INDOOR AIR ANALYSIS OF VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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INDOOR AIR ANALYSIS OF VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

The objective of this Standard Operating Procedure (SOP) is to provide guidance on the requirements needed to analyze Volatile Organic Compounds (VOCs) in air samples using gas chromatography/mass spectrometry (GC/MS). This method is based on modified National Institute for Occupational Safety and Health (NIOSH) Methods 1003, 1500, and 1501 for the analysis of VOCs in air samples. A list of compounds routinely analyzed by the Scientific, Engineering Response and Analytical Services (SERAS) laboratory is provided in Table 1, Appendix A.

This method can be used to identify and quantify most VOCs that have boiling points below 200 degrees Celsius (□C). Such compounds include aliphatic hydrocarbons, aromatic hydrocarbons, and halogenated hydrocarbons. Organic compounds that are gaseous at room temperature, reactive, polar, or oxygenated (aldehydes, some ketones and alcohols) are either inefficiently desorbed, or not adsorbed (have relatively early breakthrough).

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute United States Environmental Protection Agency (U.S. EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

The air samples are collected on two stage charcoal tubes, extracted with carbon disulfide (CS_2) and the extracts analyzed by GC/MS. Prior to GC/MS analysis, a 1 mL aliquot of the CS_2 extract is spiked with the internal standards listed in Table 2, Appendix A and analyzed for the VOCs in Table 1, Appendix A. Identification and quantitation is made by comparing the retention times and mass spectral data of unknown compounds with those of known compounds from calibration standards as follows:

The gas chromatograph (GC) is temperature programmed to separate the method analytes, which are then detected with the mass spectrometer (MS). The compounds eluting from the GC column are identified by comparing the measured mass spectra and retention times to reference spectra and retention times in a database. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for sample extracts. The concentration of each identified analyte is calculated by relating the MS response of the quantitation ion produced by that compound, to the MS response of the quantitation ion produced by a compound that is used as an internal standard.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

Charcoal used for sampling is housed in a glass tube that has been flame sealed. The tube contains 600 milligrams (mg) of charcoal and is 11 centimeters (cm) long with a 8 millimeter (mm) inner diameter (ID) and a 6 mm outer diameter (OD) containing two sections of 20/40 mesh activated charcoal separated by urethane foam. The front adsorbing section contains 400 mg of charcoal and the back adsorbing section contains 200 mg of charcoal. To preserve and store air samples collected on charcoal tubes:

1. Place plastic caps on the charcoal tube ends.
2. Place sample in a whirlpack bag. If duplicate samples are collected, place both charcoal tubes in one whirlpack bag.
3. Protect samples from light and refrigerate at 4°C (± 2°C) from the time of collection until extraction and analysis.
4. Recommended maximum holding time is 14 days from date of collection.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

1. High humidity and temperature, and high sampling flow rates may decrease the absorption capacity of activated carbon. Contaminants may migrate from the front portion to the back portion of the tube.

2. Impurities in the purge gas and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing method blanks.

3. Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) into the sample during storage and handling. Lot blanks, field blanks and trip blanks submitted and taken through the extraction and analysis serve as a check on such contamination.

4. Impurities in carbon disulfide (CS_2), the desorbing agent, may cause interferences. It is important to use a chromatographic quality grade, free of benzene.

5.0 EQUIPMENT/APPARATUS

- Micro syringes, Hamilton gas tight syringes: 10, 25, 50, 100, 500, and 1000 µL, 0.006 inch ID needle
- Charcoal tubes, 600 mg two-stage (SKC, Inc. or equivalent)
- Balance, capable of accurately weighing 0.0001 grams (g)
- Bottle, 10 milliliter (mL), crimp top with Teflon cap liner.
- Volumetric flasks, Class A with ground-glass stoppers, 5-, 10-, 25-, and 50-mL volumes
- Vials, 2 mL for GC autosampler
- Desorption vials, 4 mL, screw cap with Teflon cap liner (Supelco cat #2-2954 or equivalent)
- Sonicator
- Hewlett Packard (HP) 6890 GC and 5972 mass selective detector (MSD), equipped with a HP 6890 autosampler and controlled by HP Enviroquant (or equivalent software)

- Restek Rtx-5 (crossbonded SE-54) fused silica capillary column, 30 meter (m) x 0.25 mm ID, 0.5µm film thickness (or equivalent)

6.0 REAGENTS

1. Carbon disulfide, benzene less than 1 ppm

2. Decafluorotriphenylphosphine (DFTPP), 50 microgram/milliliter (µg/mL), commercially available. The amount in a 1 microliter (µL) injection is 50 nanograms (ng).

3. Stock calibration standards, 5000 µg/mL, custom mix, commercially available.

4. Intermediate calibration standard, 200 µg/mL, using the stock calibration standard, prepare a ½5 dilution in carbon disulfide. The intermediate calibration standard should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing working calibration standards.

5. Working calibration standards, 100, 50, 25, 10, 5, 1 µg/mL in CS_2.

6. Internal standard mix, custom mix, commercially available containing cyclohexane-d_{12}, toluene-d_8, 1,4-dichlorobenzene-d_4, naphthalene-d_8 and 1-chlorooctane in carbon disulfide.

7. Standard spiking solution, commercially available, custom mix, 5000 µg/mL containing cyclohexane, 1,2-Dichloropropane, Bromoform, Mesitylene, 1,2,4-Trichlorobenzene and 4-Phenylcyclohexene.

   Note: 1,4-Dichlorobenzene may be substituted if 4-phenylcyclohexene is not commercially available

7.0 PROCEDURES

7.1 Sample Preparation

- All charcoal tube samples and standard solutions must be allowed to warm up to ambient temperature before extraction and analysis.

- The charcoal tubes are extracted by placing the front and back sorbent sections of the sampler tube in separate 4-mL vials. Discard the foam plugs and glass wool of the tube.

- Add 2.0 mL of carbon disulfide to each vial, cap with a Teflon®-lined screw top, shake for 2 minutes, and allow to stand for a minimum of one hour with occasional agitation. Alternatively, sonicate for 15 minutes in a water bath sonicator.

- Sample extracts are now ready for analysis.

7.2 GC/MS Operating Conditions

The operating conditions used for the standards and sample analysis on the HP6890/5972 GC/MSD are listed below. Other conditions may be used as long as the QA/QC and peak identification criteria are met. Any deviation from this SOP must be documented in the case narrative.

Column Identification:	Restek Rtx-5 (cross bonded SE-54), 30 mm x 0.25 mm ID with a 0.5 □m film thickness.
Injector Temperature:	280°C
Transfer Temperature:	280 °C
Source Temperature:	Controlled by transfer line
Temperature Program:	40 °C for 1 min 4 °C/min to 120 °C 20 °C/min to 270 °C hold for 1 min
Pulsed Split Injection:	8:1 split, 14 psi pulse for 1 min
Mass Range:	35 - 360 amu for sample (35-450 amu for DFTPP)
Scan Time:	To give at least five scans per peak and not to exceed two seconds per scan
Injection Volume:	2 µL

7.3 DFTPP (Tune)

Tune the GC/MS system to meet the ion abundance criteria listed in Table 3, Appendix A by injecting 50 ng of DFTPP. Acceptable performance must be achieved every 24 hours.

7.4 Initial Calibration

1. Prepare calibration standards at a minimum of six concentration levels (1, 5, 10, 25, 50, and 100 µg/mL) for each target compound in CS_2 from the 200 µg/mL intermediate calibration standard as follows:

500 µL→	1.0 mL CS_2	100 µg/mL
250 µL→	1.0 mL CS_2	50 µg /mL
125 µL→	1.0 mL CS_2	25 µg /mL
50 µL→	1.0 mL CS_2	10 µg /mL
25 µL→	1.0 mL CS_2	5 µg /mL
5 µL→	1.0 mL CS_2	1 µg /mL

Store all standard solutions at -10 to -20 ^{0}C in crimp top vials with Teflon liners protected from light for a period up to 6 months.

2. Add 20 µL of the internal standard mix to each 1 mL aliquot of the six calibration standards resulting in a concentration of 50 µg/mL. Do not add the internal standard mix if using commercially prepared calibration standards that already contain internal standards.

3. After an acceptable DFTPP tune, inject 1 µL of each of the calibration standards.

4. Use the following equation to calculate and tabulate the relative response factor (RRF) of all target analytes and surrogates in all six calibration standards. The primary ion of the internal standard must be used for quantitation.

$$RRF = \frac{(A_X)(C_{IS})}{(A_{IS})(C_X)}$$

where:

A_X = Area of the characteristic ion for the compound to be measured
A_{IS} = Area of the characteristic ion for the specific internal standard
C_{IS} = Concentration of the internal standard
C_X = Concentration of the compound to be measured

5. A five-point calibration for bromoform, styrene, and terpinene may be used if the 1 µg/mL RRF is too low. Calculate and tabulate the average RRF and percent relative standard deviation (%RSD) for all compounds. The average RRF for each compound must not be less than 0.05 and the % RSD for each compound must be less than or equal to 30%.

$$\text{RRF average} = \frac{RRF_1 + \ldots + RRF_5}{5}$$

$$SD = \sqrt{\sum_{n=} \frac{RRF_i - RRF_{average})^2}{4}}$$

$$\%RSD = \frac{SD}{RRF_{average}} x\ 100$$

7.5 Continuing Calibration

A check of the initial calibration curve must be performed every 24 hours during sample analysis.

1. Inject 1 µL of a 25 µg/mL calibration standard that contains target analytes and internal standards.

2. Calculate and tabulate the daily RRF for all compounds.

3. Use the following equation to calculate percent difference (% D) between each daily RRF and average RRF from the initial calibration curve.

$$\%D = \frac{RRF_{Daily} - RRF_{Average}}{RRF_{Average}} \times 100$$

4. If the minimum RRF of any quantitated analyte (target) is <0.05, the initial calibration curve must be rerun.

5. If the %D of any quantitated analyte (target) is >25%, the initial calibration curve must also be rerun.

6. Reanalysis can be waived by Organic Group Leader as determined on a per project basis.

7.6 GC/MS Analysis

Sample extracts may be analyzed only after the GC/MS has met the requirements of DFTPP, initial calibration, and continuing calibration as described above. The operating conditions used for calibration standards must be employed for analysis of samples.

1. Add 20 µL of the internal standard mix into the method blank, the BS/BSD, and all the sample extracts.

2. Inject 1 µL of the extract for each sample, method blank or BS/BSD sample.

3. If the response of any analyte exceeds that of the highest calibration standard (i.e., 100 µg/mL), the sample extract must be diluted so that the analyte response falls within the linear range established in the initial calibration. Ideally, the concentration of the analyte should fall midrange of the curve after dilution.

4. After a dilution is prepared, the internal standard mix is added accordingly, to maintain the required concentration of 50 µg/mL of each internal standard in the diluted extract.

7.7 Identification of Target Analytes

The target analytes are identified by comparison of the sample mass spectra with the mass spectra of a calibration standard. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component at the GC relative retention time (RRT) as the standard component

- Correspondence of the sample component and standard component mass spectra

1. For establishing correspondence of the RRT, the sample component RRT must compare within 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

2. For comparison of standard and sample components, reference mass spectra must be obtained

from the 25 µg/mL calibration standard. The standard mass spectra may be obtained from the run used to obtain the reference RRTs. In the case of co-elution of standard components, the reference mass spectra from the National Institute of Standard and Technology (NIST) Mass Spectral Library should be used or the analyst can use professional judgment to establish the presence of target analytes. If professional judgment is used, it will be documented in the case narrative.

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

   a. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion equals 100%) *must* be present in the sample mass spectra

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

   c. Ions greater than 10% present in the *sample* spectrum but not in the *standard* spectrum must be considered and accounted for by the analyst making the comparison. All target analytes meeting the identification criteria must be reported with their mass spectra. Report the actual value of all target analytes below the quantitation limit with a flag of "J", e.g., "3 J".

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

7.8 Library Search

A library search shall be executed for non-target compounds present in method blanks and samples for the purpose of tentative identification. In this case, the NIST Mass Spectral Library (or equivalent) will be used for identification search.

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

2. Guidelines for making tentative identification:

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

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

standard spectra, the corresponding sample ion abundance must be between 30-70%.

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

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

3. If all of the above conditions for a compound are met and if the Q value of the search is 80%, that compound will be reported as a tentatively identified compound (TIC). If the Q value is < 80% or the mass spectral interpretation specialist indicates that no valid tentative identification can be made, the compound should be reported as *unknown*. The mass spectral interpretation specialist should give additional classification of the unknown compound, if possible (e.g., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). The molecular weight should be included in the TIC report if it can be distinguished from the library search.

4 Up to twenty (20) organic compounds of greatest apparent concentration that are not target analytes shall be identified by a forward library search.

8.0 CALCULATIONS

8.1 Target Analytes

The target analytes identified by the GC/MS method shall be quantitated by the internal standard method. The internal standards (IS) used shall be those listed in Table 2. The EICP area of the characteristic ions of the target analytes and IS are used. Target analyte concentrations and concentration conversions are calculated as follows:

1. Amount of analyte in total µg/sample:

$$\mu \text{/sample} = \frac{(A_s)(C_{is})}{(A_{is})\,(RRF)} \; x \; V \; x \; DE$$

where:

A_S = Area of characteristic ion for the analyte to be measured
A_{IS} = Area of characteristic ion for the internal standard
C_{IS} = Concentration of internal standard

RRF = Relative response factor of analyte
V = Extraction Volume (mL)
DE = Desorption efficiency, decimal point equivalent

The RRF is calculated from the calibration standard solution mixture using:

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

where:

A_x = Area of characteristic ion of analyte in the standard mixture
A_{is} = Area of characteristic ion of internal standard in the standard mixture
C_x = Concentration of internal standard in the standard mixture
C_{is} = Concentration of analyte in the standard mixture

2. Concentration of analyte in mg/m^3:

$$\text{Concentration}\left(\text{ng}/\text{m}^3\right) = \frac{(\text{Total}\mu\text{g sample front} + \text{Total}\mu\text{g sample back})}{\text{Liters sampled}} \times \frac{1\text{mg}}{1000\text{ng}} \text{ x } \frac{1000\text{L}}{1\text{m}^3}$$

NOTE: If any target analyte is present in the lot blank, the concentration in μg will be subtracted from the sample concentration.

When the concentration of any identified target analyte is below the quantitation limits but the mass spectrum meets the identification criteria, report the concentration by flagging the results with "J". Any concentration less than 25% of the method detection limit (MDL) will not be reported. All target concentrations are reported to two significant figures

3. Concentration of analyte in parts per billion by volume (ppbv):

$$\text{Concentration (ppbv)} = (\text{ng/m}^3) \text{ x } (24.45/\text{MW}) \text{ x } 1000$$

where:

MW = Molecular Weight of the analyte.

4. Quantitation Detection Limits (QDLs):

The QDLs in ppbv are calculated using the following equation:

$$QDL = 24.45x \frac{(C_S)(V_E)(DE)}{(V_S)(MW)}$$

where:

C_S = Concentration of lowest standard in the linear range of the six- point calibration curve
V_E = Extract volume (mL)
V_S = Sample volume (m^3)
DE = Desorption efficiency, reciprocal
MW= Molecular weight of analyte

8.2 Tentatively Identified Compounds (TICs)

An estimated concentration for tentatively identified compounds (TICs) must be calculated by the internal standard method. For quantification, the nearest preceding internal standard free of interferences shall be used. The formula for calculating concentrations is the same as in Section 8.1, except that area count or peak height of the TICs and their assigned internal standards from the total ion chromatogram is used for quantitation. A relative response factor (RRF) is assumed to be 1.0. All non-target concentrations are reported to two significant figures.

8.3 Blank Spike Recoveries

Blank spike recoveries and relative percent difference (RPD) between the recoveries of each of the compounds in BS/BSD will be calculated by the following equations:

$$\text{Blank Spike Recovery (\%R)} = \frac{\text{SBR - BR}}{\text{SA}} \text{ x } 100$$

where:

SBR = Spike blank result
BR = Lot Blank result
SA = Spike added

$$\text{RPD} = \frac{(\text{BSR} - \text{BSDR})}{(\text{BSR} + \text{BSDR})/2} \text{ x } 100$$

where:

RPD = Relative percent difference
BSR = Blank spike recovery
BSDR = Blank spike duplicate recovery

Note: RPD is always expressed as a positive value.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

9.1 Tune (DFTPP)

The GC/MS must meet the ion abundance tune criteria specified in Table 3, Appendix A, before initiating acquisition activities involving samples, blanks, or standards. The tune check ensures correct mass calibration, mass resolution, and mass transmission. It must be performed every 24 hours during sample analysis.

9.2 Initial Calibration for Target Compounds

Once the tune criteria has been met, the GC/MS system must be initially calibrated using a minimum of six concentrations (1, 5, 10, 25, 50, 100 µg/mL) to determine the linear response of the target analytes.

The initial calibration of the GC/MS is evaluated according to the magnitude and stability of the relative response factors of (RRF) of each target analyte and surrogate. The minimum RRF of each compound at all six levels must be equal to or greater than 0.05 and the %RSD must not exceed 30%. Once this criteria has been met blanks and samples may be analyzed.

9.3 Continuing Calibration for Target Compounds

After 24 hours of sample acquisition have passed, the GC/MS must be re-tuned using DFTPP and the initial calibration curve verified by the mid-level calibration standard.

1. The DFTPP tune must pass the criteria in Table 3, Appendix A.

2. The 25 µg/mL calibration standard must be used for the continuing calibration.

3. The continuing calibration of the GC/MS is evaluated based on the magnitude of RRF and %D between the *average* RRF of each compound from the initial calibration and the RRF of that compound in the continuing calibration standard. The minimum RRF of each SPCC in the continuing calibration must be equal to or greater than 0.05 and %D for each CCC must not exceed 25%. For any target compounds present in the sample at a concentration greater than the MDL, those compounds must meet the minimum RRF of 0.05 and the %D criteria of 25%.

4. If any of the requirements listed in Step 3 are not met, notify the Organic Group Leader.

9.4 Internal Standard Responses and Retention Times

The response of each of internal standard in all calibration standards, samples, and blanks is crucial for obtaining reliable analytical results because the quantitative determination of semi-volatile compounds is based on the area of each internal standard.

1. The amount of each internal standard in a 1 µL injection of sample extract must be 50 ng.

2. The response and the retention time of each internal standard are evaluated for stability. The area of each internal standard in a sample must not vary by more than a factor of 2 (i.e., -50% to +100%) from the area of the same internal standard in the continuing calibration standard. In addition, the retention time of each internal standard must be within 0.50 minutes (30 seconds) of its retention time in the continuing calibration standard.

3. If samples are quantitated by the initial calibration, the area of each internal standard at 25 µg/mL calibration standard must be used for evaluation.

4. The response of each internal standard in all samples, blanks and spikes must be tabulated. If an internal standard area is outside the QC limits, the extract must be reanalyzed to confirm a matrix effect or to determine if it was within the laboratory's control. If the reanalysis is within QC limits, report only the reanalysis if within the 14-day analysis holding time. If reanalysis confirms matrix effects, submit both sets of data but report the initial run.

9.5 Method Blank Analysis

A method blank is an aliquot of carbon disulfide that is carried through the entire analytical procedure. The purpose of a method blank is to determine the level of contaminations associated with preparation and analysis of samples.

1. One method blank must be prepared for each batch of 20 samples.

2. A method blank should contain no more than the QL of the target analytes listed in Table 1, Appendix A.

3. If a method blank exceeds the contamination limits as described above, the analytical system is considered as unacceptable. The sources of contamination must be investigated so that appropriate corrective actions can be taken and documented, before proceeding any further sample analysis. Due to the nature of the samples, re-extraction is not possible.

9.6 Solvent Blank Analysis

Prior to using a specific lot of carbon disulfide, the solvent must be analyzed and found to be free of any target analytes.

9.7 Blank Spike/Blank Spike Duplicate (BS/BSD)

The BS/BSD recoveries were determined by spiking the charcoal tubes with 50 µg of each analyte (25 µg/mL). No air was drawn through the charcoal tubes. The purpose of the BS/BSD is to evaluate the accuracy and precision of the extraction and analysis, including possible sample matrix effects.

1. One BS/BSD must be prepared every 10 samples or per project. The BS/BSD must be associated with a method blank that meets the criteria in Section 9.5and must be extracted and analyzed within holding time.

2. The spike solutions specified in Step 7 of Section 6.0 must be used.

3. Spike recoveries and relative percent difference (RPD) of each spike compound in the BS/BSD are calculated according to the equations specified in Section 8.3.

4. The quality control limits for recovery and RPD are listed below. The QC limits are advisory at this time and no further action is required if the recovery fall outside the limits.

   Recovery 70-130% RPD 20%

   Note: If the laboratory fails to meet the recovery QC limits and the RPD limits on a routine basis, the Organic Group Leader must investigate the cause and take corrective action.

9.8 Dilution Analysis

If the concentration of any target analyte in a sample extract exceeds the initial calibration range, the sample extract must be diluted and reanalyzed as described in Section 7.6.

1. Use the results from the initial analysis to estimate the approximate dilution factor needed to bring the highest concentration within the linear calibration range.

2. The dilution factor chosen should bring the highest target analyte within the upper half of the calibration range.

3. Submit the data from the original sample and the dilution in which analytes fall within the calibration range.

9.9 Method Detection Limits

The method detection limit (MDL) reported is based on the lowest point of the calibration range. Compounds detected at less than the lowest standard will be reported as "J" values. The matrix will be the charcoal tube media spiked will all the method analytes. It is recommended that a MDL study be performed once a year to verify that the values obtained are below the lowest standard used for reporting.

9.10 Precision and Accuracy

Single laboratory accuracy and precision data were obtained for the method analytes using laboratory fortified charcoal tube blanks with analytes at 5 µg/mL. Seven charcoal tube blanks were spiked with the method analytes and are used to check the instrument precision. The samples were subsequently extracted with CS_2 and analyzed by GC/MS. Calculation of theoretical MDLs were calculated using the formula:

$$\text{Theoretical MDL} = t_{(n-1,1-\alpha=0.99)}$$

where:

$t_{(n-1,1-\alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = the standard deviation of the replicate analyses

$S = [\sum(X_j - \langle X \rangle)^2/(n-1)]^{1/2}$

For seven injections $t_{(n-1,1-\alpha=0.99)} = 3.143$. Therefore, substituting into equation above yields:

Theoretical MDL = 3.143 x S

9.11 Desorption Efficiencies

The desorption efficiency (DE) is determined for each compound at 10, 50 and 200 µg levels. Three replicate charcoal tubes are spiked with a standard solution mixture at each level, extracted with CS_2 and analyzed by GC/MS. A blank is also extracted with CS_2 and analyzed to determine any contamination in the carbon disulfide. The DEs are calculated as follows:

$$DE = \frac{\text{Average Amount Recovered } \mu\text{/mL}}{\text{Spiked Amount } \mu\text{/mL}}$$

The amount recovered is calculated by:

$$\text{Amount Recovered } (\mu\text{/mL}) = \frac{(A_S)(C_s)}{(A_{IS})(RRF)}$$

where:

A_S = Area of the characteristic ion for the compound to be measured

A_{IS} = Area of the characteristic ion for the specific internal standard (IS)

C_{IS} = Amount of internal standard added in nanograms

RRF =Average relative response factor from the analysis of calibration standard

Total microgram in sample (µg/sample)

$$\mu\text{/sample} = \frac{(A_s)(C_{is})}{(A_{is})(RRF)} \times V \times DE$$

where:

V = Extraction volume (mL)

DE = Desorption efficiency

9.12 Manual Integrations

Manual integration of all target analytes, surrogates, and internal standards shall be submitted for review. The manual integration results shall be flagged with "m" if not performed by the software, and initialed and dated by the analyst. Documentation of the manual integration of quantitation ion peaks must be included in the data package. Refer to SERAS SOP# 1001, *Chromatographic Peak Integration Procedures*.

10.0 DATA VALIDATION

Data will be assessed in accordance with the guidelines set forth in the most current version of SERAS SOP #1016, *Data Validation Procedures for Routine Organic Analysis* using the criteria listed in Appendix B. However, data is considered satisfactory for submission when all the following requirements are met.

1. All samples must be analyzed under an acceptable tune, initial calibration, and continuing calibration check at the required frequency.

2. The QC requirements described in Section 9.0 should be met at all times. Any deviation or anomalous conditions should be discussed with the Organic Group Leader.

11.0 HEALTH AND SAFETY

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

12.0 REFERENCES

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13.0 APPENDICES

A - Tables
B - Data Validation Criteria

APPENDIX A
Tables
SOP #1816
June 2002

TABLE 1. Target Compound List (TCL) and Characteristic Ions

TARGET COMPOUND	PRIMARY ION	SECONDARY ION(S)
1,1,1-Trichloroethane	97	99, 61
Cyclohexene	56	84, 69
Benzene	78	52, 50
Carbon Tetrachloride	117	119, 121
Cyclohexene	67	54, 82
n-Heptane	57	71, 100
1,2-Dichloropropane	63	76, 65
Trichloroethene	130	132, 95
1,4-Dioxane	88	58
Methylcyclohexane	83	55, 98
Methylisobutyl Ketone	58	85, 100
Toluene	91	92, 65
n-Octane	57	85, 114
Tetrachloroethene	166	129, 164
Chlorobenzene	112	77, 114
Ethylbenzene	91	106, 77
para-Xylene	91	106, 77
Bromoform	173	171, 91
Styrene	104	78, 103
ortho-Xylene	91	106, 105
n-Nonene	56	69, 55
n-Nonane	57	85, 128
1,1,2,2-Tetrachloroethane	83	85, 168
Cumene	105	120, 79
Mesitylene	105	120, 91
alpha-Methylstyrene	118	117, 78
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	148, 111
1,2-Dichlorobenzene	146	111, 148
Benzyl Chloride	91	126, 89
alpha-Terpinene	93	121, 136
D-Limonene	68	93, 79
4-tert-Butyltoluene	133	105, 148
1,2,4-Trichlorobenzene	180	182, 184
Naphthalene	128	127, 129

TABLE 1 (Cont'd). Target Compound List (TCL) and Characteristic Ions

TARGET COMPOUND	PRIMARY ION	SECONDARY ION(S)
4-Phenylcyclohexene	104	158, 78
n-Decene	56	70, 55
n-Decane	57	71, 85
n-Undecene	55	70, 83
n-Undecane	57	71, 85
n-Nonanal	57	82, 98
n-Dodecane	57	71, 85
n-Tridecane	57	71, 85
n-Tetradecane	57	71, 85
n-Pentadecane	57	71, 85
n-Hexadecane	57	71, 85

TABLE 2. Volatile Compound Internal Standards List (ISL) and Characteristic Ions

TARGET COMPOUND	PRIMARY ION	SECONDARY ION(S)
Cyclohexane-d_{12}	64	96, 46
Toluene-d_8	98	100
1,4-Dichlorobenzene-d_4	150	152
Naphthalene-d_8	136	108, 137
1-Chlorooctane	91	55

TABLE 3. Ion Abundance Criteria for Decafluorotriphenyl phosphine (DFTPP) Tune

m/z	Ion Abundance Criteria
51	30 - 80 percent of mass 198
68	Less than 2 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	25.0 - 75.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 0.75 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110 percent of mass 198
443	15.0 - 24.0 percent of mass 442

NOTE: All ion abundances must be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent that of m/z 198.

TABLE 4. Volatile Compounds Internal Standards with Corresponding Compounds Assigned for Quantitation

Cyclohexane-d_{12}	Toluene-d_8	1,4-Dichlorobenzene-d_4	Naphthalene-d_8	1-Chlorooctane
1,1,1-Trichloroethane	Methylisobutylketone	Cumene	Benzyl Chloride	n-Decene
Cyclohexane	Toluene	Mesitylene	alpha-Terpinene	n-Decane
Carbon Tetrachloride	n-Octane	Alpha-methylstyrene	D-Limonene	n-Undecene
Benzene	Tetrachloroethene	1,3-Dichlorobenzene	4-tert-Butyltoluene	n-Undecane
Cyclohexane	Chlorobenzene	1,4-Dichlorobenzene	1,2,4-Trichlorobenzene	n-Nonanal
n-Heptane	Ethylbenzene	1,2-Dichlorobenzene	Napthalene	n-Dodecane
1,2-Dichloropropane	para-Xylene	4-Phenylcyclohexene		n-Tridecane
Trichloroethene	Bromoform			n-Tetradecane
1,4-Dioxane	Styrene			n-Pentadecane
Methylcyclohexane	ortho-Xylene			n-Hexadecane
	n-Nonene			
	n-Nonane			
	1,1,2,2-Tetrachloroethane			

APPENDIX B
Data Validation Criteria
SOP #1816
June 2002

INDOOR AIR ANALYSIS OF VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Data Validation Criteria: VOA using carbon tubes, Modified NIOSH 1500/1501/1003

Holding Time	14 days from collection, 15-21 days → J; >21 days □ non-detects R, hits → J
Media Blank Contamination	Average media blank subtracted from samples and QC samples
Trip, Field Blank	Sample <5x blank → U Sample >5x blank → No qualifier
Mass Spec Tuning	24 hrs; 24-25 hr → J, >25 hr → R
ICAL	Minimum six standards, RSD 30%; hits> 30% → J; non-detects: 50-90% → UJ, >90% → R
Minimum RF	0.050; <0.050 → hits J, non-hits R
CCAL	Mid-point; %D<25% ; hits> 25% □ J; non-detects: 50-90% □ UJ, >90% □ R
Internal Standards	Area counts 50-200% of calibration area, RT 0.5 min.; Outside area criteria: hits □ J, 25-50% or >200% non-detects □ UJ, <25% □
Compound Identification	Ions >10% in reference spectra, 20% in sample spectra, RRT0.06; spectra out □ Prof judgement; RRT>0.06, hits J
BS,BSD	0% recovery □ hits J, non-detects R
Desorption efficiency	within 1 yr or new media lot