3M EHS Laboratory

Method

Extraction and Analysis of Organic Compounds from Occupational Safety and Health Administration Versatile Sampler (OVS) Tubes Using Gas Chromatography/Mass Spectrometry and Liquid Chromatography/Mass Spectrometry

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Quality Assurance

1 Scope and Application

This method describes the steps for the extraction of organic compounds from Occupational Safety and Health Administration (OSHA) Versatile Sampler (OVS) air sampling tubes and subsequent analysis of extracts utilizing liquid chromatography/mass spectrometry (LC/MS) and gas chromatography/mass spectrometry (GC/MS).

This is a performance-based method and may be generally applied to the determination of organic compounds[1] from OVS tubes by solvent extraction when analysis batch quality control (QC) criteria are met. All QC samples should be prepared with an OVS tube with the same part number as the samples and the same lot number if possible. Each set of samples shall be prepared with laboratory control spikes (LCSs) and method blanks. A sample analysis batch will consist of an appropriate calibration curve (or an initial continuing calibration check standard), LCS samples, samples, and bracketing continuing calibration check standards which are analyzed on the same instrument. Preparation of additional QCs such as Laboratory Matrix Spikes (LMSs), Field Matrix Spikes (FMSs), Trip Blank Matrix Spikes (TBMS), sample replicates, etc. may be included during the sample preparation and analysis, with those results used to evaluate the sample data precision and accuracy. The batch analytical QCs must be completed and pass QC acceptance criteria (section 9) and include QCs representative of sample holding times and air sample volumes if the data from the analytical batch are to be reported.

2 Method Summary

OVS tubes typically consist of a glass fiber or quartz filter, resin (e.g. XAD or Tenax), urethane foam plugs, glass tube housing, and a retaining ring. Component parts from the OVS tube are disassembled and extracted with an appropriate solvent (e.g. acetone). The component parts may be solvent extracted individually or combined (e.g. designating a “front” section as the filter, first resin bed and first foam plug and a “back” section as the second resin bed and second foam plug). It is not acceptable to combine what is considered the backup portion of the OVS tube (e.g. the “back” section) with the “front” section in an extract.

Quantitation of the OVS tube solvent extract is typically performed using internal standard calibration. The internal standard may be added either during sample extraction (e.g. spiking the OVS sample directly or included in the extraction solvent) or just prior to analysis (e.g. adding internal standard post extraction). Alternatively, quantitation may be performed by external standard calibration.

Identification of target compounds is accomplished by comparing their retention time and mass spectra to authentic standards.

Tentative identification of an unknown compound using GC/MS may be made by comparing a full scan electron impact (or other technique) mass spectrum of the unknown to a NIST library mass spectral search, or other suitable library match (e.g. a custom library maintained by the laboratory). As the OVS tube extraction efficiency is unknown, an estimated ≥ concentration of a non-target analyte identified in a sample may be made using either the response factor of the nearest internal standard free of interferences or using the response factor of another calibrated compound. Also, a product ion scan mass spectrum using liquid chromatography-high resolution mass spectrometry (LC/HRMS) can also be used to confirm unknown compounds.

[1] Limited scope method validations for fluorochemicals are documented in 3M EHS Laboratory Reports No. W1260 and W2258.

3 Definitions

3.1 General Definitions

3.1.1 Analysis Batch

A set of samples analyzed with calibration standards and/or continuing calibration standard checks, laboratory control samples, instrument blanks, and method blanks on the same instrument. Additional QCs such as Laboratory Matrix Spikes (LMSs), Field Matrix Spikes (FMSs), Trip Blank Matrix Spikes (TBMS), and sample replicates may be included. The analysis batch must include QCs representative of sample holding times and air sample volumes.

3.1.2 Sample Extract

A solution prepared in the same solvent as the calibration standards which has been prepared from a sample.

3.1.3 Solvent Calibration Standard

A solvent solution prepared with a known amount of analyte, spiked from an intermediate or stock solution standard, for the purpose of establishing instrument response of a target/surrogate analyte.

3.1.4 Internal Standard (IS or ISTD)

A compound added to each study sample, calibration standard, laboratory control sample, procedural blank, and any additional quality control at a consistent level (typically around the mid-level of the calibration range). The internal standard(s) are typically stable isotopically labeled counterparts of one or more target analytes. If a labeled counterpart is not available, a labeled compound of similar chemical functionality or retention time characteristics may be used instead, (e.g. EPA mixes provided by vendors). The area count ratio of the target analyte to the internal standard is used for calibration.

3.1.5 Limit of Quantitation (LOQ)

The lower limit of quantitation (LLOQ) for an analytical batch is the lowest concentration that can be reliably quantitated within the specified limits of accuracy. The LLOQ is generally selected as the lowest non-zero standard in the calibration curve that meets method acceptance criteria. The LLOQ for each target analyte is established for each analysis batch as the lowest calibration standard with area counts (or area count ratio when internal standard calibration is used) that meet the established criteria discussed later in this document.

Typically, sample LLOQs are reported in ppmv or mg/m^3 as shown by the calculations provided in section 12. Reporting a sample LLOQ must take into account how the different sections of the OVS tube were separated and extracted. Also, recoveries of LCSs with air drawn through them at a similar rate and duration should demonstrate how the analytes of interest are captured on the media. For example, if an OVS tube is separated into its three component parts (filter, 1st resin bed, 2nd resin bed) and extracted as such, LCSs that demonstrate that an analyte is captured on the first resin bed and not the filter, an overall sample LLOQ may be calculated using the individual components into account (no summation is necessary). Another example, if LCSs that demonstrate that an analyte is captured on the filter and first resin bed, an overall sample LLOQ would be calculated by summing the individual components (filter and 1st resin bed).[2]

Samples that have had no air drawn through them (e.g. trip blank) are reported as mass of analyte (e.g. ng, µg). The same considerations as stated in the previous paragraph for reporting the LLOQ must be taken into account for each section separated and extracted.

[2] Example assumes that the OVS tube components were individually extracted. A different procedure may be required if the component parts are combined when extracted.

The upper limit of quantitation (ULOQ) for an analytical batch is defined as the highest concentration standard used to construct the calibration curve that meets accuracy requirements. Sample results above the ULOQ should be diluted and reanalyzed.

3.1.6 Solvent Blank

An aliquot of solvent that is not taken through the entire sample preparation process, but used to evaluate instrument background levels.

3.1.7 Sample Breakthrough

Sample breakthrough is defined as when the backup portion of the OVS tube (typically the second resin bed and puff) contains over 5% of the detected analyte in the front portion. If this occurs, samples must be flagged and reported as minimum estimates.

3.2 Mandatory Quality Control

3.2.1 Method Blank

A blank OVS tube that is extracted at the same time using the same procedure as the samples. The method blank is used to determine if analytes or other interferences are present in the matrix, laboratory environment, or the apparatus.

3.2.2 Laboratory Control Sample (LCS)

A blank OVS tube to which known quantities of the target analytes, internal standards and surrogates (when applicable), are added in the laboratory at the time when samples are prepared. The LCSs are prepared and analyzed exactly like a sample and are used to evaluate the performance of the method for that batch. LCSs are prepared for each sample analysis batch to determine method accuracy and precision.

3.2.3 Field Blank (FB)/Trip Blank (TB)

An unused OVS tube sent to the sampling location along with other samples designated for sample collection.

3.2.4 Trip Blank Matrix Spike (TBMS)

A blank OVS tube to which known quantities of the appropriate target analytes are added in the laboratory prior to the shipment to the sampling site with the sample collection vessels. The TBMS is prepared and analyzed exactly like a study sample to determine whether a loss of analyte or analytical bias could be attributed to sample holding time, sample storage and/or shipment issues. TBMS's can be sampled with representative OVS sample air flows.

3.3 Additional Optional Quality Control

3.3.1 Laboratory Matrix Spike (LMS)

An aliquot of a sample extract to which known quantities of target analytes, internal standard and surrogate (when applicable) are added in the laboratory. The LMS is analyzed exactly like a laboratory sample to determine whether the sample matrix contributes bias to the analytical results. The endogenous concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LMS corrected for these concentrations. LMS's can be sampled with representative OVS sample holding times and air flows.

3.3.2 Field Duplicate Sample (FDS, Field Dup)

A sample collected in parallel with the primary sample. The FDS is handled under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of the FDS compared to that of the primary sample gives a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures. Additional samples may be collected and labeled as such (e.g. Field Triplicate Sample, etc.).

3.3.3 Field Matrix Spike (FMS)

A sample collected in parallel with the primary sample to which known quantities of target and/or surrogate analytes are added to the OVS tube in the laboratory prior to sending it to the field for sampling. The FMS is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis. FMS's can be sampled with representative OVS sample air flows.

3.3.4 Surrogate Standard

If supported by a method validation, an isotopically labeled standard, not used as an internal standard that is added to each sample either prior to sending it to the field for sampling or during sample preparation. The surrogate would also be added to laboratory control spike samples and other quality control to serve as a means to evaluate the method performance (stability, recovery). Surrogate standard samples can be sampled with representative OVS sample holding times and air flows.

4 Warnings and Cautions

Always wear appropriate personal protective equipment (PPE) such as protective gloves, eye protection and appropriate clothing, and necessary engineering controls (fume hoods, ventilation, etc.) when working with unknown sample matrixes, solvents, chemicals and instrumentation. For potential hazard information, refer to safety data sheets, packing materials lists, the 3M Chemical Hazard Review, the 3M Guide to Laboratory Practices or other information as appropriate.

The analyst must be familiar with the described laboratory equipment and the potential hazards including, but not limited to the use of balances, centrifuges, solvents, ovens, pressurized gasses and solvent lines, and high voltage and mechanical moving parts. Refer to the appropriate equipment procedures, SOPs or the appropriate operator manuals for additional information and cautions.

5 Interferences

Impurities present in solvents and organic compounds out-gassing from the components of the analytical system are potential sources of contamination. Sample integrity can be influenced by diffusion of volatile organic materials through the septum seal of the vial.

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials should be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

Contamination by carryover can occur whenever high-concentration and low concentration samples are analyzed sequentially. The analysis of solvent blanks is used to check for contamination.

6 Instrumentation, Supplies, and Materials

A variety of vendors and models may be used. Any combination of these or other suitable equipment may be used, provided all data quality objectives are met. The instruments listed below are examples of the equipment available at the time this document was created.

6.1 GC/MS Instrumentation

Agilent Technologies 7890A GC System with 5975C inert XL EI/CI MSD with Triple-Axis Detector

Agilent Technologies 7890B GC System with 5977 EI/CI Mass Spectrometer

Agilent Technologies 6890 GC System with 5973 EI/CI Mass Spectrometer

Agilent Technologies 7890B GC System with 7200B Q-TOF Mass Spectrometer

Agilent Technologies 7890B GC with Thermal Conductivity Detector

6.2 LC/MS Instrumentation

Agilent Technologies HPLC 1100

Agilent Technologies G1311A Quaternary Pump

Agilent Technologies G1322A Solvent Degasser

Agilent Technologies G1313A Autosampler

Agilent Technologies G1316A Column Compartment (Temperature Controlled)

Agilent Technologies G1323A Hand held Controller

Agilent Technologies G1315B Diode Array Detector

Sciex API 5000, 5500, or 6500 Triple Quad Mass Spectrometer

Sciex API 5600 TOF Mass Spectrometer

Sciex Turbo Ion Spray Liquid Introduction Interface Source

Electrospray Ionization Source (ESI)

Atmospheric Pressure Chemical Ionization Source (APCI)

6.3 Supplies and Materials

The following list of supplies and materials is not exhaustive, but rather provides a guide of what the experienced analyst may use during the course of a project or study.

OVS Sampler Tubes. Supelco with XAD-4 resin, Sigma-Aldrich Tenax, Sigma-Aldrich XAD-7 resin.

GC Analytical Column. Agilent J & W DB-624, 0.25 mm, 30 m, 1.4 µm; Agilent DB-1, 0.32 mm, 60 m, 1 µm; Agilent DB-5, 0.32 mm, 60 m, 1 µm; Phenomenex Zebron ZB-SemiVolatiles, 0.25 mm, 30 m, 0.5 µm; or other column type, diameter, length or stationery phase to provide suitable analyte retention and resolution.

GC Carrier Gas. Helium, ultra-high purity or other appropriate carrier gas.

HPLC Analytical Column. Betasil C18 HPLC, 4.6 mm x 100 mm or 2.1 mm x 100 mm, 5 µm (ThermoElectron Corporation)

Miscellaneous. Gas-tight glass microsyringes, single-use plastic syringes with disposable needles, volumetric flasks, disposable pipettes, mininert re-closable valves, and gloves are some of the required supplies generally needed to complete studies using this method. Analytical balances, orbital shakers, centrifuges, and other devices may also be required. Identification of these devices and the settings used will be included in the raw data as appropriate.

7 Reagents and Standards

7.1 ASTM Type I Water

Milli-Q™ water or equivalent provided by a Milli-Q Element system, or other suitable system.

7.2 Liquid Chromatograph Mobile Phase

Chemicals, including, but not limited to, ammonium acetate, acetic acid, and formic acid may be used. The source and purity of chemicals used will be documented in the raw data.

7.3 Internal Standards (ISTD)

Purchased mixes of deuterated internal standards may be acquired and diluted appropriately. Alternatively, internal standard solutions (single component or mixtures) may be prepared in the lab using isotopically labeled compounds representative of the project's target analytes.

7.4 Surrogate Standards

Surrogates are not required for all studies, particularly for laboratory generated samples.

7.5 Solvents

Solvents, including, but not limited to, methanol, acetone, acetonitrile, methylene chloride, and ethyl acetate, may be used. The source and purity of solvents used will be documented in the raw data. It is recommended to use a solvent grade that is appropriate to the analytical technique used (i.e. HPLC grade or GC/MS grade).

8 Standard and Sample Handling

8.1 Holding Times

Samples shall be prepared and analyzed within established holding times. If a holding time has not been determined, sample stability may be monitored through the use of a QC element such as a Trip Blank Matrix Spike, a Field Matrix Spike, or an equivalent procedure such as spiking an OVS tube in the laboratory, drawing a minimal amount of air through it (to attain proper partitioning onto the media on which it will be stored), and storing it in a similar manner as the sample for a time period that encompasses the anticipated duration of sampling through analysis.

8.2 Stock Solutions

Stock solutions may be prepared in the lab from neat liquids or solids, or may be purchased as certified solutions. Stock solutions are prepared in an appropriate solvent and then further diluted to desired concentrations. Analyte concentrations are adjusted for purity as appropriate. Stock standards may be stored in a refrigerator or freezer to minimize possible losses due to volatility.

8.3 Intermediate Standard Solutions

Intermediate solutions are typically prepared in solvent using volumetric flasks. Partially fill the flask with the dilution solvent and add the appropriate volume of stock solution. Fill to volume with the dilution solvent and immediately recap. Mix by inverting the flask multiple times.

8.4 Calibration Standards

Calibration standards are prepared from the stock and intermediate standards. Solvent calibration standards are typically prepared by diluting a known volume of a stock or intermediate standard into a volumetric flask with the same solvent used to prepare samples.

9 Quality Control

Data quality objective requirements vary for different projects or studies. Unless specified in a GPO or protocol, precision and accuracy requirements are listed below. Precision and accuracy assessments based on these spike results are described in each analytical report.

9.1 Mandatory Quality Control

9.1.1 Method Blanks

A minimum of three method blanks shall be prepared and analyzed throughout the analytical sequence (at least at the beginning and at the end). Each method blank will have air drawn through them at a similar rate and duration as the LCSs. Blank contamination is estimated by extrapolation, if the concentration is below the lowest calibration standard. (Note: This extrapolation procedure is not allowed for sample results). Area counts and/or area ratio responses shall be less than half the area counts and/or area ratio response of the lowest non-zero standard in the calibration curve used to establish the lower limit of quantitation.

9.1.2 Field Blank (FB)/Trip Blank (TB)

At least one field/trip blank shall be prepared and analyzed. Blank contamination is estimated by extrapolation, if the concentration is below the lowest calibration standard. (Note: This extrapolation procedure is not allowed for sample results). Area counts and/or area ratio responses shall be less than half the area and/or area ratio response of the lowest non-zero standard in the calibration curve used to establish the lower limit of quantitation.

9.1.3 Lab Control Spike

At least three levels (two levels for surrogates) in triplicate are prepared with blank OVS tubes, with the three levels generally at the low end of the calibration curve, near the mid-range, and near the upper end of the curve. Levels may be adjusted to levels appropriate for analysis (e.g. fortifying the OVS tube at the exposure limit or at a final concentration that requires dilution if high levels are expected). Each LCS will have air drawn through it at a rate and duration similar to the samples submitted for analysis. Acceptance criteria are RSD≤20% (or RPD, if duplicates prepared) and 100%±25% accuracy to be used without technical justification. Percent recoveries should be examined for any evidence that may indicate a sample loading bias and if any analyte breakthrough is present in the backup sections of the sampler.

Sample data for target analytes outside of the LCS acceptance criteria (where nine LCSs were prepared) will be handled as follows:

If the average recovery of a single spiking level falls outside the method acceptance criteria, but at least 67% (6 out of 9) of all LCS samples are within 100±25% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 75%-125% of nominal value), the average recovery will be flagged as outside method acceptance criteria.

A successful LCS analysis coupled with a failed matrix spike analysis suggests that instrument is performing correctly but the sample matrix may affect the accuracy of results and therefore must be discussed in the report (see Section 9.2.5 Lab Matrix Spike).

9.1.4 Trip Blanks Matrix Spikes (TBMS)

At least one TBMS is prepared at a concentration near the mid-range of the calibration curve. Levels may be adjusted to levels appropriate for analysis (e.g. fortifying the OVS tube at the exposure limit). Each TBMS will have a minimal amount of air drawn through it to ensure the analyte partitions onto the media where it will be captured during sample collection.

TBMS recoveries should be within 100%±25% of the spike level. Recoveries outside this level may indicate stability or other mitigating issues with the sample storage and shipping procedures and should be evaluated accordingly, and addressed in the final report.

9.2 Additional Optional Quality Control

9.2.1 Solvent Blank

Solvent blanks are analyzed after calibration standards, continuing calibration verification (CCV) standards, after known highly concentrated samples, and periodically throughout an analytical sequence at the discretion of the analyst. If successive solvent blanks are analyzed, only the last injection need be evaluated. If a solvent blank within an analytical sequence does not meet criteria, technical justification may be made to accept the data. For example, if trace contaminants are present in a solvent blank and the next sample does not contain analyte above the LOQ, the data may be accepted because the sample is unaffected by any contamination bias shown in the previous solvent blank. Conversely, if trace contaminants are present in a solvent blank and the next sample contains analyte at a significantly higher concentration, the data may also be accepted. In this instance, subsequent samples in the sequence are evaluated for evidence of background contamination.

9.2.2 Replicate Analysis

Results should be ≤25% RPD (duplicates) or ≤25% RSD (triplicates or more) to be used without technical justification. One example of technical justification would be that replicate sample values are near the limit of quantitation where the quantitative measurements are more susceptible to variability. Replicate samples not meeting method criteria are flagged and reported as outside of QC acceptance criteria.

9.2.3 Internal Standard

Internal standard area counts may drift throughout an analytical sequence. The areas should be monitored for anomalies that suggest that a problem exists with a specific sample. Specifically, if the area of the internal standard in a sample changes by a factor of two (-50% to +100%) from the average internal standard area counts from the calibration curve, technical justification must be made in order to use the data. The above acceptance criteria does not apply when external standard calibration is used.

9.2.4 Surrogate

Recoveries should be within 100%±30% to be used without technical justification.

9.2.5 Lab Matrix Spike

A lab matrix spike (LMS) is an aliquot of a sample fortified with the target compound(s). Results are used to evaluate the method accuracy and precision including possible matrix interference(s). LMS standard solutions may be from the same source as the initial calibration standards to restrict the influence of accuracy on the determination of recovery throughout the analysis. If prepared, LMSs should be prepared at a minimum of one concentration. Acceptance criteria are 100%±30% accuracy and %RSDs or RPDs should be ≤ 25% to be used without technical justification. If an LMS recovery is outside of the 100%±30%, but within 100%±50%, then the sample result is reported and flagged as outside of QC acceptance criteria, with an expanded analytical uncertainty. If an LMS recovery is outside of 100%±50%, the sample result is not reportable.

9.2.6 Field Matrix Spikes (FMS)

FMS recovery acceptance criteria are 100%±30% after correcting for the endogenous levels of the target analyte. If an FMS recovery is outside of the 100%±30%, but within 100%±50%, then the sample result is reported and flagged as outside of QC acceptance criteria, with an expanded analytical uncertainty. If an FMS recovery is outside of 100%±50%, the sample result is not reportable.

10 Calibration and Standardization

10.1 Instrument Calibration

Samples are quantitated against a standard curve containing varying amounts of target analytes and a fixed amount of internal standard if available. The curve is calculated from the plot of individual calibration points using MassHunter, Analyst or other data reduction software. A set of six or more calibration standards is analyzed at the beginning of each project/study and within a project/study if Continuing Calibration Verification standards do not meet the acceptance criteria (see next section). The acceptance criterion for the residual of each standard is 100%±25%, but is 100%±30% at the lower limit of quantitation (LLOQ). Low or high curve points may be deactivated, depending on instrument sensitivity, linearity of response, and levels required to bracket sample concentrations.

The standard curve may be plotted by linear regression ($y = mx + b$) or a quadratic regression ($y = ax^2 + bx + c$); and may be weighted $1/x$, $1/x^2$, or non-weighted. The regression fit may include, but not be forced through, the origin. A minimum coefficient of determination (r^2) of 0.99 is required.

Samples that contain target analytes at on-column concentrations higher than the upper limit of the calibration curve must be diluted such that the on-column concentration is within the calibration range, or they must be reported as minimum estimated concentrations.

10.2 Continuing Calibration Verification (CCV)

After a successful initial calibration curve, the continued accuracy of the curve may be shown by the analysis of, one or more calibration check standards at the beginning of a new analytical sequence, after every ten samples or fewer, and at the end of the analytical sequence.

Only samples bracketed by a compliant CCV (70%–130%) may be reported without technical justification.

The CCV concentration is typically near the mid-range of the curve, but may be varied. For example, low level CCVs may be used for low level samples, whereas a low and a high CCV may be analyzed in succession to further document the continued accuracy of the entire curve range. The CCV may be a reinjected calibration curve point or a separately prepared standard.

10.3 System Suitability for GC/MS scan mode

Analyses utilizing the scan mode for a mass spectrometer operating with electron impact (EI) ionization should have an acceptable tune evaluation performed prior to analysis. This check may be performed daily or solely at the beginning of a project/study based on the data quality objectives. Most GC/MS software (e.g. Agilent MassHunter) has the capability of performing a "check tune" utilizing PFTBA. If the instrument passes the check tune (i.e. meets the manufacturers recommended specifications) analysis may continue. A failed check tune may require retuning the instrument according to the manufacturer's specifications (e.g. utilizing atune or etune on an Agilent 5977) or maintenance.

If the mass spectrometer is operated using chemical ionization (CI) using methane as a reagent gas, running a chemical ionization autotune where a summary report for PCICH4.U (positive chemical ionization) or NCICH4.U (negative chemical ionization) is generated is sufficient. The manufacturer does not have specified CI tuning criteria.

11 Procedures

The analysis of the OVS tube extracts may consist of either LC/MS or GC/MS or both depending on the project specific analyte list.

11.1 Quality Control Sample Spike Preparation

Quality Control Samples (e.g. LCSs, TBMS, etc.) are prepared by using blank OVS tubes. Carefully remove the cap of the OVS tube on the end where the retaining frit and glass fiber or quartz filter are located. Spike the analyte(s) of interest onto the filter, allow it to dry, and then draw air through the Quality Control Samples.

11.2 Sample Preparation

OVS tubes typically consist of multiple components (e.g. retaining ring, filter, 1st resin (beads), 1st foam plug, 2nd resin (beads), 2nd plug). Depending on the project specific analyte(s), these components may be individually separated or combined into "sections" into vials prior to extraction. Document the extraction method (e.g. sonication, vortex, etc.) and the volume of solvent used to extract the components/sections. It is recommended to rinse the OVS glass tube with the extraction solvent into the first/top component/section (typically containing the filter). The following is an example of an extraction procedure. This procedure may be modified as needed.

11.2.1 Section 1

Wearing gloves and working in a hood, remove the retaining ring and filter from the OVS tube, and place in a labeled vial. After removing all components as described below, rinse the empty OVS glass tube into this vial with extraction solvent.

11.2.2 Section 2

In the same manner, remove the first quantity of resin (beads) and the first urethane foam plug, and place in a second labeled vial. Care must be taken to minimize the loss of beads during this transfer due to electrostatic forces. Add extraction solvent to the vial.

11.2.3 Section 3

Remove the second quantity of resin and the second urethane foam plug, and place in a third labeled vial. Add extraction solvent to the vial. This analysis monitors for target analyte break-through of the first resin bed during sample collection.

11.2.4 Extraction

Sonicate and/or vortex mix each vial. Document any additional steps performed. Transfer a measured volume of solvent extracts from the extraction vials into sample vials. As needed, filter to remove resin particles that may plug the autosampler needle. Fortify the extracts with internal standards for the LC/MS and GC/MS analysis. Alternately, internal standard may be added to the extraction solvent.

11.3 Sample Analysis

Instrument parameters are set to provide suitable chromatography and sensitivity for the intended purpose. Analytical conditions used for a project/study will be influenced by properties such as the volatility, molecular weight, presence of isomers, and impurities present. Settings used should be documented in the raw data and the final report as appropriate.

All calibration standards, CCVs, blanks, samples, and quality control samples must be analyzed using the same settings. If changes are made after analysis has been initiated, recalibration is necessary.

12 Data Analysis and Calculations

Each dataset should be processed using chromatography software (e.g. Agilent MassHunter, Sciex Analyst). Integration parameters should be set to minimize the number of manual integrations required yet still result in uniform integration of peaks at all concentration levels. It is acceptable to perform manual integrations for any or all standards, samples, or blanks if appropriate integration parameters cannot be found, especially when near baseline resolved isomers are present. All integrations must be done consistently for all standards, samples, and blanks and in compliance with ETS-12-010.

Means (averages) will be calculated by adding the individual entities and dividing the resultant sum by the number of individual entities.

Standard deviations will be calculated using Microsoft Excel ® or other software as appropriate. The Microsoft® built-in function STDEV.S is typically used.

Sample precision will be reported as % relative standard deviation (%RSD) or as % coefficient of variation (%CV) for triplicates or above, and relative percent difference (RPD) for duplicate data. Sample %RSD will be calculated using the following equation:

$$\text{Sample \%RSD} = \left(\frac{A}{B}\right) * 100$$

Where: A = standard deviation of averaged samples and B = average of samples

The RPD is defined as the absolute value of the difference of two values divided by the average of the two values and multiplied by 100.

Calculate any matrix spike percent recoveries using the following equation:

$$\text{\% Recovery} = \frac{(\text{observed concentration} - \text{unfortified sample concentration})}{\text{spike concentration}} * 100\%$$

Calculate the air concentration as follows:

$$ppmv = \frac{(W_f + W_b)(24.45)}{(V)(MW)}$$

where,

W_f = Micrograms of analyte present in front of OVS tube

W_b = Micrograms of analyte present in the back of OVS tube

V = Total Volume of air sampled in liters through the OVS tube

24.45 (L/mol) = Molar volume of a gas at 24.8 °C and 760 mm of Hg

MW = Molecular weight of the analyte of interest

$$mg/m^3 = \frac{(W_f + W_b)}{(V)}$$

where,

W_f = Micrograms of analyte present in front of OVS tube

W_b = Micrograms of analyte present in the back of OVS tube

V = Total Volume of air sampled in liters through the OVS tube

13 Analyte Identification When Using GC/MS Scan Mode

The following section provides guidance which may be used to assist in determining qualitative analyte identification while utilizing the mass spectrometer EI scan mode of analysis. When evaluating samples, it is up to the analyst to determine if the following is applicable.

13.1 Tentatively Identified Compounds (TICs)

A library search may be required to tentatively identify compounds which are not included in the calibration curves using a library search. Guidelines for tentative identification include but are not limited to:

Additional ions present in the sample spectrum that are not included in the reference spectrum should be reviewed for possible background contamination or co-eluting compounds.

Additional 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, co-eluting peaks, or deconvolution.

If, in the technical judgement of the analyst, no valid identification can be made, report the compound as an unknown with possible classification, such as hydrocarbon.

How the estimated concentrations of the TICs was determined should be detailed in the report. Estimated values of TICs may be reported using several different approaches which may include:

Average response factor of all targets

Average response factor of closest target

Average response factor of all ISTDs

Response factor of closest target's ISTD

Response factor of closest ISTD

Relative ISTD estimation

Manual response factor (such as utilizing one specific ISTD)

All TICs should be identified with the appropriate flag in the final report. Traditional EPA flags include:

B: The associated sample TIC was also detected in the associated blank.

J: Indicates an estimated value.

N: Applied to all TIC results where the identification is based on a mass spectral library search.

A discussion should be added to the report addressing the limitations of the identification and estimation of TICs. This discussion should include the libraries searched, the quality fit factor and how it may be influenced at lower concentrations, how the concentrations were estimated (see above), how the LLOQ was determined (e.g. analyst experience, lowest standard of a target analyte, etc.), factors that may influence a TIC to be not reported (e.g. low match quality, estimated concentration below the LLOQ, low signal to noise, only the top ten TICs were requested), and any other factors that may add to the uncertainty of a compounds presence or non-presence.

All reports should include a disclaimer regarding how the response factors of the TICs relative to the target/ISTD used to estimate the concentration is unknown. All TIC concentrations are considered estimates at best, the uncertainty of TICs cannot be ascertained, and the TIC results should be used for screening purposes only.

14 Pollution Prevention and Waste Management

Follow 3M procedures for the disposal of sample vials, flammable solvent, and glass.

Follow 3M policies for all sample handling and disposal.

15 Records

Analytical records needed to reconstruct the sample preparation, sample analysis, and to reconstruct the results calculations must be included in the final data package or kept as facility records. The required documents may include, but are not limited to, the following handwritten or electronic records:

Standard Preparation Log Book Records

Sample Preparation Worksheet(s)

Liquid Chromatograph/Gas Chromatograph and Mass Spectrometer Identification and Settings

Analytical Sequence(s)

Initial Calibration Results Summary

Chromatograms

Quantitation Reports for Analyses

Notes to File

16 Attachments

None

18 References

National Institute for Occupational Safety and Health (NIOSH) Method Development Protocol DHHS (NIOSH) Publication No. 95-117

Reagen, William K., Lindstrom, Kent R., Thompson, Kathy L. and Flaherty, John M. (2004) 'Analytical Techniques and Method Validation for the Measurement of Selected Semivolatile and Nonvolatile Organofluorochemicals in Air', Journal of Occupational and Environmental Hygiene, 1:9, 559-569

19 Affected Documents

None

20 Revisions

Revision Number	Summary of Changes
0	This document is a revision of ETS-8-104.0, several analytes were removed from section 1.1 to enable distribution of this document to outside laboratories. If ETS-8-104 is revised then this document must be revised as well. Conversely, if this document is revised then ETS-8-104 must be revised to reflect the same changes. *[ETS-8-104 was discontinued on 10/17/2002]*
1	Extensive updates to broaden the scope of the method from the analysis of only fluorochemicals to organic compounds in general.