to collect soil samples. The soil is pressed into the jar to the top to eliminate any headspace. (New York State). Holding time is 14 days from sample collection to analysis.

6.3.2 Option 2.

Encore style sampler and capsules are sent to the field and a fraction of either approximately 5 gm or 25 gm are collected by field personnel and shipped back to the laboratory, chilled to 0-6°C while in transit. The laboratory then has 48 hrs from sampling to preserve the soil fractions in DI water for the low concentration fractions and Methanol for high concentration fraction.

6.3.3 Option 3.

Soil vials are prepared by laboratory personnel. For each field sample, two 40 mL VOA vials, each containing a 5 mL solution of Sodium Bisulfate (1 gm/5mL), are sealed, labeled and tarred. Another 40 mL VOA vial containing 10 mLs of Purge and Trap Methanol is sealed, labeled and tarred. A Top Loading balance, if necessary, is supplied to the field personnel and a 5 gm fraction is added to each of the three supplied vials. Optionally a Encore sampler may be used to sample these fractions, then added to the above mentioned vials. The field sampler then returns the fractions (40mL vials) back to the laboratory chilled to 0-6°C. At which time the lab weighs the vials to determine or confirm the soil content and must perform the analysis within 14 days of sampling. (See VOC-5035).

- 6.4 All samples (preserved waters and soils) must be stored at 0-6°C and must be analyzed within 14 days of collection. Aqueous samples not prepreserved with HCl must be analyzed within 7 days of collection. See SMO-GEN for further discussion of sample receipt and handling.

7. APPARATUS AND EQUIPMENT

- 7.1. See Appendix A of the Quality Assurance Manual for configuration of specific components, computer hardware and software, serial numbers and receipt of the major components of the instruments.
- 7.2. Gas chromatograph/Mass Selective Detector Systems
- 7.2.1. Gas Chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases.
- 7.2.2. GC Column Options:
- Hewlett Packard HP-624, 25 M, 0.2 mm ID fused silica, 1.12 micron film thickness, or equivalent;
 - J&W DB624, 60 M, 0.32 mm ID fused silica, 1.8 micron film thickness, or equivalent;
 - J&W DB624, 60 M, 0.25 mm ID fused silica, 1.0 micron film thickness, or equivalent;
 - J&W DB624, 20 M, 0.18 mm ID fused silica, 1.0 micron film thickness, or equivalent.

- 7.2.3. Mass Spectrometer - HP5970B, HP5971, HP5972, or HP5973 - Capable of scanning from 35 to 300 amu every 2 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.
- 7.2.4. Data System - A computer system interfaced to the mass spectrometer. The system allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software (HP Chemstation) that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). The software allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.
- 7.3. Appropriate analytical balance (0.0001 g recommended for standard preparation and 0.01 g for sample weighing), volumetric flasks, syringes, vials, and bottles for standards preparation.
- 7.4. Purge and Trap with Autosampler
- 7.4.1. Each volatile GC/MS analytical system uses a purge and trap concentrator system to introduce the sample onto the GC column. Each purge and trap has an autosampler (A/S) attached to run multiple samples, one at a time, and run unattended for extended periods of time.
- 7.4.2. Varian Archon autosamplers – these autosamplers add both Internal Standards and Surrogate Standards automatically from two individual receptacles, removing some of the inconsistencies related to the repetitive analyst setup of the older autosampler technology. In turn, the sample and standard preparation vary for both methods 5030 and 5035 using these autosamplers. The preparation of both samples and standards for method 8260B by 5030 and 5035 will be addressed below.
- 7.4.3. Centurian autosamplers – these autosamplers add both Internal Standards and Surrogate Standards automatically from two individual receptacles, removing some of the inconsistencies related to the repetitive analyst setup of the older autosampler technology. In turn, the sample and standard preparation vary using these autosamplers. The preparation of both samples and standards for method 8260B waters will be addressed below.
- 7.4.4. Adsorbent Traps: Supelco K-Traps Carboxen Vocarb 3000.

7.5. PH indicator Paper – wide range – examples: pHydriion by Mikro 1-12 or EMD colorpHast 0-14.

7.6. See VOC-5035 for further equipment related to soil sample collection, preservation, and extraction.

8. PREVENTATIVE MAINTANENCE

Typical preventive maintenance measures include, but are not limited to, the following items:

- Check gas supply
- Change in-line filters, septum, gold seal, and injection port liner, as needed
- Clip column as needed
- Clean source

Specific instructions for these maintenance activities are found in the appropriate instrument manuals.

Maintenance log - All Preventive maintenance, as well as instrument repair, should be documented in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

9. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1. Solvents must be of sufficient purity to permit usage without lessening the accuracy of the determination or introducing interferences. Solvents are to be checked for contamination before use. See ADM-CTMN.

- Methanol, purge and trap grade or equivalent. Purchased commercially. Store at room temperature for up to 3 years.

9.2. See VOC-5035 for preservatives.

9.3. **Standards storage and expiration** – All of the standards in this SOP are stored in the freezer and are allowed to warm to room temperature before using. Prepared standards expire one month from preparation or sooner if indicated by poor performance. Purchased standards expire upon manufacturer's indications or one month from opening, whichever is sooner. All ampulated gas standards expire upon manufacturer's indications or one month from opening. All dilutions made from the opened gas standard less than 100 ppb expire one week from preparation, unless verified against another source or continue to perform within 20%^D of the initial calibration.

9.4. **Standards Preparation General Information and Disclaimers**

All of the preparation instructions are general guidelines. Other technical recipes may be used to achieve the same results. Example – a 20 mg/L standard may be made by adding 1 mL of 200 mg/L to 10 mLs or may be made by adding 4 mL of 50 mg/L to 10 mLs. The preparation depends upon the final volume needed and the initial concentration of the stock. Reasonable dilution technique is used.

The initial calibration curves given are typical, but also subject to variation due to targets and detection levels needed. The curves will always be at least 5 points. The lowest concentration level shall be at the method reporting level. The remaining levels should define the working linear range of the analytical system.

Vendors and vendors' products are sometimes listed for the ease of the analyst using this SOP, but products and purchased concentrations are examples only and subject to change at any time. All purchased standards are certified by the vendor. Certificates of Analysis are kept in the department until the standards are no longer being used – at which time they are archived with QA. Certificates of Analysis are available upon request. Purchased standards are routinely checked against an independent source for both analyte identification and analyte concentration.

All Standards must be traceable using the CAS lot system (ADM-DATANTRY).

All targets are routinely spiked in the LCS, MS, and MSD.

9.5. **Internal Standards and Surrogates** - The surrogates used are Dibromofluoromethane, toluene-d₈, 4-bromofluorobenzene, and 1,2-dichloroethane-d₄. The internal standards are pentafluorobenzene, 1,4-difluorobenzene, 1,4-dichlorobenzene-d₄ and chlorobenzene-d₅. All surrogates and internal standards are added to every standard, sample, blank and spike at 50 ug/L (5 ul of a 50 ppm working standard mix to 5.0 mL sample volume) for water and soils. The initial calibration standards have additional surrogate added to attain varied calibration concentration levels. 1,2-Dichloroethane-d₄ is reported and evaluated only if requested, even though it is always added.

*See DOD Summary Attachment for DOD Specific Criteria

9.5.1. Stock standards (purchased) – used for both Archon and Centurian systems

9.5.1.1. Internal Standard Mix (2500 ug/mL) - Supelco 8260B Equity IS Mix.

9.5.1.2. Surrogate Mix (2500 ug/mL) –Ultra 8260B Surrogate Mix

9.5.2. Centurian Intermediate and Working Standards (prepared)

9.5.2.1. Centurian IS and Surr Intermediate Standards

9.5.2.1.1. Internal Standard Mix (500 ug/mL) – Dilute 1.0 mL of 2500 ug/mL Stock Internal Standard Mix to 5.0 mL with Methanol.

9.5.2.1.2. Surrogate Mix (500 ug/mL) – Dilute 1.0 mL of 2500 ug/mL Stock Surrogate Mix to 5.0 mL with Methanol.

9.5.2.2. Centurian IS and Surrogate Working standards (prepared)

9.5.2.2.1. Internal Standard Mix (50 ug/mL) – Dilute 500 uL of 500 ug/mL Internal Standard Mix to 5.0 mL with Methanol.

9.5.2.2.2. Surrogate Mix (50 ug/mL) – Dilute 500 uL of 500 ug/mL Surrogate Mix to 5.0 mL with Methanol.

9.5.2.2.3. Surrogate Mix (25 ug/mL) – Dilute 250 uL of 500 ug/mL Surrogate Mix to 5.0 mL with Methanol.

9.5.2.2.4. Combined Internal Standard/Surrogate Mix (50 ug/mL) – Dilute 500 uL of 500 ug/mL Intermediate Internal Standard Mix and 500 uL of 500 ug/mL Intermediate Surrogate Mix to 5.0 mL with Methanol.

9.5.3. Archon IS/Surr Working Standard (prepared)

9.5.3.1. Combined Internal Standard/Surrogate Mix (250 ug/mL) – Dilute 1 mL of 2500 ug/mL Internal Standard Stock and 1 mL of 2500 ug/mL Surrogate Stock to 10 mLs with methanol.

9.5.3.2. This solution is placed into an autosampler vial that acts as a reservoir for the autosampler. 1 uL is automatically added to each injection (5 mL) for a concentration of 50 ug/L. The sample or standard is transferred from the Archon through a nickel transfer line, past a ported valve that is calibrated to deliver 1 uL of IS/Surr mix. The sample fraction is transferred to a fritted sparge chamber on the Tekmar 2016 concentrator at which time the sample or standard is purged on to the absorbent trap.

9.6. **Tune Standard** (10 ug/L) – dilute 1 uL of 500 ug/mL Working Surrogate Standard (the Surrogate standard contains the BFB needed for the Tune) to 50 mLs with DI.

9.6.1. For Waters – place the whole vial on the system.

9.6.2. For Soils – place 5 mLs of the solution into a vial and place on the system.

9.7. **Preparation of Primary Standards for 8260B Full List Targets**

9.7.1. Full List Stock Standard Solutions

9.7.1.1. Targets/Gases/APP-MANN Stock Standards

- Supelco 8-61339 (2000 ug/mL) – purchased
- Supelco 4-8799-0 (2000 ug/mL) – purchased
- Supelco 86-1298 (various levels) – purchased

9.7.1.2. HSL Stock Standards

- Supelco 46831-u (2000 ug/mL)
- Chloroprene (2000 ug/mL) – Supelco 86-1145
- Acrolein (approximately 32000 ppm) – made from neat - exact concentration calculated from exact mass added (recorded to 0.1 mg).

9.7.1.3. Freons Plus Special Stock Standard

- Accustandard Primary Freons Custom 5-9219 (2000 ug/mL)
- 8260 Extras - Absolute 94237 (500-40000 ug/mL)

9.7.2. Full List Targets Working Solutions

9.7.2.1. Targets/Gases/App-MANN Higher Working solution (500-10000 ppm) – Dilute 1.25 mLs of each of the three Targets/Gases/App-MANN Stock solutions to 5.0 mLs with methanol.

9.7.2.2. HSL Working solution (500 ppm compounds and 2500 ppm acrolein) – Dilute 1.25 mLs of 2000 ppm Supelco 46831-u, 1.25 mLs of 2000 ppm chloroprene, and a volume (volume calculated to bring to desired concentration) of ~32000 ppm acrolein to 5.0 mLs with methanol.

9.7.2.3. Freons Plus Special Working Solution (500-40,000 ppm) – Dilute 1.25 mLs of 2000 ug/mL Freons Special Stock and 1.25 mL of 8260 Extras to 5.0 mLs with methanol.

9.7.2.4. Low Level Combined Working Solution – Dilute 10 uL of each of the above working solutions to 1.0 mLs with methanol.

9.7.3. Calibration Level Standards for waters by Archon (Example-varies by instrument)

Concentration of standard (VSTD)	0.5	1	2	5	10	20	50	100	150	200
Concentration of surrogate	50*	50*	50*	60	75	50*	50	100	150	200
Vol. Of low level combined working std.	5	10	20	0	0	0	0	0	0	0
Vol. of target/gases working std. (uL)	0	0	0	0.5	1	2	5	10	15	20
Vol. Of HSL working Std (uL)	0	0	0	0.5	1	2	5	10	15	20
Vol. Of Freons Special Std (uL)	0	0	0	0.5	1	2	5	10	15	20
Vol. Of 500 ppm Surrogate Stock (uL)	0	0	0	1	2.5	0	0	5	10	15

*Not used in the surrogate curve

Dilute the above volumes to 50 mLs with DI. Place each standard in its own vial. The Archon draws 5.0 mLs of the standard from the vial and adds 1 uL of the combined 50 ppm IS/Surr standard. Not all of the points are always used.

9.7.4. Calibration Level Standards for waters by Tekmar (Example-varies by instrument)

Concentration of standard (VSTD)	1	5	20	50	100	150	200
Final Concentration of surrogate (ppb)	50*	50*	20	50	100	150	200
Vol. of low-level comb. working std. (uL)	10	0	0	0	0	0	0
Vol. Of targets/gases working std. (uL)	0	0.5	2	5	10	15	20
Vol. Of HSL working Std (uL)	0	0.5	2	5	10	15	20
Vol. Of Freons working Std (uL)	0	0.5	2	5	10	15	20
Vol. Of 500 ppm Surrogate Stock (uL)	0	0	2	0	5	10	15
Vol. Of 50 ppm IS stock (uL)	0	0	5	0	0	0	0

*Not used in the surrogate curve

Dilute the volumes above to 50 mLs with DI. Remove a 5.0 mL aliquot and add 5.0 uL of 50 ppm combined IS/Surr stock to all except the 20 ppb standard which already had the Internal Standards and Surrogates added. Purge 5.0 mLs.

9.7.5. Calibration Level Standards for Soils by Archon (Example-varies by instrument)

Concentration of standard (VSTD)	5	10	20	50	100	150	200
Concentration of surrogate	50*	50*	75	50	100	125	150
Vol. Of low level combined working std. without Freons (uL)	50	100	0	0	0	0	0
Vol. of target/gases working std. (uL)	0	0	2	5	10	15	20
Vol. Of HSL working Std (uL)	0	0	2	5	10	15	20
Vol. Of 500 ppm Surrogate Stock (uL)	0	0	2.5	0	5	7.5	10

*Not used in the surrogate curve

Dilute the above volumes to 50 mLs with DI. Transfer 5.0 mLs each standard to separate vials. The Archon adds 1 uL of the combined 50 ppm IS/Surr standard to the vial of the aqueous standard and purges directly in the vial. Not all of the points are always used.

When calibrating for the analysis of soils by 5035/8260B, the standard solution above must contain the same amount of Sodium Bisulfate as the samples being analyzed.

9.8. **Preparation of Secondary Standards for 8260B Full List Targets**

9.8.1. **Secondary Stock Standards**

9.8.1.1. Secondary Targets/Gases

- Supelco 8-561298 – purchased
- Supelco 4-58799- purchased
- Supelco 8-561339 – purchased

9.8.1.2. Secondary HSL

- Supelco 456831-U- purchased
- Supelco 85561145 – purchased
- Acrolein - made from a second source of neat acrolein.

9.8.1.3. Secondary Freons

- Absolute 93034 (1000 ppm) – purchased
- Absolute 94236/8260B Extra Compound SS (2000-40,000).

9.8.2. **Working Standards**

- Secondary Targets/Gases (500-10,000 ppm)- Dilute 1.25 mLs of each of the Target/Gases purchased standards to 5.0 mL with methanol.
- Secondary HSL (500-2500 ppm) – Dilute 1.25 mLs of each of the purchased HSL standards and 0.390 mLs of the acrolein standard to 5.0 mLs with methanol.
- Secondary Freons Plus – Dilute 1.0 mL of 93034 (SS Freons – 1000 ppm) purchased standard and 94236 (SS Extras 2000-40000 ppm) standard to 5.0 mLs with methanol.

9.8.3. **ICV (50 ppb)**– Dilute 5.0 uL of Secondary Target/Gases Working stock, 5.0 uL of Secondary HSL Working Stock, and 12.5 uL of Secondary Freons Plus working stock to 50.0 mLs with DI.

9.8.4. **LCS (20 ppb)**- Dilute 2.0 uL of Secondary Target/Gases Working stock, 2.0 uL of Secondary HSL Working Stock, and 5 uL of Secondary Freons Plus working stock to 50.0 mLs with DI.

9.8.5. **MS/MSD (50 ppb)**- Add 5.0 uL of Secondary Target/Gases Working stock, 5.0 uL of Secondary HSL Working Stock, and 12.5 uL of Secondary Freons Plus working stock to 50.0 mLs of sample.

9.8.6. **Method Blank** – Analyze DI as a sample.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to the instructions in this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are only to be performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

11. PROCEDURE

11.1. Be sure the system has a current MDL and the analyst has a current Demonstration of Capability.

11.2. Sample Preparation –samples are screened according to VOC-SAMPL.

11.2.1. Water Samples

11.2.1.1. No preparation is generally required, other than dilution with reagent water to bring analytes into the upper half of the calibration range. Thus, a 5.0 mL sample volume is run straight from the sample vial for a 5.0 mL purge. Other purge volumes (10, 25 mLs for low level) may be used depending on client requirements.

11.2.1.2. After analysis, the pH of all water samples are to be checked with pH paper. The pH shall be noted in the run log. If the pH is not <2, file a pH discrepancy form and give to the Project Manager.

11.2.1.3. Samples requiring dilutions due to targets above the linear range of the instruments are prepared as follows according to ADM-DIL:

11.2.1.3.1. (1/5) = 10 mL sample adjusted to 50 mL in a 50 mL ground glass graduated cylinder inverted once and transferred to a 40 mL VOA vial

11.2.1.3.2. (1/25) = 2.0 mL sample adjusted to 50 mL in a 50 mL ground glass graduated cylinder inverted once and transferred to a 40 mL VOA vial

11.2.1.3.3. (1/50) = 1.0 mL sample adjusted to 50 mL in a 50 mL ground glass graduated cylinder inverted once and transferred to a 40 mL VOA vial

11.2.1.4. Internal standards and surrogates are added to the diluted sample by the autosampler.

Note: At no time should less than 1 mL of the original sample fraction be used for the preparation of the diluted sample. This insures a representative fraction of sample is diluted.

11.2.2. Soil samples

11.2.2.1. Follow VOC-5035 for preparation of soils by 5035.

11.2.2.2. 5.0g ± 0.05 g weighed on a certified top-loading balance or equivalent. Record the weight to two decimal places.

11.3. Instrument Performance Check –Tuning

11.3.1. Verify that the MS meets standard mass spectral abundance criteria prior to initiation of any samples by injecting the 4-bromofluorobenzene (BFB) tune standard. The tune standard must be analyzed at the beginning of the analytical sequence and every 12-hours of continuous analysis. The 12-hour clock starts at the time of the BFB injection. Evaluate the ion abundance using the following scenarios:

11.3.1.1. One scan at the apex, or one scan immediately preceding the apex or one scan immediately following the apex;

11.3.1.2. The mean of the apex and the immediate preceding or following scans;

11.3.1.3. The mean of the apex, immediately preceding scan, and immediately following scan;

11.3.1.4. Any of the three scenarios above with background subtraction. If background subtraction is necessary, a single scan, no more than 20 scans prior to the elution of BFB may be used. Do not background subtract part of the BFB peak.

11.3.2. Each volatile GC/MS system must meet the BFB ion abundance criteria shown in Table 1 for a 50 ng injection of BFB.

11.3.3. If tuning criteria cannot be met, the source may need cleaning, filaments replaced or other maintenance. Record the corrective action taken in the run log or maintenance log and re-inject the tune standard. Sample analysis may not proceed until the tune meets these criteria.

11.4. Initial Calibration – follow the CAS ICAL Policy for Organic Analytes.

11.4.1. Tune the instrument according to 11.3.

11.4.2. Run an instrument blank to demonstrate that the instrument is free of contamination before analyzing the standards.

11.4.3. A 5 point calibration must be analyzed. More points can be used for better response. The standards must be analyzed the same as the samples (example: if samples are to be heated, the standards are to be heated). Calibration levels are given in Section 9 depending on the client requirements. Analyze each calibration standard and tabulate the area response of the characteristic quantitation ions versus concentration for each compound, internal standards and surrogate. The low level standard used during calibration shall be the reporting level for the analysis. The midpoint standard of the initial calibration curve establishes the retention time window position for each analyte and surrogate.

11.4.4. The internal standards should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see instrument specific addendum - attached). If interferences are noted, use the next most intense ion as the quantitation ion.

11.4.5. Calculate the response factors (RF) for each compound and surrogate relative to the specified internal standard by:

$$RF_x = \frac{(A_x)(C_{ISTD})}{(A_{ISTD})(C_x)}$$

Where:

- A_x = Area of the characteristic quantitation ion for compound x.
 A_{ISTD} = Area of the characteristic quantitation ion for the specified internal standard.
 C_x = The concentration of the compound added (ppb).
 C_{ISTD} = The concentration of the specified internal standard (ppb).

11.4.6. Calculate the mean response factor ($\overline{RF_x}$) for each analyte and surrogate from the calibration levels. Calculate standard deviation (SD) and the percent relative standard deviations (%RSD) for each analyte from the mean with:

$$SD = \sqrt{\frac{\sum_{i=1}^N (RF_i - \overline{RF})^2}{N - 1}}$$

where:

RF_i = RF for each of the 5 calibration levels
 \overline{RF} = mean of 5 initial RFs for a compound.
 N = Number of RF values (i.e., 5)

$$\%RSD = \frac{(SD)}{(\overline{RF}_x)} 100.$$

where:

RSD = relative standard deviation.
 \overline{RF} = mean of 5 initial RFs for a compound.
 SD = standard deviation of average RFs for a compound.

11.4.7. Initial Calibration criteria

11.4.7.1. The % RSD should be less than 15% for each target compound. If the %RSD of any target is greater than 15%, see the options below.

11.4.7.2. If the % RSD for any target compound is 15% or less, linearity can be assumed over the calibration range, and the relative response factor for each analyte and surrogate is used to quantitate sample analytes.

11.4.7.3. If the % RSD of any compound is > 15%, construct a linear regression calibration curve of area ratio (A/A_{is}) versus concentration using the equation of a line ($y=mx+b$). The origin may not be used as a calibration point and the required Correlation Coefficient must be $\geq 0.990^*$. If the Calibration Correlation is not met, linear regression may not be used to quantitate the target. See the option below. It is good lab practice to mark all target compounds on a curve to identify target compounds calculated using linear regression.

11.4.7.4. The response of 5 SPCC's (System Performance Check Compounds) must meet the following minimum \overline{RF}_x :

SPCC	5 mL purge	25 mL purge
Chloromethane	>0.10	>0.010
1,1-Dichloroethane	>0.10	>0.200
Bromoform	>0.10	>0.05
Chlorobenzene	>0.30	>0.500
1,1,2,2-Tetrachloroethane	>0.30	>0.100

11.4.7.5. Initial Calibration Verification Standard (ICV)- inject and analyze the ICV to verify the initial calibration immediately after the calibration. The % recovery must meet 70-130%* for all compounds.

11.4.8. Only after the calibration has passed all of the above criteria shall samples be analyzed.

11.5. Daily GC/MS Calibration and Analytical Sequence

11.5.1. The start of a 12-hour analysis window requires a check of the Mass Spec Detector's tune via an injection of 50 ng of BFB. The acceptance criteria must be met before client samples are analyzed.

*See DOD Summary Attachment for DOD Specific Criteria

11.5.2. CCV -

11.5.2.1. Frequency - After the tuning criteria have been verified, the initial calibration must be checked and verified by analyzing a midrange Continuing Calibration Verification Standard (CCV).

11.5.2.2. Concentration - The 50 ppb level is recommended. NELAC requires this calibration check standard to vary in concentration over time. An injection of the CCV and LCS standards shall satisfy this requirement as long as the standards are two different concentrations.

11.5.2.3. Limits and Corrective Action-

11.5.2.3.1. Each SPCC compound must meet it's minimum RF (see above). This is the same check that is applied to the initial calibration. If these criteria are not met, correct the problem and obtain a compliant CCV or recalibrate before sample analysis begins.

11.5.2.3.2. The CCC compounds listed previously are used to check the validity of the initial calibration. Calculate the %D for each compound using the calculations below. The %D for each CCC must meet $\leq 20\%$ for the initial calibration to be valid.

11.5.2.3.2.1. For **linear regression calibrations**, calculate the percent drift using:

$$\% \text{ Drift} = \frac{C_c - C_T}{C_T} \times 100$$

where:

C_c = Calculated concentration of Calibration Check Compound standard.

C_T = Theoretical concentration of prepared standard.

11.5.2.3.2.2. For **calibrations based on RF**, calculate the percent difference using:

$$\% \text{ Difference} = \frac{RF_v - \overline{RF}}{\overline{RF}} \times 100$$

where RF_v is the response factor from the analysis of the verification standard and \overline{RF} is the mean response factor from the initial calibration.

11.5.2.4. If the CCC compounds are not included in the initial calibration, all compounds must meet the $\leq 20\%$ criteria.

11.5.2.5. For all other TCL compounds, the %D should meet $\leq 25\%$. Two compounds may be greater than 25%D, however must not exceed 40%D for analysis to continue. It is good lab practice to maintain $\leq 20\%$ D when a compound is positive in a sample to ensure accurate quantitation, but not required.*

11.5.3. Internal Standards - If the tune criteria and the continuing calibration criteria are met, then evaluate the retention times of all compounds, surrogates, and internal standards against the initial calibration. If the retention time for any internal standard changes by more than 30 seconds from the current initial calibration mid-point standard, the system must be inspected for malfunctions and corrections must be made, as required. If the area for any of the internal standards changes by a factor of 2 (-50% to +100%) from the current initial calibration mid-point std., corrections must be made to the system. Reanalyze any samples associated with malfunctioning system.

11.5.4. Analyze the LCS. Evaluate the LCS according to the instructions in 12.

11.5.5. Analyze a method blank to check the system for contamination. Evaluate the MB according to the instructions in 12.

11.5.6. When all of the above criteria are met, client sample analysis may begin.

11.5.7. When purging 25 mL sample volumes to obtain lower detection limits, criteria from the EPA Statement of Work, OLC 02.1 shall be followed. See Table 3.

11.6. Identification of Analytes and Data Interpretation, and Client Sample Analysis

11.6.1. Note that medium soils (prepared by method 5035) are run on water curves on any autosampler. Client samples are analyzed on an instrument running an appropriate calibration for the target compound list needed for the sample.

11.6.2. The qualitative identification of compounds determined by this method is based on retention time, and comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass

*See DOD Summary Attachment for DOD Specific Criteria

spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met. If there is no peak found for an analyte in the expected retention time window and the mass spectra does not match according to the below, then the analyte is "not found".

- 11.6.2.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.
 - 11.6.2.2. The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.
 - 11.6.2.3. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.
 - 11.6.2.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
 - 11.6.2.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
 - 11.6.2.6. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.
- 11.6.3. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification.

*See DOD Summary Attachment for DOD Specific Criteria

11.6.4. If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, dilute the sample (from a fresh vial if available) according to section 11.2 and ADM-DIL. If a fresh vial is not available, the use of a compromised vial must be documented in the runlog and on the case narrative (by use of a NCAR – see ADM-NCAR).

11.6.5. If the detector becomes saturated from a high concentration sample run a blank after the sample to demonstrate the instrument is free from carry-over. If there is contamination, take corrective action. The instrument must be demonstrated to be free from contamination before analysis may continue.

12. QA/QC REQUIREMENTS

12.1. **Method Blank** - For every 12-hour analysis window and for each analytical batch, after meeting the tune and continuing calibration criteria, at least one method blank must be run and reportable for each matrix. All blanks reported must be free from target analytes with the exception of known common laboratory contaminants. Acetone and Methylene Chloride must not be present at a level greater than 5 times the MRL and all samples affected should be marked with the appropriate lab flag. Method blanks are considered free of contamination if the result is less than half of the reporting limit. Reanalyze the MB until the system is shown to meet these criteria. Reanalyze any samples associated with a non-compliant method blank.

Exception: if a target analyte is greater than ten times the method blank contaminant, the analysis may continue since the sample concentration is high enough that possible contamination has not significantly affected its concentration.

12.2. LCS-

12.2.1. **Frequency** - With each batch of samples (20 samples maximum), a minimum of one LCS for each matrix must be analyzed to ensure instrument performance. When batches are less than 20 samples, the LCS is performed on a per batch basis. The LCS is prepared by spiking a blank with the matrix spike solution, and going through the entire extraction and analysis. LCSs may be analyzed in duplicate to avoid discarding a sequence due to mishaps such as poor desorption, improper standard preparation, or poor injection. In order to be considered as duplicates, LCSs must be run together without samples or other QC in between. When duplicate LCSs are analyzed within the sequence, the following acceptance criteria have been established:

12.2.1.1. When the first LCS of the duplicate pair meets LCS criteria, this LCS is reported and used to verify continued performance. Continue with the sequence. The second is not evaluated or reported.

12.2.1.2. When the first LCS of the duplicate pair does not meet the LCS criteria and the second LCS does meet LCS criteria, the second LCS is reported and used to verify continued performance. If known, the cause of the first failure should be noted in the run log. Continue with the sequence. The first LCS is not reported.

12.2.1.3. When some or all compounds are outlying within the first or second or both LCSs, the results shall not be merged to report an acceptable LCS. If the outliers are high bias and the associated samples prior to and following the LCS are non-detect for those compounds, the LCS may be used to verify the performance and reported with the high bias. Otherwise the sequence is not valid since the LCS cannot be used to close the previous samples or open for the following samples. The unacceptable LCS and associated samples shall be reanalyzed.

12.2.2. Acceptance Criteria

12.2.2.1. Calculate percent recovery (%R) as follows:

$$\%R = X/TV \times 100$$

Where: X = Concentration of the analyte recovered
TV = True value of amount spiked

12.2.2.2. Acceptance criteria for lab control samples are listed in Appendix C of the Quality Assurance Manual*.

Exceptions: Client-specific QAPP requirements also may supercede lab control limits listed in Appendix C of the Quality Assurance Manual.

12.2.3. **Corrective Action** - If the LCS recovery for any control analyte* fails acceptance limits, corrective action is required except as described below. If instrument corrective action is not applicable or ineffective, re-analysis of the associated samples is required. If any other analyte fails the acceptance limits, the analyst must evaluate the impact on data quality and take any necessary corrective action, which may include re-analysis of the associated samples. Project-specific requirements may require all

*See DOD Summary Attachment for DOD Specific Criteria

compounds to be treated as control analytes, or dictate use of project acceptance criteria.

12.2.4. Sample analysis may continue under the following circumstances when controlled compound* recoveries fall outside the control limits listed in Appendix C of the Quality Assurance Manual.

- High outlying recovery associated with a non-detect sample result since the high bias would have negligible effect on non-detect sample results.
- Reanalysis would result in a worse quality scenario such as holding time issues or insufficient sample volume.
- Low outlying recoveries associated with non-detect sample results as long as the response factors for these compounds are adequate to show the compound's presence in the sample.

12.3. MS/MSD –

12.3.1. **Frequency** - For each batch of samples (20 samples maximum), a minimum of one MS/MSD pair for each matrix must be analyzed to assess sample matrix and to ensure instrument performance. If there is not enough sample to process MS/MSD, a Blank Spike and Blank Spike Duplicate will be processed to show precision in the batch. See below.

12.3.2. **Recovery Limits** - The limits for MS recovery and MS/MSD RPD are given in Appendix C of the Quality Assurance Manual*.

12.3.3. Recovery Corrective Action

12.3.3.1. Although all targets are evaluated, only the method specific compounds (1,1-Dichloroethene, trichloroethene, benzene, toluene, and chlorobenzene) are typically reported from the MS/MSD analyses. The results of the MS/MSD analysis is used for client assessment of sample matrix and is not used to control the analysis. Outlying MS/MSD recoveries associated with an acceptable LCS may indicate sample matrix interferences, but does not warrant reanalysis or confirmation. All data shall be reported with the appropriate flags or mentioned in the Case Narrative.

12.3.3.2. If the MS/MSD does not pass precision or accuracy requirements, evaluate the associated LCS. If the LCS passes QC requirements it is presumed that matrix has affected the

*See DOD Summary Attachment for DOD Specific Criteria

spiked samples and the run may continue. If the concurrent LCS fails for the same compound or any other compound the validity of the LCS should be examined and any samples prior to the LCS and after the last CCV should be reanalyzed, including the MS/MSD.

12.3.4. **RPD Limits** – given in Appendix C of the Quality Assurance Manual

12.3.5. **RPD Corrective Action** - if the RPD value between samples or MS/MSD results exceed limits listed in Appendix C of the QAM, examine the chromatograms and benchsheets for potential matrix interferences. Examples may include product layers on aqueous samples that may result in non-homogenous subsampling, non-homogenous soil samples, chromatographic interferences resulting in poor peak resolution and inconsistent integrations, or poor purging efficiencies (indicated by surrogate recovery). Reanalyze the pair if deemed appropriate. The outlying RPD should be mentioned in the Case Narrative so that data may be flagged appropriately.

12.4. **BS/BSD** – (Blank Spike/Blank Spike DUP) - only run when there is insufficient sample for MS/MSD at the MS/MSD frequency. The RPD must meet RPD limits listed for the MS/MSD. If it does not, the outlying RPD must be mentioned in the case narrative.

12.5. **Calibration** - The acceptance criteria for tuning verification, initial, and continuing calibration verification are discussed in the procedure (Section 11).

12.6. **Surrogates and Internal Standards** –

12.6.1. **Frequency** – Added to all injections

12.6.2. **Acceptance Criteria** - The limits for surrogate recovery is given in Appendix C of the Quality Assurance Manual. Dichloroethane-d4 is evaluated and reported only if requested. The limit for internal standards is (-50% to 100%).

12.6.3. **Corrective Action** - When instances of Surrogate or internal area count failures occur, the associated sample is repeated and the results are compared. If the questioned samples fail a second analysis, the first run is reported to the client and the sample flagged with an “**” indicating a probable matrix interference exists. In the case where Tier package work is required and the appropriate forms need to be generated, the second analytical analysis is also reported to the client. If the second analysis passes, report these data.

12.6.4. If a surrogate(s) fails acceptance, the sample must be evaluated for matrix interferences and "historical results". Reanalyze the sample to confirm the interference. If needed contact client and flag the data in the report. If surrogates are diluted more than 10 times, report as "D", diluted below calibration. For package reports, include initial and confirmation analysis results. High outlying recoveries associated with non-detect sample results need not be reanalyzed. They need only be noted in the case narrative as high bias with non-detect results.

13. DATA REDUCTION AND REPORTING

13.1. Calculations

The GC/MS data stations, in current use, all use the H-P RTE Integrator to generate the raw data used to calculate the standards \overline{RF}_x values, the sample amounts, and the spike values. The software does three passes through each data file. The first two identify and integrate each internal standard and surrogate. The third pass uses the time-drift information from the first two passes to search for all method analytes in the proper retention times and with the proper characteristic quantitation ions. The primary and secondary quantitation ions are given in Table 2. The internal standard with which the analytes are associated changes with each column and is documented in the Initial Calibration Summary Report. The current associations per instrument are attached to this SOP in the Instrument Specific Addendum.

13.1.1. The results for a water sample are calculated as follows when \overline{RF}_x is used:

$$A_x = \frac{(Resp_x)(Amt_{ISTD})}{(Resp_{ISTD})(\overline{RF}_x)} \times DilFactor$$

Where:

A_x = the amount, in ppb, of the analytes in the sample;

$Resp_x$ = the peak area of the analytes of interest;

$Resp_{ISTD}$ = the peak area of the associated internal standard;

Amt_{ISTD} = the amount, in ppb, of internal standard added; and

\overline{RF}_x the average response from the five-point for the analytes of interest.

13.1.2. The results for a soil sample are broken into two types, the low-level type and the high-level type.

13.1.2.1. The low-level type is a direct heated purge of soil and requires its own separate five-point. For soil, 5 grams is weighed out into the sample vial, and is purged with 5 mL of blank reagent water at a temperature of $40^\circ\text{C} \pm 2^\circ$. The results for low-level soil work are calculated by taking the normal print out, in ppb,

*See DOD Summary Attachment for DOD Specific Criteria

(see the water results outlined above) and correcting for the total, dry soil sample actually purged (the dry weight is determined according to GEN-DWPS in the General Chemistry Department and the 8260 correction is made in LIMS):

$$(A_x) * \frac{(5 \text{ grams})}{(ASW_t \text{ gr})(\% \text{ Solids})} = A_x \text{ Low - Level Soil}$$

Where:

A_x = the amount, in ppb, from the data station;

5 grams = the nominal amount of soil that is heated and purged;

ASW_t = the actual soil wet weight, in grams, that is purged

% Solids = the correction factor for dry weight in decimal form.

13.1.2.2. The high-level type is based on an extraction (see VOC-5035).

In general, a four-gram wet weight of soil is extracted with 10 mL of purge-and-trap methanol. A 100 ul aliquot of this extract is run against the results for a high-level soil extract are calculated as follows:

$$(A_x) * \frac{(\text{Dilution})(5 \text{ ml})}{(ASW_t)(\% \text{ Solids})} = A_x \text{ High - Level Soil Amt.}$$

Where:

A_x = the data station results, in ppb;

Dilution = the dilution of the extract.

5 mL = the amount of methanol used to extract the soil;

ASW_t = the actual wet weight of soil extracted

% Solids = the dry soil correction in decimal form.

It should be noted that some states and governing agencies require differing amounts of soil and Methanol ratio be maintained these ratios are generally, 1:2.5, 1:2, 1:1. The amount of extract added is never greater than 100 ul per 5 mL DI. As an example, the Archon autosampler would require the addition of 1.0 mL to 49 mL DI. This is then transferred to a 40 mL VOA vial. See the included table in method 5035 for specific state regulation on soil to Methanol ratios.

13.2. All sample data and QC data, including calibration verification must reference the name (date or filename) of the ICAL on the raw data report.

13.3. Manual Integration – When the data system incorrectly quantitates or identifies analytes, manual integration is necessary. Data must be integrated consistently between standards, samples, and QC. See ADM-INT.

*See DOD Summary Attachment for DOD Specific Criteria

13.4. Reporting

Most reports are generated using STARLIMS. All data is transferred electronically from the instrument into STARLIMS. The data is reviewed by a qualified peer with applicable checklists (see ADM-DREV) before the data is acceptable and able to be reported to the client.

14. METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

Demonstration of Capability is performed upon instrument set-up, whenever a new analyst begins independent analysis, and annually thereafter according to ADM-TRANDOC and section 19 below. The documentation of this method performance is retained by the Quality Assurance office

Accuracy and Precision Data is available in SW-846 method 8260B.

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

- 15.1. It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.
- 15.2. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.
- 15.3. Excess, unused sample and testing byproducts are disposed following the procedures in the *SMO-SPDIS*.

16. CORRECTIVE ACTION FOR OUT OF CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18. REFERENCES

- 18.1. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods*, USEPA SW-846, Third Edition, December 1996.

19. TRAINING OUTLINE

- 19.1. Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.
- 19.2. Observe Sample Preparation and Analysis. Follow GC/MS Training Plan Form.
- 19.3. Participate in the methodology, documentation, and data reduction with guidance
- 19.4. Demonstrate Competency by performing the analysis independently. Analyze four replicates of the LCS. If recovery is within the limits of the LCS in Appendix C of the Quality Assurance Manual, complete Training Plan Form, summary spreadsheet, and IDC certificate and file with QA. An IDC study must be acceptable before the new analyst may analyze samples independently. Continuing Demonstration of Capability is demonstrated annually with the acceptable performance of a Proficiency sample, or new four replicate study.

20. METHOD MODIFICATIONS

None

21. INSTRUMENT-SPECIFIC ADDENDUM

Attached are the printouts from the GC/MS instruments running 8260B showing which analytes are associated with which internal standard. The instrument is the third item in the first line (Data File) of the report. Example: Data File: J:\ACQUDATA\MSVOA#. The internal standards are the first compound in each section (always have an AvgRF and CCRF of 1.000) and the associated analytes are listed below the internal standard.

22. ATTACHMENTS

Table 1 BFB Tune QC Criteria
Table 2 Characteristic Masses for Purgeable Organic Compounds
Attachment I SIM MODE
Attachment II CURRENT IS/ANALYTE ASSOCIATIONS PER INSTRUMENT
Attachment III DOD Summary and QC Criteria

23. CHANGES FROM PREVIOUS REVISION

- Updated DoD requirements to QSM V3 throughout
- 7-Added column option – 60M, 0.25 mm ID, 1 micron.
- 7-Added paragraph describing Centurian
- 8-Updated maintenance – added need to change gold seal – eliminated references to guard columns and jet separators.
- Throughout - Removed references to Tekmar since the Tekmars are no longer being used
- 9-Changed the Tekmar IS and Surr standards prep to Centurian
- 9-Changed the tune standard from 1 ug/L to 10 ug/L.
- 9-Updated the manufacturer's standards used
- 11-Eliminated the grand mean option and the associated 30% RSD ICAL criteria for CCCs.
- 11-Added the minimum \overline{RF}_x for 25 mL purge SPCCs to table in 11 instead of referencing the attached Table 3 from OLC02.1. Eliminated Table 3.
- 12-Added BS/BSD
- Incorporated the SIM Mode Addendum into the SOP in an Attachment.

TABLE 1

4-BROMOFLUOROBENZENE CHARACTERISTIC ION ABUNDANCE CRITERIA

Mass/é ratio	Ion Abundance Criteria
50	15 - 40% of mass/é 95
75	30 - 60% of mass/é 95
95	base peak, 100% relative abundance
96	5 - 9% of mass/é 95
173	<2% of mass/é 174
174	>50% of mass/é 95
175	5 - 9% of mass/é 174
176	>95%; <101% of mass/é 174
177	5 - 9% of mass/é 176

*See DDO Summary Attachment for DOD Specific Criteria

Table2

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	58	49
Chlorodibromomethane	129	208, 206
Chloroethane	64 (49*)	66 (51*)
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	85, 106
Chloroform	83	85
Chloromethane	50 (49*)	52 (51*)
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174

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*See DOD Summary Attachment for DOD Specific Criteria

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d ₄	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	83	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141

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*See DOD Summary Attachment for DOD Specific Criteria

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
β -Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	66
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates:		
Benzene-d ₆	84	83
Bromobenzene-d ₅	82	162
Bromochloromethane-d ₂	51	131
1,4-Difluorobenzene	114	
Chlorobenzene-d ₃	117	
1,4-Dichlorobenzene-d ₂	152	115, 150
1,1,2-Trichloroethane-d ₃	100	
4-Bromofluorobenzene	95	174, 176
Chloroform-d ₁	84	
Dibromofluoromethane	113	

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Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Dichloroethane-d ₂	102	
Toluene-d ₈	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

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**ATTACHMENT I
SIM MODE**

*See DOD Summary Attachment for DOD Specific Criteria

SIM MODE

SCOPE

This SOP uses EPA method 8260B for the determination of low concentration levels of specific volatile organic compounds (VOCs) in aqueous, soil, sludge, sediment, and various types of waste. A mass spectrometer operating under the selective ion monitoring (SIM) mode is used for the analysis. The compounds that are routinely determined by this procedure are listed in SIM MODE Table 1. Other VOCs are available upon request. The list may be used in entirety or in part by meeting established method criteria for the compounds of interest. The reported MRL may be adjusted higher; however, the capability of achieving lower MRLs for specific project requirements must be demonstrated.

METHOD SUMMARY

Gas chromatographic/mass spectrometric (GC/MS) conditions are detailed in the 8260B SOP. The compounds are detected by a mass selective detector (MSD) using the SIM mode. The retention time and the ratio of two characteristic ions of each analyte are used for identification. The response of either the primary ion or the secondary ion is used for quantitation. Additional ions may be used to confirm the presence of each compound.

PROCEDURE

All applicable procedure and quality control (QC) requirements discussed in the 8260B SOP apply, only the linear range reduces based upon level of quantitation requested. Thus associated QC (LCS, CCVs, MS/MSD, Internal Standards, and Surrogates) spiking concentrations also reduce in concentration. For example, a typical linear range may be 0.05-5.0ppb with internal and surrogate standards spiked at 1.0 ppb, the CCV spiked at 1.0ppb, and an LCS spiked at 0.5ppb. Preparation of standards need only to include the compounds of interest.

INTERFERENCES

Due to the low concentration levels being sought in SIM mode, cleanliness is extremely important to avoid laboratory contamination. Multiple instrument blanks are recommend to be analyzed prior to any SIM-mode analyses. Good laboratory practices must be maintained through out the preparation of standards and samples and analysis to avoid contamination.

SIM MODE Table 1
List of Target Analytes and Reporting Levels*

Compound	Reporting Limit (ug/L)
Benzene	0.05
Toluene	0.05
Ethylbenzene	0.05
Xylene, total	0.05
Vinyl Chloride	0.10
Carbon tetrachloride	0.05
Tetrachloroethane	0.05

*See DOD Summary Attachment for DOD Specific Criteria

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ATTACHMENT II
CURRENT IS/ANALYTE ASSOCIATIONS PER
INSTRUMENT

*See DOD Summary Attachment for DOD Specific Criteria

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOA3\DATA\103002\C5527.D Vial: 29
Acq On : 30 Oct 102 8:28 am Operator: DROOT
Sample : ccv Inst : MS #3
Misc : Multiplr: 1.00

Method : J:\ACQUDATA\MSVOA3\METHODS\EXP1021.M
Title : 8260voa
Last Update : Tue Oct 22 08:08:39 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

	Compound	AvgRF	CCRF	%Dev	Area	Dev (min)
1	Pentafluorobenzene	1.000	1.000	0.0	107	0.00
2	Dichlorodifluoromethane	0.535	0.577	-7.9	126	0.03
3 p	Chloromethane	1.230	1.223	0.6	118	0.03
4 c	Vinyl Chloride	0.799	0.851	-6.6	131	0.02
5	Bromomethane	0.366	0.350	4.4	100	0.02
6	Chloroethane	0.458	0.497	-8.5	128	0.02
7	FREON 21	1.049	0.984	6.2	98	0.02
8	Trichlorofluoromethane	0.573	0.597	-4.2	127	0.00
9	Diethyl Ether	0.761	0.815	-7.0	119	0.02
10	FREON 123A	0.859	0.925	-7.7	119	0.02
11	Acrolein	0.155	0.165	-6.3	120	0.03
12	FREON 113	0.214	0.231	-8.3	137	0.00
13	FREON 123	0.811	0.857	-5.7	116	0.00
14 c	1,1-Dicethene	0.482	0.513	-6.4	129	0.02
15	Acetone	0.338	0.312	7.7	106	0.02
16	Iodomethane	0.272	0.283	-4.2	101	0.02
17	Carbon Disulfide	2.239	2.596	-16.0	120	0.00
18	2-PROPANOL	0.074	0.077	-3.7	113	0.03
19	Acetonitrile	0.172	0.181	-5.3	111	0.03
20	Allyl Chloride	0.372	0.407	-9.5	129	0.00
21	Methylene Chloride	0.731	0.745	-1.9	122	0.02
22	TBA	0.077	0.082	-6.8	117	0.03
23	Acrylonitrile	0.415	0.462	-11.3	122	0.00
24	Methyl-t-Butyl Ether	1.850	1.938	-4.7	118	0.02
25	trans-1,2-Dichloroethene	0.584	0.645	-10.3	130	0.00
26 p	1,1-Dicethane	1.239	1.316	-6.2	127	0.00
27	Vinyl Acetate	0.598	2.505	-319.0#	509#	0.00
28	2-Chloro-1,3-butadiene	1.027	1.174	-14.3	118	0.00
29	2,2-Dichloropropane	0.561	0.800	-42.8#	172	0.00
30	2-Butanone	0.610	0.664	-8.9	119	0.00
31	Ethyl Acetate	1.184	0.644	45.6#	60	0.14
32	cis-1,2-Dichloroethene	0.658	0.705	-7.2	123	0.00
33	Propionitrile	0.146	0.160	-9.5	121	0.00
34	Methacrylonitrile	0.378	0.405	-7.3	122	0.00
35	Bromochloromethane	0.309	0.314	-1.5	116	0.00
36 c	Chloroform	0.985	1.018	-3.3	126	0.00
37	Tetrahydrofuran	0.398	0.403	-1.3	121	0.00
38	1,1,1-Trichloroethane	0.605	0.673	-11.1	132	0.00
39 I	1,4 - Difluorobenzene	1.000	1.000	0.0	106	0.00
40 s	surr4,Dibrflmethane	0.293	0.319	-9.0	106	0.00
41	Carbontetrachloride	0.228	0.253	-11.2	133	0.00

(#) = Out of Range
C5527.D EXP1021.M

Wed Oct 30 09:29:20 2002

GCMS *MW 30* Page 1

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOA3\DATA\103002\C5527.D Vial: 29
Acq On : 30 Oct 102 8:28 am Operator: DROOT
Sample : ccv Inst : MS #3
Misc : Multiplr: 1.00

Method : J:\ACQUDATA\MSVOA3\METHODS\EXP1021.M
Title : 8260voa
Last Update : Tue Oct 22 08:08:39 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

	Compound	AvgRF	CCRF	%Dev	Area%	Dev(min)
42	1,1-Dichloropropene	0.404	0.445	-10.2	136	0.00
43	Iso-Butyl Alcohol	0.030	0.031	-5.9	116	0.00
44	Benzene	1.337	1.412	-5.6	127	0.00
45 S	surr1, 1,2-Diclcethane	0.335	0.350	-4.5	108	0.00
46	1,2-Dichloroethane	0.427	0.408	4.6	116	0.00
47	N-Heptane	0.433	0.613	-41.7#	175	0.00
48	Trichloroethene	0.354	0.309	12.6	105	0.00
49 c	1,2-Diclp propane	0.447	0.467	-4.6	122	0.00
50	Methyl Methacrylate	0.317	0.353	-11.2	125	0.00
51	1,4-Dioxane	0.004	0.004	-3.5	121	0.00
52	Dibromomethane	0.228	0.226	0.7	114	0.00
53	Bromodichloromethane	0.409	0.415	-1.6	118	0.00
54	2-Nitropropane	0.116	0.137	-18.5	135	0.00
55	2-Chloroethylvinyl Ether	0.350	0.362	-3.4	115	0.00
56	cis-1,3-Dichloropropene	0.594	0.640	-7.7	125	-0.01
57 I	d5 - Chlorobenzene	1.000	1.000	0.0	114	0.00
58	4-Methyl-2-Pentanone	0.808	0.777	3.8	115	0.00
59 c	Toluene	1.356	1.374	-1.3	130	0.00
60	trans-1,3-Dichloropropene	0.584	0.600	-2.9	123	0.00
61	Ethyl Methacrylate	0.669	0.684	-2.2	124	0.00
62	1,1,2-Trichloroethane	0.336	0.330	1.8	119	0.00
63 s	surr3, Toluene-d8	1.247	1.292	-3.6	108	0.00
64 s	surr2, bfb	0.462	0.523	-13.3	117	0.00
65	Tetrachloroethane	0.268	0.276	-3.0	136	-0.01
66	2-Hexanone	0.530	0.532	-0.4	115	0.00
67	1,3-Diclp propane	0.710	0.708	0.3	121	-0.01
68	Dibromochloromethane	0.316	0.311	1.5	119	0.00
69	1,2-Dibromoethane	0.353	0.343	2.9	116	0.00
70 p	Chlorobenzene	0.790	0.790	0.1	128	0.00
71	1,1,1,2-Tetrachloroethane	0.270	0.272	-0.6	122	0.00
72 c	Ethylbenzene	1.371	1.417	-3.3	131	0.00
73	(m+p) Xylene	0.468	0.491	-4.9	134	0.00
74	o-Xylene	0.470	0.475	-1.0	129	0.00
75	Styrene	0.864	0.887	-2.6	129	0.00
76 p	Bromoform	0.206	0.213	-3.6	121	0.00
77	Isopropylbenzene	1.082	1.138	-5.1	132	0.00
78	Cyclohexanone	0.074	0.042	43.7#	70	0.00
79 I	d4 - Dichlorobenzene	1.000	1.000	0.0	117	0.00
80 p	1,1,2,2-Tetrachloroethane	0.954	1.208	-26.6#	162	0.00
81	Trans-1,4-Dichloro-2-butene	0.315	0.348	-10.5	143	0.00

(#) = Out of Range
C5527.D EXP1021.M

Wed Oct 30 09:29:27 2002

GCMS

Page 2

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOA3\DATA\103002\C5527.D Vial: 29
Acq On : 30 Oct 102 8:28 am Operator: DROOT
Sample : ccv Inst : MS #3
Misc : Multiplr: 1.00

Method : J:\ACQUDATA\MSVOA3\METHODS\EXP1021.M
Title : 8260voa
Last Update : Tue Oct 22 08:08:39 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

	Compound	AvgRPF	CCRF	%Dev	Area	% Dev (min)
82	1,2,3-Trichloropropane	0.278	0.261	6.2	123	0.00
83	n-Propylbenzene	3.209	3.320	-3.5	135	0.00
84	Bromobenzene	0.704	0.671	4.7	122	0.00
85	1,3,5-Trimethylbenzene	1.762	1.811	-2.8	134	0.00
86	2-Chlorotoluene	1.983	1.995	-0.6	130	0.00
87	4-Chlorotoluene	2.213	2.193	0.9	129	0.00
88	tert-Butylbenzene	1.405	1.449	-3.1	137	0.00
89	1,2,4-Trimethylbenzene	1.773	1.785	-0.7	131	0.00
90	sec-Butylbenzene	2.198	2.283	-3.9	135	0.00
91	p-Isopropyltoluene	1.625	1.722	-6.0	139	0.00
92	1,3-Dclbenz	1.174	1.153	1.8	128	0.00
93	1,4-Dclbenz	1.214	1.149	5.4	124	0.00
94	n-Butylbenzene	1.614	1.780	-10.3	149	0.00
95	1,2-Dclbenz	1.154	1.118	3.2	125	0.00
96	1,2-Dibromo-3-chloropropane	0.172	0.166	3.8	124	0.00
97	Nitrobenzene	0.000	0.000	0.0	133	0.02
98	1,2,4-Tc benzene	0.527	0.545	-3.5	133	0.00
99	Hexachlorobt	0.174	0.199	-14.6	147	0.02
100	Naphthalen	1.454	1.527	-5.0	133	0.00
101	1,2,3-Tclbenzene	0.482	0.497	-3.2	130	0.02
102	TOTAL XYLENE	0.000	0.000	0.0	0#	0.03

(#) = Out of Range SPCC's out = 0 CCC's out = 0
C5527.D EXP1021.M Wed Oct 30 09:29:30 2002 GCMS Page 3

*See DOD Summary Attachment for DOD Specific Criteria

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOA5\DATA\102902\A4331.D Vial: 85
Acq On : 30 Oct 102 12:23 am Operator: B.ALLGEIER
Sample : CCV Inst : 5971 - In
Misc : Multiplr: 1.00

Method : J:\ACQUDATA\MSVOA5\METHODS\EXP1021.M
Title : 8260voa
Last Update : Tue Oct 22 10:50:10 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

Compound	AvgRRF	CCRF	%Dev	Area%	Dev(min)	
1	Pentafluorobenzene	1.000	1.000	0.0	89	0.02
2	Dichlorodifluoromethane	0.495	0.525	-6.1	93	0.00
3 p	Chloromethane	0.652	0.698	-7.1	92	0.00
4 c	Vinyl Chloride	0.495	0.527	-6.4	95	0.00
5	Bromomethane	0.363	0.339	6.7	88	0.00
6	Chloroethane	0.317	0.341	-7.4	96	0.00
7	Trichlorofluoromethane	0.583	0.653	-11.9	96	0.00
8	Diethyl Ether	0.395	0.407	-3.1	91	0.00
9	Acrolein	0.084	0.065	22.5	70	0.01
10	FREON 113	0.190	0.210	-10.6	97	0.01
11 c	1,1-Dichlethene	0.364	0.374	-2.7	95	0.00
12	Acetone	0.156	0.168	-7.7	105	0.01
13	Iodomethane	0.444	0.605	-36.4#	98	0.00
14	Carbon Disulfide	1.649	1.758	-6.6	87	0.02
15	Acetonitrile	0.016	0.017	-5.3	94	0.00
16	Allyl Chloride	0.240	0.262	-9.3	91	0.00
17	Methylene Chloride	0.507	0.521	-2.8	92	0.02
18	TBA	0.039	0.038	1.7	86	0.00
19	Methyl-t-Butyl Ether	1.289	1.368	-6.1	93	0.00
20	Acrylonitrile	0.200	0.212	-6.4	93	0.00
21	trans-1,2-Dichloroethene	0.434	0.453	-4.3	93	0.02
22 p	1,1-Dichlethane	0.963	1.054	-9.4	94	0.01
23	Vinyl Acetate	0.099	0.063	36.5#	55	0.01
24	2-Chloro-1,3-butadiene	0.782	0.875	-11.8	87	0.02
25	2,2-Dichloropropane	0.683	0.664	2.8	83	0.01
26	2-Butanone	0.318	0.330	-3.6	94	0.00
27	cis-1,2-Dichloroethene	0.494	0.528	-6.9	93	0.01
28	Propionitrile	0.076	0.079	-3.0	91	0.01
29	Methacrylonitrile	0.225	0.229	-1.8	92	0.00
30	Bromochloromethane	0.268	0.290	-8.5	96	0.02
31	Tetrahydrofuran	0.184	0.182	0.7	89	0.01
32 c	Chloroform	0.907	1.008	-11.1	97	0.00
33	1,1,1-Trichloroethane	0.645	0.725	-12.5	97	0.02
34	1,4-Difluorobenzene	1.000	1.000	0.0	93	0.00
35 s	surr4,Dibrflmethane	0.332	0.358	-7.9	94	0.00
36	Carbontetrachloride	0.303	0.332	-9.6	98	0.02
37	1,1-Dichloropropene	0.395	0.415	-5.0	94	0.00
38	Iso-Butyl Alcohol	0.014	0.012	12.9	77	0.02
39	Benzene	1.196	1.228	-2.7	92	0.00
40 s	surr1,1,2-Dichlethane	0.364	0.411	-12.9	96	0.00
41	1,2-Dichloroethane	0.441	0.461	-4.6	98	0.00

(#) = Out of Range
A4331.D EXP1021.M

Wed Oct 30 11:09:15 2002

Page 1

*See DOD Summary Attachment for DOD Specific Criteria

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOA5\DATA\102902\A4331.D Vial: 85
Acq On : 30 Oct 102 12:23 am Operator: B.ALLGEIER
Sample : CCV Inst : 5971 - In
Misc : Multiplr: 1.00

Method : J:\ACQUDATA\MSVOA5\METHODS\EXP1021.M
Title : 8260voa
Last Update : Tue Oct 22 10:50:10 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

	Compound	AvgRF	CCRF	%Dev	Area%	Dev(min)
42	Trichloroethene	0.280	0.320	-14.4	103	0.01
43 c	1,2-Dicloropropane	0.378	0.391	-3.5	92	0.01
44	Methyl Methacrylate	0.232	0.232	-0.1	91	0.01
45	1,4-Dioxane	0.003	0.002	15.8	77	0.02
46	Dibromomethane	0.200	0.208	-3.9	94	0.01
47	Bromodichloromethane	0.411	0.463	-12.7	98	0.02
48	2-Nitropropane	0.092	0.098	-7.3	94	0.02
49	2-Chloroethylvinyl Ether	0.236	0.248	-5.0	94	0.02
50	cis-1,3-Dichloropropene	0.573	0.590	-3.0	91	0.02
51	4-Methyl-2-Pentanone	0.464	0.465	-0.2	94	0.00
52 c	Toluene	1.210	1.259	-4.1	92	0.00
53	trans-1,3-Dichloropropene	0.522	0.551	-5.5	92	0.00
54	Ethyl Methacrylate	0.478	0.502	-5.0	93	0.00
55	1,1,2-Trichloroethane	0.274	0.288	-5.3	94	0.02
56 s	surr3,Toluene-d8	1.138	1.200	-5.5	92	0.02
57 s	surr2,bfb	0.493	0.573	-16.2	97	0.02
58	d5-Chlorobenze	1.000	1.000	0.0	93	0.02
59	Tetrachloroethene	0.281	0.296	-5.6	95	0.00
60	2-Hexanone	0.319	0.315	1.3	95	0.02
61	1,3-Dichloropropene	0.550	0.558	-1.5	92	0.02
62	Dibromochloromethane	0.320	0.344	-7.7	98	0.02
63	1,2-Dibromoethane	0.293	0.303	-3.3	95	0.02
64 p	Chlorobenzene	0.807	0.832	-3.1	93	0.02
65	1,1,1,2-Tetrachloroethane	0.280	0.298	-6.2	96	0.02
66 c	Ethylbenzene	1.374	1.389	-1.1	90	0.02
67	(m+p)Xylene	0.484	0.487	-0.5	90	0.02
68	o-Xylene	0.485	0.501	-3.4	92	0.03
69	Styrene	0.832	0.861	-3.4	91	0.02
70 p	Bromoform	0.218	0.240	-10.1	97	0.02
71	Isopropylbenzene	1.230	1.293	-5.1	93	0.02
72	Cyclohexanone	0.000	0.000	0.0	90	0.02
73	d4-1,4-Dichlorobenzene	1.000	1.000	0.0	93	0.02
74 p	1,1,2,2-Tetrachloroethane	0.932	0.854	8.3	85	0.02
75	1,2,3-Trichloropropene	0.198	0.209	-5.3	94	0.02
76	Trans-1,4-Dichloro-2-Butene	0.241	0.243	-1.2	90	0.02
77	n-Propylbenzene	3.262	3.204	1.8	88	0.02
78	Bromobenzene	0.708	0.747	-5.6	97	0.02
79	1,3,5-Trimethylbenzene	1.790	1.633	8.8	82	0.02
80	2-Chlorotoluene	2.020	2.040	-1.0	91	0.02
81	4-Chlorotoluene	2.015	1.996	0.9	89	0.02

(#) = Out of Range
A4331.D EXP1021.M

Wed Oct 30 11:09:19 2002

Page 2

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOA5\DATA\102902\A4331.D Vial: 85
Acq On : 30 Oct 102 12:23 am Operator: B.ALLGEIER
Sample : CCV Inst : 5971 - In
Misc : Multiplr: 1.00

Method : J:\ACQUDATA\MSVOA5\METHODS\EXP1021.M
Title : 8260voa
Last Update : Tue Oct 22 10:50:10 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

Compound	AvgRF	CCRF	%Dev	Area%	Dev(min)
82 tert-Butylbenzene	1.636	1.632	0.3	88	0.02
83 1,2,4-Trimethylbenzene	1.680	1.511	10.1	79	0.02
84 sec-Butylbenzene	2.523	2.522	0.0	88	0.00
85 p-Isopropyltoluene	1.872	1.751	6.4	82	0.02
86 1,3-Dclbenz	1.269	1.276	-0.6	91	0.02
87 1,4-Dclbenz	1.270	1.252	1.4	89	0.02
88 n-Butylbenzene	1.703	1.490	12.5	76	0.02
89 1,2-Dclbenz	1.262	1.266	-0.3	90	0.02
90 1,2-Dibromo-3-chloropropane	0.154	0.166	-7.8	95	0.02
91 Nitrobenzene	0.000	0.000	0.0	83	0.02
92 1,2,4-Tcbenzene	0.580	0.529	8.7	83	0.02
93 Hexachlorobt	0.295	0.278	5.7	85	0.02
94 Naphthalen	1.235	1.181	4.3	85	0.00
95 1,2,3-Tclbenzene	0.537	0.500	7.0	82	0.00
96 TOTAL XYLENE	0.000	0.000	0.0	0#	-2.30#

(#) = Out of Range
A4331.D EXP1021.M

SPCC's out = 0 CCC's out = 0
Wed Oct 30 11:09:21 2002

Page 3

*See DOD Summary Attachment for DOD Specific Criteria

Evaluate Continuing Calibration Report

Data File : J:\ACQUATA\MSVOA6\DATA\103002\Q9582.D Vial: 2
Acq On : 30 Oct 2002 10:26 am Operator: PDEPALMA
Sample : CCV Inst : GC/MS Ins
Misc : 8260B/OLM4.2 for W.A.P Multiplr: 1.00
MS Integration Params: INTP35.P

Method : J:\ACQUATA\MSVOA6\METHODS\SOW1022W.M (RTE Integrator)
Title : EPA Method 8260B OLM4.2 CPD LIST
Last Update : Wed Oct 30 12:33:47 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

	Compound	AvgRF	CCRF	%Dev	Area%	Dev(min)
1	Pentafluorobenzene	1.000	1.000	0.0	55	-0.02
2	Dichlorodifluoromethane	0.410	0.504	-22.9	68	-0.02
3 P	Chloromethane	0.243	0.222	8.6	52	-0.01
4 c	Vinyl Chloride	0.241	0.225	6.6	51	-0.01
5	Bromomethane	0.173	0.167	3.5	56	-0.01
6	Chloroethane	0.149	0.138	7.4	50	-0.01
7	Trichlorofluoromethane	0.680	0.750	-10.3	60	-0.02
8 c	1,1-Dicethene	0.268	0.275	-2.6	57	-0.01
9	Freon 113	0.322	0.337	-4.7	58	-0.02
10	Acetone	0.109	0.104	4.6	55	-0.02
11	Carbon Disulfide	0.868	0.852	1.8	54	-0.02
12	Methyl Acetate	0.188	0.177	5.9	51	-0.02
13	Methylene Chloride	0.320	0.321	-0.3	56	-0.02
14	Methyl-t-Butyl Ether	1.146	1.168	-1.9	57	-0.02
15	trans-1,2-Dichloroethene	0.316	0.319	-0.9	55	-0.02
16 P	1,1-Dicethane	0.595	0.616	-3.5	58	-0.02
17	cis-1,2-Dichloroethene	0.351	0.373	-6.3	56	-0.02
18	2-Butanone	0.109	0.101	7.3	49#	-0.02
19 c	Chloroform	0.732	0.844	-15.3	63	-0.02
20	1,1,1-Trichloroethane	0.766	0.914	-19.3	65	-0.02
21	1,4-Difluorobenzene	1.000	1.000	0.0	50	-0.02
22 s	surr4,Dibrflmethane	0.318	0.356	-11.9	59	-0.02
23	Cyclohexane	0.412	0.385	6.6	50	-0.02
24	Carbontetrachloride	0.542	0.722	-33.2#	69	-0.02
25	Benzene	0.973	1.055	-8.4	55	-0.02
26	1,2-Dichloroethane	0.497	0.660	-32.8#	66	-0.01
27	Trichloroethene	0.286	0.350	-22.4	62	-0.02
28	Methyl Cyclohexane	0.406	0.407	-0.2	52	-0.02
29 c	1,2-Dicpropene	0.230	0.247	-7.4	53	-0.01
30	Bromodichloromethane	0.450	0.574	-27.6#	64	-0.02
31	cis-1,3-Dichloropropene	0.431	0.519	-20.4	60	-0.02
32	4-Methyl-2-pentanone	0.154	0.158	-2.6	49#	-0.01
33 s	SURR3,Toluene-d8	1.057	1.139	-7.8	55	-0.02
34 c	Toluene	1.073	1.176	-9.6	57	-0.02
35	trans-1,3-Dichloropropene	0.468	0.560	-19.7	59	-0.02
36	1,1,2-Trichloroethane	0.218	0.255	-17.0	58	-0.01
37	Dibromochloromethane	0.337	0.441	-30.9#	65	-0.01
38 s	SURR2,BFB	0.380	0.418	-10.0	61	-0.01
39	d5-Chlorobenzene	1.000	1.000	0.0	51	-0.01

(#) = Out of Range
Q9582.D SOW1022W.M

Wed Oct 30 12:40:06 2002

Page 1

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOA6\DATA\103002\Q9582.D Vial: 2
Acq On : 30 Oct 2002 10:26 am Operator: PDEPALMA
Sample : CCV Inst : GC/MS Ins
Misc : 8260B/OLM4.2 for W.A.P Multiplr: 1.00
MS Integration Params: INTP35.P

Method : J:\ACQUDATA\MSVOA6\METHODS\SOW1022W.M (RTE Integrator)
Title : EPA Method 8260B OLM4.2 CPD LIST
Last Update : Wed Oct 30 12:33:47 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

	Compound	AvgRF	CCRF	%Dev	Area%	Dev (min)
40	Tetrachloroethene	0.285	0.375	-31.6#	65	-0.01
41	2-Hexanone	0.138	0.150	-8.7	53	-0.01
42	1,2-Dibromoethane	0.289	0.346	-19.7	58	-0.01
43 P	Chlorobenzene	0.819	0.997	-21.7	61	-0.01
44 c	Ethylbenzene	0.389	0.473	-21.6#	62	-0.01
45	(m+p)Xylene	0.465	0.554	-19.1	61	-0.01
46	o-Xylene	0.436	0.528	-21.1	63	-0.01
47	Styrene	0.737	0.896	-21.6	62	-0.01
48 P	Bromoform	0.267	0.371	-39.0#	67	-0.01
49	Isopropylbenzene	1.070	1.327	-24.0	64	-0.01
50	1,4-Dichlorobenzene-d4	1.000	1.000	0.0	55	-0.01
51 P	1,1,2,2-Tetrachloroethane	0.689	0.730	-6.0	56	-0.01
52	1,3-Diclbzene	1.374	1.629	-18.6	66	-0.01
53	1,4-Diclbzene	1.384	1.682	-21.5	68	-0.01
54	1,2-Diclbzene	1.280	1.549	-21.0	68	-0.01
55	1,2-Dibromo-3-chloropropane	0.145	0.183	-26.2#	71	0.00
56	1,2,4-Tcbzene	0.447	0.547	-22.4	71	0.00

(#) = Out of Range SPCC's out = 0 CCC's out = 1
Q9582.D SOW1022W.M Wed Oct 30 12:40:08 2002 Page 2

*See DOD Summary Attachment for DOD Specific Criteria

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOA7\DATA\102202\V7572.D Vial: 2
Acq On : 22 Oct 2002 1:52 pm Operator: Herring
Sample : ccv Inst : GC/MS Ins
Misc : Multiplr: 1.00
MS Integration Params: RTEINT.P

Method : J:\ACQUDATA\MSVOA7\METHODS\EXP1004.M (RTE Integrator)
Title : 8260voa
Last Update : Fri Oct 04 19:07:24 2002
Response via : Multiple Level Calibration

R. Herring 10/22

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

	Compound	AvgRF	CCRF	%Dev	Area%	Dev(min)
1	Pentafluorobenzene	1.000	1.000	0.0	105	-0.04
2	Dichlorodifluoromethane	0.555	0.598	-7.7	102	-0.03
3 p	Chloromethane	0.690	0.788	-14.2	113	-0.03
4 c	Vinyl Chloride	0.488	0.486	0.4	101	-0.02
5	Bromomethane	0.472	0.449	4.9	93	-0.04
6	Chloroethane	0.467	0.458	1.9	101	-0.03
7	FREON 21	1.108	1.121	-1.2	110	-0.03
8	Trichlorofluoromethane	0.733	0.733	0.0	102	-0.03
9	Diethyl Ether	0.570	0.561	1.6	100	-0.03
10	FREON 123A	0.826	0.826	0.0	112	-0.04
11	FREON 123	0.838	0.862	-2.9	111	-0.04
12	Acrolein	0.122	0.144	-18.0	110	-0.04
13	FREON 113	0.248	0.243	2.0	103	-0.04
14 c	1,1-Dicethene	0.535	0.537	-0.4	103	-0.04
15	Acetone	0.249	0.214	14.1	96	-0.04
16	2-Propanol	0.047	0.046	2.1	98	-0.03
17	Iodomethane	0.473	0.375	20.7	81	-0.04
18	Carbon Disulfide	2.168	2.321	-7.1	110	-0.04
19	Acetonitrile	0.179	0.165	7.8	100	-0.04
20	Allyl Chloride	0.345	0.325	5.8	100	-0.04
21	Methylene Chloride	0.723	0.688	4.8	103	-0.04
22	TBA	0.056	0.053	5.4	98	-0.04
23	Acrylonitrile	0.324	0.303	6.5	96	-0.04
24	Methyl-t-Butyl Ether	1.580	1.521	3.7	99	-0.04
25	trans-1,2-Dichloroethene	0.657	0.655	0.3	104	-0.04
26 p	1,1-Dicethane	1.122	1.108	1.2	100	-0.05
27	Vinyl Acetate	1.888	2.013	-6.6	107	-0.04
28	2-Chloro-1,3-butadiene	0.937	1.053	-12.4	117	-0.04
29	2,2-Dichloropropane	0.811	0.764	5.8	97	-0.05
30	2-Butanone	0.482	0.439	8.9	98	-0.05
31	Ethyl Acetate	0.000	0.000	0.0	98	-0.05
32	cis-1,2-Dichloroethene	0.741	0.728	1.8	103	-0.05
33	Propionitrile	0.116	0.110	5.2	97	-0.05
34	Methacrylonitrile	0.321	0.295	8.1	97	-0.05
35	Bromochloromethane	0.349	0.339	2.9	101	-0.05
36 c	Chloroform	1.037	1.025	1.2	100	-0.05
37	Tetrahydrofuran	0.276	0.255	7.6	95	-0.05
38	1,1,1-Trichloroethane	0.792	0.782	1.3	102	-0.05
39 I	1,4 - Difluorobenzene	1.000	1.000	0.0	106	-0.04
40 s	surr4,Dibrflmethane	0.356	0.358	-0.6	107	-0.05

(#) = Out of Range
V7572.D EXP1004.M

Tue Oct 22 15:01:42 2002

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Evaluate Continuing Calibration Report

Data File : J:\ACQUADATA\MSVOA7\DATA\102202\V7572.D Vial: 2
Acq On : 22 Oct 2002 1:52 pm Operator: Herring
Sample : ccv Inst : GC/MS Ins
Misc : Multiplr: 1.00
MS Integration Params: RTEINT.P

Method : J:\ACQUADATA\MSVOA7\METHODS\EXP1004.M (RTE Integrator)
Title : 8260voa
Last Update : Fri Oct 04 19:07:24 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

	Compound	AvgRF	CCRF	%Dev	Area%	Dev(min)
41	Carbontetrachloride	0.366	0.365	0.3	101	-0.06
42	1,1-Dichloropropene	0.486	0.466	4.1	101	-0.05
43	Iso-Butyl Alcohol	0.022	0.020	9.1	93	-0.04
44 s	surl,1,2-Diclcethane	0.343	0.336	2.0	104	-0.05
45	Benzene	1.521	1.452	4.5	102	-0.04
46	1,2-Dichloroethane	0.486	0.450	7.4	103	-0.04
47	N-Heptane	0.760	0.739	2.8	95	-0.04
48	Trichloroethene	0.389	0.382	1.8	104	-0.05
49 c	1,2-Diclcpropane	0.481	0.442	8.1	100	-0.05
50	Methyl Methacrylate	0.312	0.288	7.7	93	-0.05
51	1,4-Dioxane	0.004	0.004	0.0	105	-0.05
52	Dibromomethane	0.296	0.279	5.7	101	-0.05
53	Bromodichloromethane	0.488	0.488	0.0	102	-0.05
54	2-Nitropropane	0.000	0.000	0.0	100	-0.05
55	2-Chloroethylvinyl Ether	0.347	0.327	5.8	103	-0.05
56	cis-1,3-Dichloropropene	0.664	0.651	2.0	102	-0.05
57 I	d5 - Chlorobenzene	1.000	1.000	0.0	107	-0.05
58	4-Methyl-2-Pentanone	0.704	0.651	7.5	98	-0.05
59 c	Toluene	1.607	1.590	1.1	102	-0.05
60	trans-1,3-Dichloropropene	0.637	0.613	3.8	100	-0.05
61	Ethyl Methacrylate	0.666	0.610	8.4	97	-0.05
62	1,1,2-Trichloroethane	0.361	0.347	3.9	100	-0.06
63 s	surr3,Toluene-d8	1.272	1.253	1.5	104	-0.05
64 s	surr2,bfb	0.517	0.522	-1.0	106	-0.05
65	Tetrachloroethene	0.405	0.399	1.5	101	-0.05
66	2-Hexanone	0.481	0.440	8.5	96	-0.05
67	1,3-Dichloropropane	0.729	0.671	8.0	99	-0.06
68	Dibromochloromethane	0.406	0.392	3.4	100	-0.06
69	1,2-Dibromoethane	0.446	0.423	5.2	98	-0.05
70 p	Chlorobenzene	1.055	1.027	2.7	101	-0.05
71	1,1,1,2-Tetrachloroethane	0.350	0.339	3.1	103	-0.06
72 c	Ethylbenzene	1.797	1.783	0.8	102	-0.05
73	(m+p)Xylene	0.657	0.640	2.6	101	-0.05
74	o-Xylene	0.656	0.632	3.7	102	-0.06
75	Styrene	1.160	1.115	3.9	98	-0.05
76 p	Bromoform	0.297	0.287	3.4	97	-0.05
77	Isopropylbenzene	1.610	1.605	0.3	102	-0.05
78	Cyclohexanone	0.071	0.040	43.7#	58	-0.05
79 I	d4 - Dichlorobenzene	1.000	1.000	0.0	106	-0.06

(#) = Out of Range

V7572.D EXP1004.M

Tue Oct 22 15:01:43 2002

Page 2

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOA7\DATA\102202\V7572.D Vial: 2
Acq On : 22 Oct 2002 1:52 pm Operator: Herring
Sample : ccv Inst : GC/MS Ins
Misc : Multiplr: 1.00
MS Integration Params: RTEINT.P

Method : J:\ACQUDATA\MSVOA7\METHODS\EXP1004.M (RTE Integrator)
Title : 8260voa
Last Update : Fri Oct 04 19:07:24 2002
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 25% Max. Rel. Area : 200%

	Compound	AvgRF	CCRF	%Dev	Area%	Dev(min)
80 p	1,1,2,2-Tetrachloroethane	1.195	1.129	5.5	97	-0.05
81	Trans-1,4-Dichloro-2-butene	0.329	0.300	8.8	95	-0.05
82	1,2,3-Trichloropropane	0.319	0.257	19.4	97	-0.05
83	n-Propylbenzene	4.441	4.412	0.7	104	-0.05
84	Bromobenzene	0.878	0.877	0.1	101	-0.05
85	1,3,5-Trimethylbenzene	2.551	2.491	2.4	99	-0.05
86	2-Chlorotoluene	2.817	2.778	1.4	101	-0.05
87	4-Chlorotoluene	2.662	2.590	2.7	101	-0.06
88	tert-Butylbenzene	2.158	2.132	1.2	102	-0.05
89	1,2,4-Trimethylbenzene	2.586	2.592	-0.2	100	-0.06
90	sec-Butylbenzene	3.621	3.540	2.2	100	-0.05
91	p-Isopropyltoluene	2.690	2.681	0.3	102	-0.06
92	1,3-Dclbenz	1.554	1.532	1.4	102	-0.05
93	1,4-Dclbenz	1.553	1.569	-1.0	107	-0.06
94	n-Butylbenzene	2.978	2.972	0.2	99	-0.05
95	1,2-Dclbenz	1.512	1.476	2.4	100	-0.05
96	1,2-Dibromo-3-chloropropane	0.245	0.206	15.9	98	-0.06
97	Nitrobenzene	0.000	0.000	0.0	93	-0.05
98	1,2,4-Tcbenzene	1.066	1.014	4.9	98	-0.07
99	Hexachlorobt	0.380	0.360	5.3	102	-0.07
100	Napthalen	2.256	1.939	14.1	88	-0.07
101	1,2,3-Tclbenzene	0.933	0.878	5.9	97	-0.07

(#) = Out of Range
V7572.D EXP1004.M

SPCC's out = 0 CCC's out = 0
Tue Oct 22 15:01:43 2002

*See DOD Summary Attachment for DOD Specific Criteria

Evaluate Continuing Calibration Report

Data File : J:\ACQUDATA\MSVOAS\DATA\101104\F1124.D Vial: 5
Acq On : 11 Oct 2004 11:43 am Operator: Herring
Sample : CCV Inst : GCMS#2
Misc : Multiplr: 1.00
MS Integration Params: RTEINT.P

Method : J:\ACQUDATA\MSVOAS\METHODS\WAT1008.M (RTE Integrator)
Title : 8260voa
Last Update : Mon Oct 11 18:55:59 2004
Response via : Multiple Level Calibration

Min. RRF : 0.000 Min. Rel. Area : 50% Max. R.T. Dev 0.50min
Max. RRF Dev : 20% Max. Rel. Area : 200%

	Compound	AvgRF	CCRF	%Dev	Area%	Dev(min)
1 I	Pentafluorobenzene	1.000	1.000	0.0	109	0.00
2	Dichlorodifluoromethane	0.569	0.646	-13.5	115	0.00
3 p	Chloromethane	0.886	0.863	2.6	110	0.00
4 c	Vinyl Chloride	0.674	0.712	-5.6	112	0.00
5	Bromomethane	0.382	0.442	-15.7	135	0.00
6	Chloroethane	0.442	0.438	0.9	113	0.00
7	FREON 21	1.314	1.362	-3.7	118	0.00
8	Trichlorofluoromethane	0.805	0.864	-7.3	115	0.00
9	Diethyl Ether	0.486	0.523	-7.6	117	0.00
10	FREON 123A	0.739	0.782	-5.8	118	0.00
11	FREON 123	0.810	0.824	-1.7	119	0.00
12	Acrolein	0.076	0.081	-6.6	124	0.00
13	FREON 113	0.214	0.218	-1.9	114	0.00
14 c	1,1-Dicethene	0.432	0.433	-0.2	113	0.00
15	Acetone	0.177	0.176	0.6	106	0.00
16	2-Propanol	0.023	0.019	17.4	98	0.01
17	Iodomethane	0.152	0.152	0.0	94	0.00
18	Carbon Disulfide	1.708	1.770	-3.6	120	0.00
19	Acetonitrile	0.050	0.057	-14.0	113	0.00
20	Allyl Chloride	0.250	0.285	-14.0	126	0.00
21	Methylene Chloride	0.615	0.609	1.0	116	0.00
22	TBA	0.034	0.033	2.9	107	0.00
23	Acrylonitrile	0.205	0.218	-6.3	119	0.00
24	Methyl-t-Butyl Ether	1.515	1.655	-9.2	120	0.00
25	trans-1,2-Dichloroethene	0.524	0.562	-7.3	111	0.00
26 p	1,1-Dicethane	1.086	1.152	-6.1	114	0.00
27	Vinyl Acetate	0.676	0.770	-13.9	128	0.00
28	2-Chloro-1,3-butadiene	0.981	1.102	-12.3	121	0.00
29	2,2-Dichloropropane	0.906	0.985	-8.7	121	0.00
30	2-Butanone	0.292	0.300	-2.7	118	0.00
31	cis-1,2-Dichloroethene	0.594	0.613	-3.2	116	0.00
32	Propionitrile	0.068	0.068	0.0	113	0.00
33	Methacrylonitrile	0.208	0.215	-3.4	120	0.00
34	Bromochloromethane	0.251	0.263	-4.8	118	0.00
35 c	Chloroform	1.012	1.058	-4.5	114	0.00
36	Tetrahydrofuran	0.165	0.181	-9.7	126	0.00
37	1,1,1-Trichloroethane	0.859	0.901	-4.9	115	0.00
38 I	1,4 - Difluorobenzene	1.000	1.000	0.0	111	0.00
39 s	surr4, Dibrflmethane	0.328	0.373	-13.7	125	0.00
40	cyclohexane	0.542	0.537	0.9	111	0.00

(#) = Out of Range
F1124.D WAT1008.M

Mon Oct 11 19:23:33 2004

Page 1

*See DOD Summary Attachment for DOD Specific Criteria