CS109

Standard Operating Procedure

Air Analysis by Method 8260B
Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)

Approvals and Signatures

Laboratory Director Date

QA Officer Date

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1.0 IDENTIFICATION OF THE TEST METHOD

1.1 This SOP is based on USEPA Method 8260B, Revision 2 (1996).

2.0 APPLICABLE MATRICES

2.1 This method is used for analysis of the volatile organic compounds in soil vapor and/or air samples.

3.0 METHOD DETECTION LIMIT

3.1 Method detection limits (MDL) have been determined for this method using the procedure described by 40 CFR Part 136, Appendix B.

3.2 The MDL's have been determined in laboratory reagent water.

3.3 The MDL's and reporting limits are tabulated in Table 1 in Section 23.

3.4 The MDL's are calculated using Excel tables. When a new Excel calculation is set up or when changes are made to Excel formulas, the formula is validated with a calculator.

4.0 SCOPE AND APPLICATION

4.1 The standard compound list and reporting limits are listed in Table 1 in Section 23. This method may be applied to most volatile organic compounds that have boiling points below 200º C.

4.2 Purge and trap concentration is the method by which these compounds are introduced into the GC/MS system. ChemSolutions uses EPA Method 5030 for the introduction of air samples into the purge and trap concentrator.

4.3 Air samples are analyzed with 500-mL sample volumes to achieve the method specified reporting limits. Lower volumes of high level samples may need to be analyzed to avoid saturating the system.

4.4 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as quantitative tools.

5.0 SUMMARY OF METHOD

5.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method directly to a narrow-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

5.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

6.0 DEFINITIONS

6.1 Low level samples are defined as containing analytes of interest at a concentration under 1 ug/L.

6.2 High level air samples contain analytes of interest at a concentration greater than 1 ug/L, or contain high levels of interfering materials such as petroleum hydrocarbons. High level samples can be analyzed with a sample volume of less than 500 mLs.

7.0 INTERFERENCES

7.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explained this in text accompanying the uncorrected data.

7.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

7.3 Many higher molecular weight analytes exhibit low purging efficiencies from a 5-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. The purge vessels are removed, rinsed with water and oven baked after each analysis. This will reduce sample-to-sample carryover.

7.4 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatograph carrier gas lines and purge gas plumbing are constructed from copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

7.5 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

7.6 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

8.0 SAFETY

8.1 The main hazardous compound associated with this method is methanol. Methanol is highly flammable, it should not be used around an open flame.

8.2 Methanol is also toxic if ingested. Do not eat or drink while working with methanol.

8.3 Many of the target analytes for this method are toxic and/or known or suspected carcinogens. ChemSolutions buys the standards for this method as dilute solutions to minimize exposure of laboratory personnel.

9.0 EQUIPMENT AND SUPPLIES

9.1 Purge-and-trap device for vapor samples –The purge and trap system consists of a Tekmar LSC2000 concentrator, a Tekmar ALS2016 autosampler, and a Supelco VOCARB 3000 trap. Needle spargers are used with 19mm x 150mm test tubes. The glassware and sparger positions are adjusted so that the purge gas is introduced at a point 5 mm from the base of the water column.

9.2 Injection port liners (HP Catalog #18740-80200, or equivalent). A 0.25-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

9.3 Gas chromatography/mass spectrometer/data system

9.3.1 Gas chromatograph – A Hewlett-Packard 5890 Series II gas chromatograph is used for this analysis. The GC can be run in the splitless injection mode when injecting BFB and is interfaced to the purge and trap concentrator for standard and sample analysis. The system includes all required accessories, including syringes, analytical columns, and gases.

9.3.1.1 The GC is equipped with variable constant differential flow controllers so that the column flow rate remains constant throughout desorption and temperature program operation.

9.3.1.3 The capillary column is directly coupled to the mass spectrometer source.

9.3.2 Gas chromatographic columns

9.3.2.1 Column 1 – A Restek Rtx-502.2 30 m x 0.25 mm ID capillary column is used for this analysis. The film thickness is 1.4 um.

9.3.3 Mass spectrometer – The mass spectrometer is a Hewlett Packard 5971 set up to scan from 35 to 350 amu at a rate of 2.39 scans/second, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer is tuned to produce a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 2 when 50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

9.3.4 GC/MS interface – The GC is interfaced to the MS by direct coupling, where the GC column is inserted into the mass spectrometer.

9.3.5 Data system - The computer system is a Windows NT system with a 300 GByte hard drive and HP ChemStation software. The computer allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The Chem Station software allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). The software also allows integrating the abundances in any EICP between specified time or scan-number limits. The NBS 75K Mass Spectral Library is also available on this computer.

9.4 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000-μL.

9.5 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

9.6 Syringes - 5-, 10-, or 25-mL, gas-tight.

9.7 Balance - Top-loading, capable of weighing 0.1 g.

9.8 Tedlar bags – 1 Liter, used to collect samples.

9.9 Disposable pipets - Pasteur.

9.10 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

9.11 Spatula - Stainless steel.

10.0 REAGENTS AND STANDARDS

10.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

10.2 Organic-free reagent water – ChemSolutions uses Eldorado Springs bottled water for our reagent water. This water has been tested and shown to be free of organic chemicals.

10.3 Methanol, CH_3OH – Fisher purge and trap grade or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

10.4 Stock solutions - Stock solutions are purchased as certified solutions. The certificates are stored in the Standards 3 ring binder.

10.5 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in purge and trap methanol containing the compounds of interest, either singly or mixed together. The dilutions are documented on form CS0001-01 and stored in the Standards 3 ring binder. Secondary dilution standards must be stored with minimal headspace and are checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Secondary standards for gases are replaced after one week unless the acceptability of the standard can be documented. The premixed certified solutions are stored according to the manufacturer's documented holding time and storage temperature recommendations. The standards are only briefly removed from the freezer for standard mixing or diluting and are returned to the freezer as soon as this is complete to prevent the evaporation of volatile target compounds.

10.6 Surrogate standards – ChemSolutions uses the surrogates toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. A stock surrogate solution in methanol is purchased as described above, and a surrogate standard spiking solution is prepared from the stock at a concentration of 50 μg/mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 5 μL of the surrogate spiking solution prior to analysis. This gives a concentration in the sample of 50 ug/L.

10.7 Internal standards – ChemSolutions uses the internal standards fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. An internal standard stock solution in methanol is purchased as described above. The secondary dilution standard is prepared at a concentration of 50 ug/mL of each internal standard compound. Addition of 5 μL of this standard to 5.0 mL of sample or calibration standard is the equivalent of 50 μg/L.

10.8 4-Bromofluorobenzene (BFB) standard - A standard solution containing 50 ng/μL of BFB in methanol is prepared.

10.9 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

10.9.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution stock standards. The normal concentrations for this method are: 10, 25, 50, 100 250 and 500 ng. These standards are prepared from a 10 ug/mL or a 100 ug/mL secondary dilution standard. The standards are prepared by adding 1, 2.5, 5 and 10 uL respectively, of each mix to a 5 mL syringe containing reagent water.

10.9.2 Continuing calibration check standards are prepared at a concentration of 100 ng from an alternate source of secondary dilution standards. These standards are at a concentration of 200 ug/mL. 0.5 uL of these mixes are added to a 5 mL syringe containing organic-free reagent water.

10.9.3 It is the intent of ChemSolutions that all target analytes for a particular analysis be included in the initial calibration and continuing calibration check standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

10.9.4 The calibration standards must also contain the internal standards chosen for the analysis.

10.11 Laboratory control spikes (LCS) standards – ChemSolutions uses a quality control sample (QCS) for preparing all LCS's. The QCS is from a secondary source, so it serves as a check of the accuracy of the calibration standards. This mix is purchased as a 200 ug/mL certified stock solution. 1 uL of this mix spiked into a 5 mL syringe yields a 200 ng spike. A LCS and LCS duplicate is analyzed with each set of samples up to a maximum of 20 samples.

10.11.1 All analytes must be recovered with an accuracy of plus or minus 30%. If this accuracy is not achieved the problem must be solved before sample analysis continues.

10.12 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Sample Collection and Preservation

11.1.1 Collect vapor samples in 1 liter Tedlar bags.

11.1.2 The samples must be chilled to about 4 degrees C when collected and maintained at that temperature until delivery to the laboratory.

11.2 Sample Storage

11.2.1 Samples are refrigerated immediately upon receipt by ChemSolutions.

11.2.2 Sample refrigerator is free of any solvents, high level samples, etc. that could cause contamination. Blanks are stored in the refrigerator and analyzed periodically to monitor contaminant levels.

11.3 Sample Handling

11.3.1 The samples must be analyzed within 2 days of collection.

11.3.2 Samples are only removed from the refrigerator for analysis.

12.0 QUALITY CONTROL

12.1 ChemSolutions maintains a formal quality assurance manual. The laboratory also maintains records to document the quality of the data generated.

12.2 The quality control elements used during routine laboratory performance on this method are listed below:

12.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 14.3.1 and 14.4.1.

12.2.2 There must be a valid initial calibration as described in Sec. 13.2.1.

12.2.3 There must be a valid continuing calibration as described in Sec. 13.3.1.

12.2.4 There must be a clean method blank as described in Sec. 7.4.3. This includes the method requirement for initial demonstration of low system background and the requirement for on-going demonstration of low system background. Sample

analysis cannot take place until the system has been shown to be free of contamination.

12.3 Initial Demonstration of Laboratory Accuracy and Precision. Analyze 4 replicates of a laboratory fortified blank at a concentration of 100 ng. This procedure is performed initially when bringing the method on-line, when new analysts are performing the test and when there have been major system changes.

12.3.1 Calculate the measured concentration of each analyte for each replicate, the mean concentration in all replicates, the mean % recovery (accuracy) and the relative standard deviation (precision). These data are stored in the Method 8260B QC file as Table 1.

12.4 Initial calculation of MDL's. Analyze 7 replicates of a laboratory fortified blank at a concentration of 10 ng. This procedure is performed initially when bringing the method on-line, when new analysts are performing the test and when there have been major system changes.

12.4.1 Calculate the measured concentration of each analyte for each replicate, the mean concentration in all replicates, the mean % recovery (accuracy), the relative standard deviation (precision) and the MDL using the equation MDL= S*t. These data are stored in the Method 8260B QC file as Table 2 and are tabulated at the end of this SOP in Table 1.

12.4.2 The formulas used to calculate the parameters is Section 12.4.2 are set up in Excel. All formulas are validated with a hand held calculator.

12.5 The analyst carefully monitors the quantitation ion area for all internal standards and surrogate standards in all samples, standards and blanks. An abrupt change is diagnostic of a matrix or hardware problem. When this happens the problem is corrected and the affected sample is reanalyzed. There will be some drift over time. If any areas drift by more than 50% from the current initial calibration corrective action takes place eventually resulting in a new initial calibration.

12.6 Surrogate recoveries - The surrogate standard mix described in Sect. 5.7 is added to all standards, samples, blanks and spikes at a concentration of 50 ug/L. ChemSolutions intends to chart the recoveries of these surrogates as soon as we have analyzed sufficient samples. In the mean time acceptable recoveries are 80-120. If the recoveries are outside of these limits the sample must be reanalyzed.

12.7 Laboratory Control Spike (LCS) – A blank spiked at a level of 200 ng with each analyte of concern is analyzed with each batch of samples. The maximum number of samples in a batch is 20. The data from this analyses are evaluated as described in Sect. 8.3.1 above to document the labs ability to achieve the MDL. Control charts of these data will be generated as sufficient data is generated.

13.0 CALIBRATION

13.1 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and continuing calibration check standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

13.2 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution stock standards. The normal concentrations for this method are: 10, 25, 50, 100, 250 and 500 ng. Prepare the standards as described in Section 10.10.1.

13.2.1 Calculate a RF for each analyte at each concentration as described in Sect. 15.1. Calculate %RSD for each analyte as described in Sect. 15.2. These steps are performed by the software. Print an initial calibration table after updating all levels in the software.

13.2.2 The first step in evaluating the initial calibration is to check the 5 SPCC compounds to see if they meet the minimum response factor requirement. Chloromethane, 1,1 dichloroethane and bromoform must have a response factor of at least 0.1. Chlorobenzene and 1,1,2,2 tetrachloroethane must have a response factor of at least 0.3.

13.2.3 The RSD for all analytes should be less than or equal to 15%. The RF for the following CCC compounds must be less than 30%. The CCC compounds are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene and vinyl chloride.

13.2.4 If any analyte has an RSD of greater than 15%, a linear regression must be used for all quantitations. Do not force through the origin and do not include the origin as a sixth calibration point. The correlation coefficient must be between 0.99 and 1 for the calibration to be considered valid.

13.3 The initial calibration must be verified every 12 hours of analysis time by the analysis of a mid-point or continuing calibration verification (CCV) standard. CCV standards are purchased at a concentration of 200 ug/mL. 1 uL of these mixes are added to a 5 mL syringe containing organic-free reagent water to give a 100 ng standard

13.3.1 Update this CCV as level cc in the Chem Station software. Print a continuing calibration check table. The calibration verification is valid if all surrogates and target compounds of interest have a RF with a % Difference of less than or equal to 20% compared to the average RF from the initial calibration and if the SPCC requirements above (13.2.2) are met.

14.0 PROCEDURE

14.1 For this SOP purge and trap concentration is the only form of sample introduction used. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

14.1.1 As described in the Apparatus Section the purge and trap instrumentation consists of a Tekmar LSC2000 concentrator and an ALS2016 autosampler. The instrumental operating parameters are stored as Method 1 in the LSC2000. The parameters are:

Ambient purge		LSC 2000 Mount Temp	80°C
Purge time	15 minutes	LSC 2000 Valve Temp	120°C
Dry purge	3 minutes	Transfer Line Temp	120°C
Desorb preheat	245°C	ALS2106 Valve Temp	120°C
Desorb for 2' at	250°C	Transfer Line Temp	120°C
Bake for 6' at	260°C		

14.1.2 Purge-and-trap - This method uses a 500 mL sample volume.

14.1.2.1 The purge-and-trap of vapor samples is performed at ambient temperature, with a purge gas flow rate of 40 mL/minute. The sample is injected into the sparge cell at a rate of 40 mL/minute after a 2.5 minute initial purge to remove IS and SS standards.

14.1.2.2 After the 15 minute purge, the purge and trap operates in the dry purge mode for 3 minutes. The purpose of this step is to eliminate some of the water off of the trap before sample desorption.

14.1.2.3 Next the purge and trap switches to desorb preheat. When the temperature reaches 245 C, the instrument switches to desorb. The sample is desorbed for 2 minutes at a temperature of 250C.

14.2 Chromatographic conditions

14.2.1 Column 1

Carrier gas (He) flow rate:	1 mL/min
Column:	Restek Rtx-502.2 30 m, 0.25m ID, 1.4um df
Initial temperature:	35°C, hold for 5 minutes
Temperature program:	8°C/min
Final temperature:	220°C, hold 3 minutes or until all expected compounds have eluted.
Injector temperature:	250°C
Transfer line temperature:	280°C

14.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

Mass range:	35 - 350 amu
Scan time:	2.39 scans/second

14.3.1 The GC/MS system must be hardware-tuned to meet the criteria in Table 2 for a 50 ng injection of 4-bromofluorobenzene (1-μL injection of the BFB standard). Analyses must not begin until these criteria are met. The MS tune must be verified at the beginning of each 12 hour period of sample analysis.

14.3.1.1 The mass spectrum of BFB is acquired in the following manner. The peak apex scan is acquired, a single scan no more than 20 scans prior to the elution of BFB is subtracted. Do not background subtract part of the BFB peak.

14.3.1.2 The resulting mass spectra is evaluated using the BFB mass intensity criteria in Table 2 as tuning acceptance criteria.

14.3.1.3
NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

14.3.2 Set up the purge and trap system as outlined in Sec. 1.1.1. The normal sample volume is 500 mLs. This may be reduced to as little as 5 mLs depending on the level of target compounds in the sample. A set of at least five different calibration standards is necessary. Calibration must be performed using the sample introduction technique that will be used for samples.

14.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a 5 mL gas tight syringe. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the syringe. Remove the needle as quickly as possible after injection. Add 5 μL of internal standard and surrogate standard. Immediately connect the syringe to the leur lock fitting on the purge and trap and inject the aqueous standard into the purge and trap glassware.

14.3.2.2 The internal standards selected in Sec. 5.10 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. If interferences are noted, use the next most intense ion as the quantitation ion.

14.3.3 Proceed with the analysis of the calibration standards following the procedure described above.

14.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

14.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 2 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

14.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis. This is accomplished by analyzing a 100 ug/L continuing calibration check standard. Update this standard as level cc in the quantitation data base and report as a continuing calibration. The RF for each target analyte and surrogate must be within 20% of the mean RF. If any analytes of concern do not meet this criteria reanalyze the calibration check, or the initial calibration or perform maintenance until the criteria pass.

14.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

14.4.4 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

14.4.5 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

14.5 GC/MS analysis of samples

14.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. This is normally done by purge and trap gas chromatography with PID and FID detectors.

14.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

14.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

14.5.4 Remove the plunger from a 5-mL syringe. Add 5 mLs of reagent water. Replace the syringe plunger and compress the sample. Adjust the sample volume to 5.0 mL

14.5.5 Add 5 μL of the internal standard and surrogate spiking solution. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 5 μL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 250 ng of each surrogate and internal standard.

14.5.6 Analyze the sample following the purge and trap procedure described for the standards.

14.5.7 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a lower volume. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

14.5.7.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

14.5.7.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

15 Calculations

15.1 A quantitation data base has been set up in the Chem Station software in method 8260. This data base will tabulate the area response of the characteristic ions against the concentration for each target analyte and each internal standard. The software then calculates response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte is the internal standard that has a retention time closest to the analyte being measured.

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.

A_{is} = Peak area (or height) of the internal standard.

C_s = Concentration of the analyte or surrogate.

C_{is} = Concentration of the internal standard.

15.2 The Chem Station software uses the equations below to calculate the %RSD for the 5 point initial calibration. The criteria for a successful initial calibration is that the %RSD for all target compounds of interest and surrogate compounds is less than or equal to 15%. If this criteria is not met reanalyze standards or perform appropriate maintenance until the criteria are met.

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

where:

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

RF_i = RF for each of the calibration standards

$\overline{RF}$ = mean RF for each compound from the initial calibration

n = Number of calibration standards, e.g., 5

15.3 The ChemStation software also calculates an average RF for each target compound. This average RF is used to calculate all sample and QC results until it is replaced during a new initial calibration.

16.0 METHOD PERFORMANCE

16.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. Section 12.4 describes how the MDL's were determined for this method. The MDL's are tabulated in Table 1 in Section 23.

16.2 This SOP includes Method Performance Criteria (accuracy and precision). The 3 QC procedures used to monitor method performance include surrogate standards, matrix spikes and LCS's. Surrogates are used to monitor accuracy in every sample and QC sample. LCS's or blank spikes are used to document accuracy in a clean matrix for every QC batch and to document measurement uncertainty. Matrix spikes and matrix spike duplicates are used to monitor precision and accuracy in a project specific matrix for each QC batch.

16.3 When this method is used initially the method specified limits for accuracy and precision are used. When 20 data points for a specific compound and matrix are available in-house criteria are calculated, filed and posted.

16.4 The QA Officer is responsible for ensuring that the most current QC limits are available to the analysts and the data reviewers. The current QC limits are filed according to method and matrix in the QC files. A copy is also posted near each analytical instrument.

17.0 POLLUTION PREVENTION

17.1 The primary source of potential pollution from this method is from the methanol used to make up standards and from expired standards.

17.2 Any waste methanol and expired standards are stored as flammable waste and disposed of according to all applicable laws.

18.0 DATA ASSESSMENT

18.1 Qualitative analysis

18.1.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum is generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass 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 are identified as present when the following criteria are met.

18.1.1.1 The intensities of the characteristic ions of a compound maximize in

the same scan or within one scan of each other. The Chem Station data system selects a peak based on the presence of a target chromatographic peak containing ions specific for the target compound at the compound-specific retention time.

18.1.1.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

18.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

18.1.1.4 Structural isomers that produce very similar mass spectra are 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. On this GC column o-xylene is reported as an individual isomer. M- and p-xylene are reported as isomeric pairs.

18.1.1.5 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.

18.1.1.6 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 may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

18.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

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

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

18.2 Quantitative analysis

18.2.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

18.2.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the sample may be determined using the average response factor (RF) from initial calibration data (13.2.1).

18.2.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 18.1.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

18.2.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

19.1 High Level Dilutions – If sample analysis results in any analyte are higher than the concentration range the sample will be reanalyzed at a dilution to bring the results within the calibration range.

19.2 QC Failure – When any of the QC data associated with an analytical batch is out of control the associated samples are reanalyzed after corrective action.

20.0 CONTINGENCIES FOR HANDLING UNACCEPTABLE DATA

20.1 Unacceptable data are any that do not meet the QC criteria described in Sections 12 and 13.

20.2 When this occurs every attempt is made to correct the problem and reanalyze the associated samples and QC within the sample holding time.

20.3 If it is obvious that the problem cannot be corrected in time the samples are subcontracted to another certified lab.

21.0 WASTE MANAGEMENT

21.1 All waste is handled according to local and national regulations.

21.2 Methanol waste is handled as flammable waste.

21.3 Contaminated samples are disposed of at the sampling site whenever possible. If this is not possible they are stored as either flammable or chlorinated waste.

21.4 Uncontaminated samples may be disposed of in the trash or down the sink.

22.0 REFERENCES

1. SW-846, Test Methods for Evaluating Solid Waste, Method 8260B Revision 2, December 1996. U.S. Environmental Protection Agency, Office of Solid Waste.

10/6/2008

Table 1
CHEMSOLUTIONS
EPA 8260 in Air Method Detection Limits

Direct Purge, 0.25 Liter Sample Volume

Spike Amount = 0.01 ug/L, 0.05 ug/L for Ketones With the Following Exceptions:

M and P- Xylene= 0.04 ug/L

Compound	ChemSolutions Calculated MDL (ug/L)	ChemSolutions Calculated Reporting Limit (ug/L)	Prather Spring Reporting Limit (ug/L)
1,2,4-Trimethylbenzene	0.0084	0.0167	0.05
1,3,5-Trimethylbenzene	0.0112	0.022	0.05
Benzene	0.0110	0.022	0.05
Carbon Disulfide	0.0144	0.029	0.05
Ethyl Benzene	0.0094	0.019	0.05
m-and p-Xylene	0.024	0.048	0.05
o-Xylene	0.0105	0.021	0.05
Toluene	0.0107	0.021	0.05
n-Butyl benzene	Not Available	Not Available	0.05
sec-Butyl benzene	Not Available	Not Available	0.05
t-Butyl benzene	Not Available	Not Available	0.05
Naphthalene	Not Available	Not Available	0.05
Isopropyl benzene	Not Available	Not Available	0.05
n-Propyl benzene	Not Available	Not Available	0.05
p-Isopropyl toluene	Not Available	Not Available	0.05

TABLE 2

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

[a] Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers" instructions), provided that method performance is not adversely affected.