

Standard Operating Procedure

TITLE: Volatile Organic Compounds
By Gas Chromatography/Mass Spectrometry (GC/MS)

DEPARTMENT: Volatile Organics Laboratory

APPLICATION: The method outlined within is used for the analysis of volatile organic compounds by method 8260B when soil and water samples are received from the consultant.

REFERENCES: EPA SW-846, Methods 8260B, December 1996
EPA SW-846, Methods 5035, December 1996
EPA SW-846, Methods 5030B, December 1996
EPA SW-846, Methods 8000B December 1996

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1.0 PROCEDURE SUMMARY:

- 1.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other techniques. The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a micro-bore capillary column for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).
- 1.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a direct connection. Micro-bore capillary columns may be directly interfaced to the ion source. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ions relative to an internal standard using a six point calibration curve.
- 1.3 This method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

2.0 SAMPLE HANDLING AND PRESERVATION WITH RECOMMENED HOLDING TIMES:*

2.1 Soils options

- analyzed
5035)
- 2.1.1 ZHE glass 2 oz jar - 20 grams of soil preserved immediately with methanol within 21 day of collection. (Used as a high level option for prep SW846)
 - 2.1.2 En Core 5 gram sampler, preserving sample within 48 hours with 1 gram of Sodium Bisulfate and 5 mls organic free water into a 40 ml VOA vial (for soil samples that do not effervesce) - analyzed within 14 days of collection.
 - 2.1.3 En Core 5 gram sampler, preserving sample within 48 hours with 5 mls organic free water into a 40 ml VOA vial (for soil samples that effervesce) - analyzed within 14 days of collection.
 - 2.1.4 25 gram En Core sampler preserved within 48 hours of collection - analyzed within 21 day of collection.
 - 2.1.5 ZHE glass 2 oz jar - no headspace (Only where programs allow this technique) - analyzed within 14 days of collection. Note that this collection technique leads to low biased results. Reports will be flagged indicating this condition.

* Sampling techniques change rapidly. Techniques available will be added as approved by regulatory agencies.

2.2 Waters¹

- 2.2.1 3-40 ml vials no headspace preserved with HCl - analyzed within 14 days of collection.
- 2.2.2 3-40 ml vials no headspace unpreserved - analyzed within 7 days of collection.

3.0 INTERFERENCES:

- 3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials outgas organic compounds which will be concentrated in the trap during the purge operation. 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.
- 3.2 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 been established.
- 3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics)

¹ HCl preserved water samples can affect certain compound integrity. It is advised that the consultant discuss the targeted list of compounds with the lab prior to sampling for appropriate preservation techniques. All sample vials must be packed in ice to prevent loss and insure sample integrity. Many States have different hold times that are updated yearly.

3.4 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 chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or 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.

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

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

4.0 APPARATUS AND MATERIALS:

4.1 Purge-and-trap device for aqueous samples -

4.1.1 Archon Autosampler or Dynatech PTA-30 Autosampler

4.1.2 Tekmar 3000 Purge and Trap Concentrator.

4.2 Purge-and-trap device for solid samples - Described in Method 5035

4.2.1 Archon Autosampler or Dynatech PTA-30 Autosampler

4.2.2 Tekmar 3000 Purge and Trap Concentrator.

4.3 Air sampling device known as an impinger or ORBO-100 charcoal tube

4.4 Gas chromatography/mass spectrometer/data system

4.4.1 Gas chromatograph: An analytical system complete with a temperature programmable gas chromatograph suitable for split/splitless injection equipped with Electronic Pressure Control (EPC) with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.4.1.1 The GC should be equipped with Electronic Pressure Control (EPC) so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.4.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore; a subambient oven controller may be necessary.

4.4.1.3 The capillary column is directly coupled to the source..

4.44.4.1 Gas chromatographic columns

4.4.2 Column 2 - 20m X 0.18mm ID DB-624, J&W Scientific, Inc., with a 1.0 um film thickness.

4.4.3 Mass spectrometer Hewlett-Packard 5972- Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4 Bromofluorobenzene (BFB) which meets all of the criteria in Table 1 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.

a 4.4.3.1 Direct coupling, by inserting the column into the mass spectrometer using capillary column inlet/adapter (generally used for 0.25 to 0.32 mm ID columns).

4.4.4 GC/MS interface

4.4.4.1 Any enrichment device or transfer line may be used, if all of the performance specifications described in including acceptable calibration at 50 ng or less can be achieved. GC/MS interfaces constructed entirely of glass or of glass lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.4.5 Data system A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances or scan number. This type of plot is defined as an Extracted Ion

versus time
Current Profile

of
accomplished

(EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan number limits. The most recent version the EPA/NIST Mass Spectral Library should also be available. This is by using Enviroquant or Target data acquisition software.

- 4.5 Syringes: 5 and 50 ml Hamilton gastight with Luer-lock tip; 10, 25, 50, 100, 500, 1000 μ l gastight microsyringes.
- 4.6 Balance Analytical, capable of weighing 0.01 g, and top loading, capable of weighing 0.1 g.
- 4.7 Standard solution storage containers - 1.5 ml, 7 ml, 14 ml amber vials with PTFE-lined screw caps.
- 4.8 Disposable pipets Pasteur.
- 4.9 Volumetric flasks, Class A 10-mL, 25-ml, 50-ml, and 100-mL, with ground glass stoppers.
- 4.10 Spatula Stainless steel.
- 4.11 Repipeters capable of delivering 5 mL of Sodium Bisulfate solution and OFW
- 4.12 Disposable 20 mL beakers
- 4.13 pH strip capable of indicating a reading of < 2 S.U.
- 4.14 Disposable magnetic stirring bars - Fischer brand or equivalent.
- 4.15 40-mL glass vials with screw caps

5.0 REAGENTS:

- 5.1 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.
- 5.2 Organic Free Water (OFW): Organic Free Water is water with organics present below MDL for most compounds.
- 5.3 Methanol, Burdick & Jackson Purge-and-Trap Grade or equivalent
- 5.4 Hydrochloric acid (1:1 v/v), HCl Carefully add a measured volume of concentrated HCl to an equal volume of organic free reagent water.
- 5.5 Sodium Bisulfate solution, made from NaHSO₄-ACS reagent grade or equivalent. Concentration of solution: 1g NaHSO₄ to 5.0 mL OFW
- 5.6 Gases: Helium, UHP grade

5.7 Ottawa Sand

5.8 Standards

5.8.1 Primary Standard Sources:
Restek Custom Kit Mixes.

5.8.2 Secondary Sources:
Restek VOC Mixes (Custom and standard stock mixes, different lot numbers)
Restek Internal Std. Mix.
Restek Surrogate Std. Mix.
Restek 4-Bromofluorobenzene Solution.

5.9 Stock standards - Stock standards may be prepared from neat standards and/or prepared mixes can be purchased. A reference standard prepared from a neat standard is made up at a 10,000 ug/mL concentration as follows.

5.9.1 Place about 9.8 ml of methanol into a 10 ml ground-glass stoppered volumetric flask.

5.9.2 Allow the flask to stand unstoppered for a few minutes until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

5.9.3 Using a 100 µl gastight syringe, add about 20-25 drops of the neat standard to the flask to obtain about 100 mg of standard. Let the drops fall just above the surface of the methanol but do not let the syringe needle touch the sides of the flask neck.

5.9.4 Reweigh the flask, dilute to volume, stopper, then mix by inverting the flask several times.

5.9.5 Store without headspace in a 7 mL amber vial in a freezer.

5.9.6 All data regarding standard preparation must be entered into the standard preparation logbook. A number is assigned to each prepared standard solution and that number is entered on all logs where a solution is used. The vial prepared standard solution must be labeled in accordance with the En Chem policy, and include the assigned log number. A brief description of the standard must also appear on the label.

5.9.7 Secondary dilution standards - Using stock standard solutions, prepare in methanol, secondary dilution standards containing the compounds of interest, either singularly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.10 Frequency of Standard Preparation

5.10.1 Stock solutions that are certified by the manufacturer will be purchased. Open a new stock standard every two months or sooner if comparison with check standards indicates a problem. Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented.

Dichlorodifluoromethane and chloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.10.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2 chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.11 Working Standards

5.11.1 Prepare working standards of the volatile target compounds at 100 ug/mL and the surrogates at 250 ug/ml in P&T methanol.

5.11.2 Prepare an Internal Standard and an Internal Standard/Surrogate solution (IS/SS) at a concentration of 250 ug/mL in P&T methanol. GCMS#4 has a 1.25 µl sample loop, therefore, the IS/SS and IS standards should be at 166.7 ug/mL..

5.11.3 Record all data regarding preparation of each standard solution in the standard logbook as described above for stock standards.

5.11.4 Label the working standard vials as described above for the stock standards.

5.11.5 All standards should be stored in a freezer. Prepared standard solutions in methanol are stable for about 4 weeks when stored at -15 to -20°C.

5.12 Surrogate standards - The surrogates are toluene-d8,4-bromofluorobenzene,and dibromofluoromethane. Other compounds may be used as surrogates,depending upon the

- analysis requirements. A stock surrogate solution will be purchased, 2500 ul of this will be brought up to 25 ml in meoh. Each sample undergoing GC/MS analysis must be spiked with this secondary surrogate spiking solution that is equivalent to 50 ug/L prior to analysis; either by spiking directly into sample vial or using Dynatech/Archon standard syringe.
- 5.13 Internal standards - The internal standards are chlorobenzene-d5, 1,4-difluorobenzene, 1,4-dichlorobenzene-d4, and pentafluorobenzene. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Internal standard stock will be purchased. It is recommended that the secondary dilution standard should be prepared at a concentration of 250 mg/L of each internal standard compound (2500 uL of 2500ppm internal standard mixture up to 25 ml in meoh). Addition of 10 uL of this standard to 50 mL of sample or calibration standard would be the equivalent of 50 ug/L.
- 5.14 4-Bromofluorobenzene (BFB) standard - A standard solution containing 50 ng/uL of BFB in methanol should be prepared from a purchased stock of a 2500 ug/ml certified standard.
- 5.15 Calibration standards There are two types of calibration standards used for this method: initial calibration standards and continuing calibration check standards. Concentration levels compounds are adjustable to the project plan submitted according to the action limits of the of interest.
- 5.15.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards or from a premixed certified solution. Prepare these solutions in organic free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte of interest in the samples submitted.

5.15.1.1 The "standard" calibration concentrations are prepared as follows:

Calibration Level _{ug/L}	Working Standard Amt. _{uL}	IS/SS - Standards Addition _{uL}	Volumetric/Syringe Size _{mL}
1	5	2	500
5	2.5	1	50
20	10	4	50
50	25	10	50
100	50	20	50
200	100	40	50

5.15.2 Continuing calibration check standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards or from a premixed certified solution. Prepare these solutions in organic free reagent water. Each Continuing standard should contain each analyte of interest in the samples submitted. calibration check standards must be prepared daily.

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

5.16 Matrix spiking and laboratory control sample (LCS) standards Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike will include 1,1 dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.16.1 Specific permits or programs can require that all compounds reported be spiked in the matrix spike matrix spike duplicate and Laboratory control samples. Precision and accuracy charting are done on a subset of target compounds..

5.17.2 The spiking solutions are not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the continuing calibration check standards may be used for the LCS and matrix spikes.

5.17.3 It cannot be stressed more strongly - Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10C to -20C in amber bottles with Teflon lined screw-caps.

Certain applications will require the addition of a 1 ppb standard to meet the project and quality control objectives.

** Compounds currently not analyzed for at the Green Bay facility.

6.0 PROCEDURE

6.1 Various sample gathering methods dictate the preparation for method prior to analysis. These are discussed in separated standard operating procedures. The series of steps outlined address the sample preparation techniques used specifically at this laboratory.

6.1.1 Purge-and-trap This includes purge-and-trap for aqueous samples (Method 5030B) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

6.1.1.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

above 6.1.1.2 Aqueous and soil/solid samples may also be purged at temperatures those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

volatile 6.1.2 Automated static headspace this technique is used for the pre-screening of organics from solid and aqueous samples (Method 5021) before introduction into the GC/MS system.

6.2 Chromatographic conditions

6.2.1 General:

Injector temperature: 220C
Transfer line temperature: 280C

6.2.2 Column:

Carrier gas (He) flow rate: 0.5 mL/min
Initial temperature: 35C and hold for 4 minutes
Temperature program: 8C/min. to 180C
and hold for 2.88 min.
Final temperature: 180C

Direct inject to the DB624 column. 17 ml/min split/splitless flow with a column flow rate of 0.5 ml/min.

6.3 Initial calibration

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

Mass range: 35 300 amu
Scan time: 0.6 2 sec/scan
Source temperature: According to manufacturer's specifications

6.3.1 Each GC/MS system must be hardware tuned to meet the criteria in Table 1 for a 50 ng injection or purging of 4 bromofluorobenzene (1-uL injection of the BFB standard). Analyses must not begin until these criteria are met.

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

6.3.1.1 Condition a new trap by baking for 30 minutes at 270C. To keep the trap in performance, condition the trap daily for 10 minutes at 260C while backflushing.

Method than for 25 mL. is done with whichever 6.3.2 A set of at least six different calibration standards is necessary as directed by SW846 8000. Calibration must be performed using the sample introduction technique that will be used for samples. For example 5030B, the purging efficiency for 5 mL of water is greater. Therefore, the development of the standard curve volume of sample analyzed.

the 6.3.2.1 A set of at least six calibration standards containing the method analytes is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit for that compound; the other calibration standards should contain analytes at concentrations that define range of the method. Prepare a calibration standard in a 50 mL syringe by adding an appropriate volume of intermediate solutions to 50 mL organic free water. Immediately transfer the contents of the syringe to a 40 mL vial. For soil method 5035, 5 mL of this calibration standard can be transferred to teflon screw-cap 40 mL VOA vial with a stir bar. For a methanol calibration curve, 1 add 1 mL of methanol to 49 mL of water in to a 50 mL syringe.

retention
the internal
specific internal
Table 3). If
intense ion as the

6.3.2.2 The internal standards selected in Sec. 5.15 should permit most of the components of interest in a chromatogram to have times of 0.80 to 1.20 minutes, relative to one of standards. Use the base peak ion from the standard as the primary ion for quantitation (see interferences are noted, use the next most quantitation ion.

relative
the
standard
measured.

6.3.4 Tabulate the area response of the characteristic ions (see TABLE 4) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte to one of the internal standards. The internal standard selected for calculation of the RF for a target analyte should be the internal that has a retention time closest to the analyte being

The RF is Calculated as follows:

where:

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

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.

calibration
calibration curve is
Compounds, or SPCCs)
factor. These compounds are
chlorobenzene; and 1,1,2,2
check compound instability and
lines or active sites in the system.

6.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (6 point) curve. A system performance check should be made before this used. Five compounds (the System Performance Check are checked for a minimum average response chloromethane; 1,1 dichloroethane; bromoform; tetrachloroethane. These compounds are used to to check for degradation caused by contaminated Example problems include:

6.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

transfer
quantitation ion (m/z

6.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if he purge flow is too slow. Cold spots and/or active sites in the lines may adversely affect response. Response of the 173) is directly affected by the tuning of BFB at ions m/z

174/176.
95 may improve bromoform

Increasing the m/z 174/176 ratio relative to m/z
response.

6.3.5.3 Tetrachloroethane and 1,1 dichloroethane are degraded by contaminated transfer lines in purge and trap systems and/or active sites in trapping materials.

6.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

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

6.3.6 Calibration check compounds (CCCs)

6.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of SW846 8000.

6.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^n (RF_i - \overline{RF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

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

6.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. The CCCs are:

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

6.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

6.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.10 relative retention time units. Late eluting compounds usually have much better agreement.

6.3.8 Linearity of target analytes

6.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation.

6.3.8.2 If the average response factor varies more than 15 % for a particular compound, a linear regression calculation for reporting may be performed for that particular compound in the analysis if the correlation coefficient is greater than 0.99. A new calibration curve can be performed to re-assess the use of average response factors at this time.

NOTE: SW846 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

6.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The 20% RSD criteria in SW846 8000 pertains to GC and HPLC methods other than GC/MS.

6.4 GC/MS calibration verification -

Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

6.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 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 4 before sample

analysis begins. These criteria must be demonstrated each 12 hour shift during which samples are analyzed.

- 6.4.2 The initial calibration curve (Sec. 5.17) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 6.4.4 through 6.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

- 6.4.3 A method blank should be analyzed after the calibration standard to ensure that the total system (introduction device, transfer lines and GC/MS 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.

6.4.4 System Performance Check Compounds (SPCCs)

6.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 6.3.5.4). This is the same check that is applied during the initial calibration.

6.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

6.4.5 Calibration Check Compounds (CCCs)

6.4.5.1 After the system performance check is met, the CCCs listed in Sec. 6.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration.

6.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore

not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

6.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new six point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

6.4.6 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 the 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.

6.4.7 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.

6.5 GC/MS analysis of Aqueous samples

6.5.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. The Automated static headspace technique is used for the pre-screening of volatile organics from solid and aqueous samples (Method 5021) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) before introduction into the GC/MS system (Sec 6.1.3). It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. When used only for screening purposes, the quality control requirements in the methods may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to protect a particularly expensive investment in equipment.

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

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

6.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe or vial could be used to hold two 5-mL aliquots although a dilution is required into a 40 mL vial to place in the auto sampler for proper operation. If the second aliquot is to be taken from the syringe or vial, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

6.5.4.1 Adjust the purge gas (helium) flow rate to 40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Section 6.3.5). Purge flow should be checked periodically.

6.5.4.2 Place 40 mL sample vials on the Archon or Dynatech auto sampler. Fill the standard syringe with working IS or IS/SS standard mixture. The concentration of this standard is about 250 ppm, so that the amount of all components injected will be equivalent to 50 ug/L. Fill the rinse water bottle with OFW, and discard the waste water bottle.

6.5.4.3 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delay until the diluted sample is in a 40 mL teflon screw-cap vial.

6.5.4.3.1 Dilutions may be made in 50 mL syringes. Intermediatedilutions may be necessary for extremely large dilutions.

6.5.4.3.2 Calculate the approximate volume of OFW reagent water to be added to the 50 mL. Appropriate dilution aliquot will be directly injected in the 50 mL syringe. Invert the syringe a minimum of three times, and then transfer to 40 mL teflon screw-cap vial. The sample vials will be placed on the Dynatech/Archon auto sampler.

6.5.5 The Dynatech or Archon system will drawn 5 mL aliquot from 40 mL sample vial, and combined approximately 1 uL of IS or IS/SS from standard syringe into 5 mL sparge tube.

6.5.5.1 Sample desorption - occurs at 250C.

6.5.5.2 After the 11 minute purge, Dynatech/Archon steps into desorb and starts the GC/MS program.

6.5.5.3 The MS starts data acquisition after a 1 minute solvent delay. (Desorb mode)

6.5.5.4 The trapped materials are introduced to the GC column by rapidly heating the trap to 250C while backflushing the trap with an inert gas for 2 minutes.

6.5.5.5 Hold the column temperature at 35C for 4 minutes, then program at 8C rise per minute to a temperature of 180C and hold for 0.88 min.

6.5.5.6 After desorbing the sample for 2 minutes, bake the trap at 260-C for 10 minutes.

6.5.5.7 During bake time, the sparge tube will be flushed with DI water 3 times.

6.5.5.8 When the trap is cool, the next sample can be purged.

6.5.5.9 If the initial analysis of sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range or if the sample is suspected to be high, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

6.5.5.10 For matrix spike analysis, add appropriate amount of the matrix spike to the 40 mL of sample vial. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

6.5.5.11 All dilutions should keep the response of a major constituents (previously saturated peaks) near the upper half of the linear range of the curve, exception a larger dilution may be report if the chromatogram is very complex or late elution peaks are present. Proceed to Sections 6.7 and 6.8 for qualitative and quantitative analysis.

6.5.5.12 Water-miscible liquids

6.5.5.12.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50 fold OFW reagent water.

with

6.5.5.12.2 Initial and serial dilutions can be prepared by pipetting 1 mL of the sample to a 50 mL di water syringe. Transfer immediately to a 40 mL vial.

6.6 GC/MS analysis of Sediment/Soil and Waste samples

6.6.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. The Automated static headspace technique is used for the pre-screening of volatile organics from solid and aqueous samples (Method 5021) using a gas chromatograph (GC) equipped with a photoionization detector (PID) before introduction into the GC/MS system (Sec 6.1.3). It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. When used only for screening purposes, the quality control requirements in the methods may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to protect a particularly expensive investment in equipment. Use the screening data to determine whether to use the low-concentration method (0.005-1 mg/Kg) or the high-concentration method (> 1 mg/Kg).

6.6.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples. (TABLE 1)

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

6.6.4 Low Compound concentration method - This is designed for samples containing individual purgeable compounds of < 0.2 mg/Kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all blanks and standards under the same conditions as the samples.

6.6.4.1 Use a 5 g sample if the expected concentration is <0.2 mg/Kg or a 1 g sample for expected concentrations between 0.2 and 1 mg/Kg.

6.6.4.2 A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-concentration method. Follow the initial and daily calibration instructions, except for the addition of a 40C purge temperature.

6.6.4.3 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Do not mix the contents of the sample container with a narrow metal spatula. Weigh the amount as determined in Section 6.6.4.1 into a tared 40ml VOA vial, 5ml of OFW, and a stir bar. Note and record the actual weight to the nearest 0.1 g. It is preferable to obtain a representative sample without mixing if possible, and proceed the procedures in Section 6.5.4.2.

6.6.4.4 For samples received in a 5 gram En Core sampler, prior to extruding the sample, an effervesence check is made to determine which preservation technique is used. This step will have been completed and the volatiles area will have received either 2-40ml VOA vial with a stir bar and 1 gram of Sodium Bisulfate and 5 mls of DI water or 2-40ml VOA vial with a stir bar OFW if sample effervesence was indicated. A third 5g or 25g sample preserved in methanol at a 1:1 ratio is also provided for high level analysis. This is done so that if the sample cannot be analyzed within 48 hours of sample collection, it is properly preserved. During the preparation of the sample, noted and recorded electronically are the actual weights to the nearest 0.1 g for use in later calculations.

6.6.4.5 Determination of the percent solids found in the samples is accomplished by the procedures as listed in the SOP using the determinative method SM2540G. Waste samples are to be reported on a "wet-weight" basis in order to minimize the contamination to ovens used for more than one task.

NOTE: The procedures in Sections 6.6.4.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes, especially Methylene Chloride.

6.6.4.6 Heat the sample to 40-C +/- 1-C and purge the sample for 11.0 +/- 0.1 minutes. Be sure the trap is cooler than 25C.

6.6.4.7 Proceed with the analysis as outlined in Section 6.5.5.10.

6.6.4.7.1 For low-concentration sediment/soils, add 2.5uL of the 100ppm matrix spike solution to the 5 mL of organic-free reagent water. The concentration for a 5 g sample would be equivalent to 50 ug/Kg of each matrix spike standard. Additionally, spike 5ml of DI water and add it to a 40ml VOA vial with a stir bar for the LCS/LCSD. If additional samples were not submitted for matrix spiking, then spike the same above amounts for a LCS/LCSD-pair.

6.6.5 High-concentration method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. An aliquot of the extract is added to OFW. This is purged at ambient temperature. All samples with an expected concentration of >200 ug/Kg should be analyzed by this method.

6.6.5.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Do not mix the contents of the sample container with a narrow metal spatula.

6.6.5.2 For waste that is soluble in methanol, weigh 20 g (wet weight) into a tared 2 oz. jar.

6.6.5.3 Add 20 ml of methanol and an appropriate amount of surrogate-20 ul of 2500ppm surrogate mixture.

6.6.5.4 Cap and shake for 2 min and sonicate for 20 minutes.

NOTE: The procedures in Sections 6.6.4.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes, especially Methylene Chloride.

6.6.5.5 These extracts may be stored at 4C, prior to analysis. The addition of a 1mL aliquot of each of these extracts in Sec. 6.6.5.3 will give a concentration equivalent to 50 ug/Kg of each surrogate standard.

6.6.5.6 Determine the volume of solvent extract to add to the 50mL of OFW for analysis. Use the estimated concentration from the screening procedure to determine the appropriate volume of solvent extract. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start a low ul amount and work up to a maximum of 1mL, while keeping a major peak near the upper half of the linear range of the curve. Exceptionally larger dilutions may be reported if chromatogram is complex or if late eluting peaks are present. This will protect the system from running a sample with high levels of target and non-target compounds..

6.6.5.7 Remove the plunger from a 50 mL Luerlock type syringe, fill until overflowing with OFW. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 49 mL or Pull the plunger back to 50 mL to allow volume for the addition of the sample extract. Then add the volume of solvent extract determined in Section 6.6.5.6 and a volume of extraction or dissolution solvent to total 1mL. Invert the syringe twice, and transfer to 40 mL vial.

- 6.6.5.8 Place 40 mL vial on the Dynatech/Archon autosampler.
- 6.6.5.9 Proceed with the analysis. Analyze all blanks on the same instrument as that used for the samples. The standard and blanks should also contain 1 mL of the dilution solvent to simulate the sample conditions.
- 6.6.5.10 For a matrix spike in the high-concentration sediment/soil samples, add 10 mL of methanol, 10 μ L of surrogate spike solution, and 50 μ L of matrix spike solution as in section 6.6.5.5. Add a 1 mL aliquot of this extract to 49 mL of organic-free reagent water for purging. Due to varying high level sample concentrations it is sometimes necessary to run a LCS/LCSD instead of a matrix spike as a matrix spike is project specific and may not indicate effects associated with other samples from differing sources.

6.7 Qualitative Analysis

- 6.7.1 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 must be 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.
 - 6.7.1.1 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.
 - 6.7.1.2 The relative retention time (RRT) of the sample component is within \pm 0.10 RRT units of the RRT of the standard component.
 - 6.7.1.3 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%.) A Q value is reported along with the concentration. Q values below 80% should be looked at closely for the above criteria. Ion chromatograms of all positive hits should be examined in Target Review.

6.7.1.4 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.

6.7.1.5 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.

6.7.1.6 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.

6.7.2 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. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. 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 $\pm 20\%$. (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.
- (6) Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

6.8 Quantitative Analysis

internal
analyte

- 6.8.1 When 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. Quantitation will take place using the internal standard technique. The standard used shall be the one nearest the retention time of that of a given (e.g. see Table 5).
- 6.8.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data (Sec. 6.3.8.1).
- 6.8.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec.6.8.5) should be estimated. The same formula 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.
- 6.8.4 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.
- 6.8.5 Calculate the concentration of each identified analyte in the sample as follows:

6.8.5.1 Aqueous samples

$$\text{concentration (ug/L)} = \frac{(A_{(x)})(I_{(s)})}{(A_{(is)})(RF)(V_{(o)})}$$

where:

$A_{(x)}$ = Area of characteristic ion for compound being measured.

$I_{(s)}$ = Amount of internal standard injected (ng).

$A_{(is)}$ = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Sec.6.3.4).

$V_{(o)}$ = Volume of water purged (mL), taking into consideration any dilutions made.

6.8.5.2 Sedimenty/Soil and Sludge samples

$$\text{concentration (ug/Kg)} = \frac{(A_{(x)})I_{(s)}(V_{(t)})}{(A_{(is)})(RF)(V_{(i)})(W_{(s)})(D)}$$

where:

- A_(x), I_(s), A_(is), RF, = Same as for water.
- V_(t) = Volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made).
- V_(i) = Volume of extract added (uL) for purging.
- W_(s) = Weight of sample extracted or purged (g).
- D = % dry weight of sample/100, or 1 for a wet-weight basis.

7.0 QUALITY CONTROL

7.1 Chapter One and SW846 8000 give guidance in general terms for quality control (QC) procedures. Quality control procedures to ensure the proper production operation in all of the various sample preparation and/or sample introduction techniques are found in SW846 3500 and 5000. En Chem maintains a formal quality assurance program. The laboratory also maintains records to document the quality of the data generated.

7.2 Discussed in previous sections of this SOP are found the specific requirements that must be met before samples are analyzed. Also found are alternatives when these criteria fail and corrective actions that are followed to insure that the data generated is of known quality to the end user. Below these steps are reiterated and where these steps can be found in the SOP.

7.2.1 Retention time windows are crucial to the identification of target compounds. Retention time windows are established to compensate for minor shifts that occur as a result of sample loading and normal chromatographic variability. of the width of this window is of considerable importance. A window that is "tight" may lead in the reporting of both false negative and false positive results. Re-analysis occurs in this situation due to the non-identification of surrogate components in the analysis. "Wide" retention times lead to false positive results that cannot be confirmed upon re-analysis.

7.2.1.1 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.10 relative retention time units. Late eluting compounds usually have much better agreement. (Sec. 6.3.7) The retention times will be adjusted daily off of the first standard run that day. Recommended retention times are found in TABLE 3.

7.2.2 Criteria for BFB tuning are discussed in Sec. 6.3.1 and TABLE 1

- allowable
- 7.2.3 Criteria for the Initial Calibration of the Instrument are discussed in Sec. 5.17.1.1
- 7.2.4 Criteria for System Performance Check Compounds (SPCCs) are discussed in Sec. 6.3.5
- 7.2.4.1 SPCC criteria are mandatory for every time clock. The maximum time clock is 12 hours.
- 7.2.5 The initial calibration curve (Sec. 6.3) for each compound of interest should be verified, once every time clock or 12 hours, whichever is more frequent, prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 6.4.4 through 6.4.7.
- 7.2.6 Sample Quality Control for Preparation and Analysis - En Chem has in place procedures for documenting the effect of the matrix on method performance (precision and accuracy). Development of limits is done by randomly choosing 40 points by matrix from the previous year. When new compounds are added for analysis, default limits of 50-150% are utilized until new limits can be established. The average percent recovery (p) and standard deviation (s) are calculated and the upper and lower warning and control limits are established by the following equations:

Warning Limits-

$$\begin{aligned}\text{Upper Warning Limit (UWL)} &= p+2s \\ \text{Lower Warning Limit (LWL)} &= p-2s\end{aligned}$$

Control Limits-

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= p+3s \\ \text{Lower Control Limit (LCL)} &= p-3s\end{aligned}$$

Relative Percent Difference Limits -

$$\%RPD = p'+3s'$$

where:

p' = is the average relative percent difference

s' = is the standard deviation of the relative percent difference.

NOTE: If %RPD control limits are calculated to be below 10%, the limit for that individual compound will be set at 10%. This limit allows for assessment of the data without compromising the known quality in a production setting. Most samples received are not for research.

7.2.6.1 Continuous charting for precision and accuracy is done. Limits are set yearly for Blank Spikes (BS) and Matrix Spikes (MS) and surrogates.

7.2.6.2 When results of sample spikes indicate atypical method performance, if possible the sample is reanalyzed to confirm matrix interferences.

NOTE: The large number of analytes analyzed present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined. Remember that even for a 95% confidence interval, 1 out of every 20 observations is likely to fall outside of the control limits established.

7.2.6.3 MDL studies are performed yearly. Detection, quantitation and reporting limits are set using the the data generated from these studies. The studies conform to the processes as described Chapter One of SW846 and CFR 40 part 136 and the Wisconsin Administrative Code 149.

7.2.7 Before processing any samples, the analyst will demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank will be analyzed as a safeguard against chronic laboratory contamination. The blanks are carried through all stages of sample preparation and measurement. An acceptable blank establishes cleanliness of the instrument system at or below the MDL for compounds of interest for aqueous samples or a reporting limit if allowed. Soils analysis allows for blanks to be cleaner than the reporting limit unless MDL reporting is required.

7.2.8 Documenting the effect of the matrix includes the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then the section may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the section will use a matrix spike and matrix spike duplicate pair.

7.2.8.1 For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate/duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs but not to exceed 1 per 20 samples). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

7.2.8.2 A Laboratory Control Sample (LCS) and Duplicate (LCSD) also known as a Blank Spike (BS) and Duplicate (BSD) pair is included with each analytical batch. The pair consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The pair is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix

spike analysis indicate a potential problem due to the sample matrix itself, the pair results are used to verify that the laboratory was in control.

7.2.9 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. Development of limits is done by randomly choosing a minimum of 20 points by matrix from the previous year. The average percent recovery (p) and standard deviation (s) are calculated and the upper and lower control limits are established by the following equations:

Control Limits-

$$\begin{aligned} \text{Upper Control Limit (UCL)} &= p+3s \\ \text{Lower Control Limit (LCL)} &= p-3s \end{aligned}$$

NOTE: Remember that even for a 95% confidence interval, 1 out of every 20 observations is likely to fall outside of the control limits established.

7.2.9.1 When results of sample spikes indicate atypical method performance, if possible the sample is reanalyzed to confirm matrix interferences.

7.2.10 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

INITIAL VALIDATION METHOD

7.2.11 If compounds that are tested are not comparable to the established matrix or blank spike limits generated, analysts will proceed to the corrective actions listed below and document these in maintenance log books kept for each GC/MS system:

7.2.11.1 A quality control (QC) reference sample concentrate is required containing each analyte. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions.

7.2.11.2 Prepare a QC reference sample to contain 20 ug/L of each analyte.

7.2.11.3 Four 5 mL aliquots of the well mixed QC reference sample are analyzed according to the method.

7.2.11.4 Calculate the average recovery (\bar{x}) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte using the four results.

7.2.11.5 Compare s and \bar{x} for each analyte to the laboratory recovery and precision data limits generated. Results are comparable if the calculated standard deviation of the recovery does not exceed 2.6 times the laboratory RSD or 20%, whichever is greater, and the mean recovery lies within the interval $\bar{x} \pm 3S$ or $\bar{x} \pm 30\%$, whichever is greater.

7.2.11.6 When one or more of the analytes tested are not comparable proceed as follows:

7.2.11.6.1 Locate and correct the source of the problem and repeat the test for all analytes. Document the changes made in the maintenance log.

7.2.11.6.2 Repeat the test only for those analytes that are not comparable. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem. Document the changes made in the maintenance log.

7.2.11.6.3 Repeat the test for all compounds of interest until resolved.

problem.
log.

7.2.11.7 For aqueous and soil matrices, surrogate recoveries compared with the control limits generated by the laboratory. If the recovery is not within established control limits the samples is re-analyzed to confirm matrix interferences (Sec. 7.2.9.2). Prior to re-analysis:

should be
laboratory. If the
limits the samples is re-
(Sec. 7.2.9.2). Prior to re-

7.2.11.7.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

standards.
accordingly.

7.2.11.7.2 Check instrument performance. If an instrument performance problem is identified, correct the problem, document the changes made in the appropriate log book and re-analyze the extract.

7.2.11.7.3 If no problem is found, re-extract and re-analyze the sample.

7.2.11.7.4 If, upon re-analysis, the recovery is again not within limits, flag the data as " Surrogate recovery was outside of established control limits. This was confirmed by a second GC/MS analysis on as a matrix interference."

mm/dd/yy

8.0 METHOD PERFORMANCE ESTABLISHED BY EN CHEM - GREEN BAY

- 8.1 MDL generated by En Chem are made available to analysts by the QC Department through the section supervisor
- 8.2 Accuracy and Precision data relating to Blank, Matrix and Surrogate Recoveries are made available to analysts by the QC Department through the section supervisor

TABLE 1

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.

TABLE 2

ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES^a

Estimated Quantitation Limits

5-mL Ground Water Soil/Sediment ^b Purge (mg/L)	Ketones and poor purgers	Methanol Limits Low mg/kg
1	5	50 5(m/p-Xylene = 10)

- a. Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.
- b. EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices Factor^c

Water miscible liquid waste	50
High concentration soil and sludge	125

- c. $EQL = [EQL \text{ for low soil sediment (Table 2)}] \times [Factor]$.

For non-aqueous samples, the factor is on a wet-weight basis. Wisconsin requires LOD/LOQ reporting. Other regulatory agencies may also require this practice. Analytical EQL reporting may be adjusted to fit the reporting requirements of the project as long as the objectives are met and are scientifically defensible.

TABLE 3
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes)			En Chem Standard Column ^d
	Column 1 ^a	Column 2 ^b	Column 2 ^c	
Dichlorodifluoromethane	1.35	0.70	3.13	1.64
Chloromethane	1.49	0.73	3.40	1.85
Vinyl Chloride	1.56	0.79	3.93	1.98
Bromomethane	2.19	0.96	4.80	2.39
Chloroethane	2.21	1.02	--	2.53
Trichlorofluoromethane	2.42	1.19	6.20	2.87
Acrolein	3.19			3.47
Iodomethane	3.56			3.84
Acetonitrile**	4.11			---
Carbon disulfide	4.11			3.93
Allyl chloride	4.11			4.23
Methylene chloride	4.40	2.06	9.27	4.45
1,1-Dichloroethene	4.47	1.57	7.83	3.63
Acetone	4.47			3.73
trans-1,2-Dichloroethene	4.47	2.36	9.90	4.93
Acrylonitrile	5.00			4.87
1,1-Dichloroethane	6.14	2.93	10.80	3.63
Vinyl acetate	6.43			5.78
2,2-Dichloropropane	8.10	3.80	11.87	6.60
2-Butanone	--			6.66
cis-1,2-Dichloroethene	8.25	3.90	11.93	6.62
Propionitrile**	8.51			---
Chloroform	9.01	4.80	12.60	7.17
Bromochloromethane	--	4.38	12.37	6.99
Methacrylonitrile**	9.19			---
1,1,1-Trichloroethane	10.18	4.84	12.83	7.44
Carbon tetrachloride	11.02	5.26	13.17	7.71
1,1-Dichloropropene	--	5.29	13.10	7.72
Benzene	11.50	5.67	13.50	8.04
1,2-Dichloroethane	12.09	5.83	13.63	8.07
Trichloroethene	14.03	7.27	14.80	9.11
1,2-Dichloropropane	14.41	7.66	15.20	9.45
Bromodichloromethane	15.39	8.49	15.80	9.93
Dibromomethane	15.43	7.93	5.43	9.63
Methyl methacrylate**	15.50			---
1,4-Dioxane**	16.17			---
2-Chloroethyl vinyl ether	--			10.46
4-Methyl-2-pentanone	17.32			10.94
trans-1,3-Dichloropropene	17.47	--	16.70	11.60
Toluene	18.29	10.00	17.40	11.21
cis-1,3-Dichloropropene	19.38	--	17.90	17.90

TABLE 3 (cont.)

Compound	Retention Time (minutes)			En Chem Standard Column ^d
	Column 1 ^a	Column 2 ^b	Column 2 ^c	
1,1,2-Trichloroethane	19.59	11.05	18.30	11.89
Ethyl methacrylate**	20.01			---
2-Hexanone	20.30			12.34
Tetrachloroethene	20.26	11.15	18.60	12.14
1,3-Dichloropropane	20.51	11.31	18.70	12.16
Dibromochloromethane	21.19	11.85	19.20	12.54
1,2-Dibromoethane	21.52	11.83	19.40	12.70
1-Chlorohexane**	--	13.29	--	---
Chlorobenzene	23.17	13.01	20.67	13.56
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	13.72
Ethylbenzene	23.38	13.39	21.00	13.78
p-Xylene	23.54	13.69	21.30	
m-Xylene	23.54	13.68	21.37	
m/p-Xylene	---	---	---	13.99
o-Xylene	25.16	14.42	22.27	14.66
Styrene	25.30	14.60	22.40	14.68
Bromoform	26.23	14.88	22.77	14.97
Isopropylbenzene (Cumene)	26.37	15.46	23.30	15.32
cis-1,4-Dichloro-2-butene	27.12			15.94
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	15.84
Bromobenzene	27.46	15.86	24.00	15.80
1,2,3-Trichloropropane	27.55	16.23	24.13	15.89
n-Propylbenzene	27.58	16.41	24.33	16.05
2-Chlorotoluene	28.19	16.42	24.43	16.17
trans-1,4-Dichloro-2-butene	28.26			15.42
1,3,5-Trimethylbenzene	28.31	16.90	24.83	16.38
4-Chlorotoluene	28.33	16.72	24.77	16.36
Pentachloroethane**	29.41			---
1,2,4-Trimethylbenzene	29.47	17.70	31.50	17.03
sec-Butylbenzene	30.25	18.09	26.13	17.34
tert-Butylbenzene	30.59	17.57	26.60	16.94
p-Isopropyltoluene	30.59	18.52	26.50	17.61
1,3-Dichlorobenzene	30.56	18.14	26.37	17.49
1,4-Dichlorobenzene	31.22	18.39	26.60	17.65
Benzyl chloride**	32.00			---
n-Butylbenzene	32.23	19.49	27.32	18.34
1,2-Dichlorobenzene	32.31	19.17	27.43	18.30
1,2-Dibromo-3-chloropropane	35.30	21.08	--	19.69
1,2,4-Trichlorobenzene	38.19	23.08	31.50	21.21
Hexachlorobutadiene	38.57	23.68	32.07	21.58
Naphthalene	39.05	23.52	32.20	21.63
1,2,3-Trichlorobenzene	40.01	24.18	32.97	22.08

TABLE 3 (cont.)

Compound Retention Time (minutes)	Column 1 ^a	Column 2 ^b	Column 2 ^c	En Chem Standard Column ^d
INTERNAL STANDARDS/SURROGATES				
Pentafluorobenzene	--			7.55
1,4-Difluorobenzene	13.26			8.71
Chlorobenzene-d5	23.10			13.51
1,4-Dichlorobenzene-d4	31.16			17.61
4-Bromofluorobenzene	27.83	15.71	23.63	15.56
1,2-Dichlorobenzene-d4	32.30	19.08	27.25	---
Dichloroethane-d4	12.08			---
Dibromofluoromethane	--			7.42
Toluene-d8	18.27			11.11
Fluorobenzene	13.00	6.27	14.06	---

- a. Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.
- b. Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.
- c. Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.
- d. En Chem Column - 20 meter x 0.18 mm ID DB-624 narrow-bore capillary 1.0 um film thickness (DB-624)
 Note that times listed are updated daily. Actual times may vary as daily conditions change. Hold at 35°C for 4 minutes, then 8°C/min to 180°C and hold for 2.88 min.

TABLE 4 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**	56	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	65, 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

TABLE 4 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d4	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	63	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

TABLE 4 (cont.)

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
b-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	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates:		
Benzene-d6**	84	83
Bromobenzene-d5**	82	162
Bromochloromethane-d2**	51	131
1,4-Difluorobenzene	114	
Chlorobenzene-d5	117	
1,4-Dichlorobenzene-d4	152	115, 150
1,1,2-Trichloroethane-d3**	100	
4-Bromofluorobenzene	95	174, 176
Chloroform-d1**	84	
Dibromofluoromethane	113	

TABLE 4 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Dichloroethane-d4**	102	
Toluene-d8	98	
Pentafluorobenzene	168	
Fluorobenzene**	96	77

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

TABLE 5 VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
 ASSIGNED FOR QUANTITATION

<u>Pentafluorobenzene</u>	<u>1,4-Difluorobenzene</u>
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromofluorobenzene (surrogate)
Allyl chloride	Carbon tetrachloride
Bromochloromethane	1,2-Dibromoethane
Bromomethane	Dibromomethane
2-Butanone	1,2-Dichloroethane
Carbon Disulfide	1,2-Dichloroethane-d(4) (surrogate)
Chloroethane	1,2-Dichloropropane
Chloroform	1,1-Dichloropropene
Chloromethane	cis-1,3-Dichloropropene
Dichlorodifluoromethane	trans-1,3-Dichloropropene
Dichlorofluoromethane	Diethoxymethane
1,1-Dichloroethane	2-Hexanone
1,1-Dichloroethene	4-Methyl-2-pentanone
cis-1,2-Dichloroethene	Toluene
trans-1,2-Dichloroethene	Toluene-d(8) (surrogate)
2,2-Dichloropropane	1,1,2-Trichloroethane
Di-Isopropyl Ether	Trichloroethene
Ethyl ether	
Methylene chloride	
Methyl tert Butyl Ether	<u>1,4-Dichlorobenzene-d(4)</u>
1,1,1-Trichloroethane	Bromobenzene
Trichlorofluoromethane	n-Butylbenzene
Trichlorotrifluoroethane	sec-Butylbenzene
Tetrahydrofuran	tert-Butylbenzene
Vinyl Acetate	2-Chlorotoluene
Vinyl Chloride	4-Chlorotoluene
	1,2-Dibromo-3-chloropropane
<u>Chlorobenzene-d(5)</u>	1,2-Dichlorobenzene
Bromoform	1,3-Dichlorobenzene
Chlorodibromomethane	1,4-Dichlorobenzene
Chlorobenzene	Hexachlorobutadiene
2-Chloroethylvinyl Ether	Isopropyl benzene
cis-1,4-Dichloro-2-Butene	p-Isopropyltoluene
trans-1,4-Dichloro-2-Butene	Naphthalene
1,3-Dichloropropane	n-Propylbenzene
Ethylbenzene	1,1,2,2-Tetrachloroethane
Styrene	1,2,3-Trichlorobenzene
1,1,1,2-Tetrachloroethane	1,2,4-Trichlorobenzene
Tetrachloroethene	1,2,3-Trichloropropane
Xylene	1,2,4-Trimethylbenzene
	1,3,5-Trimethylbenzene

APPENDIX A

MODIFICATIONS MADE TO PROMULGATED METHODS

Exclusions from SW846 Method 8260B and 5030B/5035

- 1.) Autosampler devices used in the method are an Archon 5100 or a Dynatech PTA-30 W/S which are connected to a Tekmar 3000 purge and trap.
- 2.) 50 ml gastight syringes are used for initial calibrations, check standards, and sample dilutions because of the vial autosamplers.
- 3.) The addition of the internal standard, IS/SS, and surrogates are done automatically by the autosampler prior to transfer of the sample to the purge and trap. For methanol samples, the internal standard is only added to the sample prior to purging.
- 4.) The sample is introduced by the autosampler without breaking the seal of the 40 ml vial.
- 5.) The desorb time of the purge and trap is 2 minutes on the VOCARB 3000 trap.
- 6.) The surrogates used are Dibromofluoromethane, Toluene-d8, and 4-Bromofluorobenzene, and not 1,2-Dichloroethane-d4.
- 7.) The internal standards used are Pentafluorobenzene, 1,4-Difluorobenzene, Chlorobenzene-d5, and 1,4-Dichlorobenzene-d4. Fluorobenzene is not used in En Chem's method.
- 8.) The concentration of BFB for tuning purposes is 50 ng/ul and 1ul is injected, not 25 ng/ul and 2 ul's due to the narrow bore column used in the analysis.
- 9.) The matrix spike and standard concentration is 100 ug/ml, not 25 ug/ml, because of the vial autosamplers.
- 10.) The concentrations of the internal and surrogate standards are 250 ug/ml, not 25 ug/ml, and 1 ul of the IS and IS/SS is introduced by the autosampler prior to sample transfer into the sparge tube. GCMS#4 has a 1.25 μ l IS loop, therefore the IS/SS and IS concentrations must be 166.7 ug/mL.
- 11.) The split injection ratio is 38:1 in the injection port.
- 12.) A LCS/LCSD is analyzed for Wisconsin methanol samples only. The LCS/LCSD is analyzed in conjunction with a MS/MSD for waters, low level soils, and medium level methanol soil samples out of the state of Wisconsin.

APPENDIX B

Data Verification and Data Entry Autoprograms

1.0 Data Verification

- 1.1 Compare the internal standard areas of the unknown to that of the CCC; areas must be +100% -50%. Also compare surrogate recovery to En Chem established limits. Rerun where conditions are not met.
- 1.2 Verify spectra of all unknown compounds versus the reference spectra from the daily CCC.
- 1.3 In Target Review, delete all false positives that do not verify according to retention times and spectral comparisons as established in method 8260B.
- 1.4 Save the file and proceed through entire data package.
- 1.5 Print out Forms 1 of the method blank, form 2,3,4, and form 8 in Quick forms. Convert the Form 2 and 3 to text files in Explorer, and copy to the network QC directory.

2.0 Import Data into Conifer

- 2.1 Create CSV files in Target and copy them onto a 3 1/2" floppy diskette.
- 2.2 Insert floppy disk into the "A-drive" and logon to computer.
- 2.3 Double click the mouse button on "Conifer", type in your name and your password and hit "OK".
- 2.4 Click on "User Extention", click on "Import Volatiles Data", click on "Target HP Chemstation", choose the instrument number of the GCMS needed and hit enter. After the files are read, exit out of the DOS prompt.
- 2.5 Click on back, twice, and click on "Import Data" once again. Click on the browse button, and go into the U:\VMSDATA\MS# directory, where # = the GCMS number where the data is stored. Select the "all files (*.*)" option and click on the "output.dat" option. Hit "Start import".
- 2.6 This will then bring you into an import spreadsheet. Using the right had scroll bar, check to make sure all files were brought in.
- 2.7 Click on "Send to LIMS" icon. Hit yes to "custom worksheet" and enter description of worksheet in the description line. If all goes well, nothing should be left in the spreadsheet except surrogates (if PVOC/BTEX, etc....) or "SPECVOA-*". If more than this remains, DO NOT append to LIMS. Delete any sample numbers that do not transfer and investigate what problem is. If just surrogates and SPECVOA-* left, then "append to LIMS" icon is clicked on. Exit to Main Menu.
- 2.8 Click on "Enter sample results" , click on "Worksheet" and choose appropriate worksheet that you just created. Click on "calculate LOD". Review data for any compounds that might have been missed during QDEL at the instrument. Click on "Calc Results". Click "Status" and enter Prep date, followed by the data of prep and the initials of the analyst prepping the samples. Exit to Main Menu.
- 2.9 Enter comments by clicking on "user extension" and enter comments. Put data files in file holder for second analyst to approve the data.
 - 2.9.1 Second analyst repeats process in "Enter sample results (section 2.8) and after verifying data, clicks on "Status" icon and marks the "approved" check box. Make sure to enter date approved and the initials of the analyst approving the data. Exit to Main menu.