3M Environmental Laboratory

Method

Analysis of Organic Compounds in Solvent Using Gas Chromatography/Mass Spectrometry

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Quality Assurance

1 Scope and Application

This method is used to quantitate organic compounds in solvent that elute as peaks from a GC column and are amenable to quantitation using a mass spectrometer (MS) or other suitable detectors, such as a thermal conductivity detector (TCD) or flame ionization detector (FID). Appropriate MS modes of detection include: scan mode, selected ion monitoring (SIM) mode, combined SIM/scan or MS/MS mode of operation using either electron impact or chemical ionization techniques.

This is a performance-based method and may be generally applied to the determination of volatile organic compounds (VOCs) and/or semivolatile organic compounds (SVOCs) in solvent extracts when analysis batch quality control (QC) criteria are met. 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), QC samples (LCSs and method blanks are required), samples, and bracketing continuing calibration check standards which are analyzed on the same instrument. Additional sample specific QCs prepared such as Laboratory Matrix Spikes (LMSs), Field Matrix Spikes (FMSs), 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 laboratory is permitted to modify the GC/MS instrument parameters including, but not limited to, the following: GC column, the temperature-programmed oven, and MS conditions. Method modifications should be implemented to improve method performance or to meet data quality objectives for the project/study. In all cases, the batch analytical QCs must be completed and pass QC acceptance criteria (section 9) if the data from the analytical batch are to be reported.

This method does not include specific sample preparation procedures. Sample preparation may follow an established laboratory method SOP, an appropriate literature method, or a sample preparation method developed in-house specific for a given project. At a minimum, the sample preparation method utilized with this analytical method should be described in the appropriate project documentation (General Project Outline (GPO), study protocol, and/or final report).

2 Method Summary

Organic compounds are introduced into the gas chromatograph by injecting the sample extract (solvent solution) through a septum into an inlet which vaporizes and introduces the compounds of interest to the carrier gas (typically helium) and onto a narrow-bore fused-silica capillary column. The gas chromatograph is temperature-programmed to separate the compounds in the sample mixture which are then detected on a mass spectrometer or other detector.

Quantitation is typically performed using stable isotope internal standard calibration. The internal standard may be added either during sample extraction (e.g. spiking the 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 (for TCD or FID) and/or mass spectra to the electron impact[1] (or electron impact like) spectra of authentic standards. Tentative identification of an unknown compound may be made by comparing a full scan electron impact 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). 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.

3 Definitions

3.1 Analysis Batch

A set of study samples analyzed with calibration standards and/or continuing calibration standard checks, laboratory control samples, instrument blanks, and method blanks on the same instrument.

3.2 Sample Extract

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

3.3 Solvent Calibration Standard

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

3.4 Extracted Calibration Standard

A solvent solution where a known amount of analyte is spiked onto a surrogate matrix and prepared the same as the samples for the purpose of establishing instrument response of a target/surrogate analyte.

3.5 Laboratory Control Sample (LCS)

A mandatory QC element to which known quantities of the target analytes, internal standards and surrogates (when applicable), are added to a surrogate matrix or blank sampling media 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.

3.6 Laboratory Matrix Spike (LMS)

An optional QC element that uses an aliquot of a sample or 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.

3.7 Field Duplicate Sample (FDS, Field Dup)

An optional QC element that uses a sample collected in duplicate at the same time from the same location as 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.).

[1] Positive or negative chemical ionization (CI) mass spectra may be used if deemed appropriate for the given analytes.

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

A mandatory QC element when samples are not generated in the laboratory that uses a surrogate matrix similar to the samples sent to the sampling location along with other samples (e.g. wipes, sorbent media, impinger solvent) designated for sample collection.

3.9 Field Matrix Spike (FMS)

An optional QC element that uses a sample to which known quantities of the target analytes are added in the laboratory before sent to the field for sampling or are added to the sample in the field by the sample collector. The FMS is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

3.10 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, including typical EPA mixes provided by vendors. The area count ratio of the target analyte to the internal standard is used for calibration.

3.11 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 precision and 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 that meet the established criteria discussed later in this document. The LLOQ may also be determined by a specified procedure outlined in a GPO or protocol.

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 precision and accuracy requirements. Sample results above the ULOQ should be diluted and reanalyzed.

3.12 Method Blank

A mandatory QC element which is a surrogate matrix (not spiked with target analytes) 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.

3.13 Surrogate Standard

An optional QC element that uses an isotopically labeled standard, not used as an internal standard that is added to each sample. The surrogate may also be added to laboratory control spike samples and other quality control to serve as a means to evaluate the method performance (stability, recovery).

3.14 Trip Blank Matrix Spike (TBMS)

An optional QC element that uses an aliquot of surrogate matrix 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. See Section 8.1 for additional options for establishing holding times.

4 Warnings and Cautions

The operator must be familiar with GC/MS systems and their associated hazards, such as high temperature, effluent venting, solvent use, moving autosampler parts, and low-pressure vacuum system. Refer to 3M Environmental Laboratory SOP ETS-9-004 titled "Working with Compressed Gases" and the appropriate equipment procedures, methods, SOPs, or operator manuals for additional information and cautions.

All exhaust vents, including the split vent and mass spectrometer pump exhaust must be connected to a laboratory hood or vented instrument enclosure to keep potentially hazardous effluent from mixing with laboratory air.

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 EHSS Environmental Laboratory's Chemical Hazard Review, the 3M Guide to Laboratory Practices or other information as appropriate.

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 blank samples is used to check for cross-over contamination. Carryover may be reduced by adjusting analytical parameters such as carrier gas split flows and additional syringe washes.

6 Instrumentation, Supplies, and Materials

A variety of vendors and models for GC/MS systems 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. Other models and different vendors of equipment may be added at a later date.

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 Supplies and Materials

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

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.

Miscellaneous. Gas-tight glass microsyringes, single-use plastic syringes with disposable needles, volumetric flasks, disposable pipettes, mininert re-closable valves, gloves, and solvents of suitable grade for the intended use are some of the required supplies generally needed to complete studies using this method. Analytical balances, orbital shakers, centrifuges, incubators, 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 Internal Standards (ISTD)

Purchased mixes of deuterated internal standards may be acquired and diluted appropriately (e.g. EPA 8270 internal standard mix from Restek or custom preparations from o2si, etc). 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.

Examples of internal standards are provided below:

EPA 8260 Mix from Restek (fluorobenzene, chlorobenzene-d_5, 1,4-dichlorobenzene-d_4)

SV Mix from Restek (acenaphthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, naphthalene-d_8, perylene-d_{12}, phenanthrene-d_{10})

Method 525.2 Mix from Restek (acenaphthene-d_{10}, chrysene-d_{12}, phenanthrene-d_{10})

7.3 Surrogate Standards

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

Examples of surrogate standards include: phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. [2]

7.4 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. GC grade solvents are recommended.

8 Standard and Sample Handling

8.1 Holding Times

Samples should 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 a surrogate matrix in the laboratory and storing it in a similar manner as the sample for a time period that encompasses the anticipated duration of sampling through analysis.

[2] The example surrogate standards are from EPA method 8270D. Depending on the project/study objectives, it is assumed that any of the recommended surrogates may be used as an ISTD and vice versa.

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 appropriate working 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.

Extracted calibration standards are typically prepared by spiking a blank sample matrix with stock and intermediate standards and extracting the sample matrix using the same procedure as the samples.

Internal standards and surrogates are added based on the requirements of the GPO or protocol.

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. Method blanks and Laboratory Control Samples (LCSs) are required for each sample preparation batch. Additional quality control samples may be prepared as described below.

9.1 Method Blanks

A mandatory QC element that is prepared with each sample preparation batch and used to document possible contamination resulting from the analytical process. It is carried through the complete sample preparation and analytical procedure. A minimum of three method blanks shall be prepped and analyzed throughout the analytical sequence (at least at the beginning and at the end). 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).

9.2 Instrument Blank

An instrument blank is an aliquot of solvent that is not taken through the entire sample preparation process, but used to evaluate instrument background levels. Instrument 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 instrument blanks are analyzed, only the last injection need be evaluated. If an instrument 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 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 blank. Conversely, if trace contaminants are present in a 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.

9.3 Replicate Analysis

Replicate analysis is optional.

A replicate analysis is defined as separate aliquot(s) from the same study sample. 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. The number of replicates for analysis should be defined in the GPO or protocol.

9.4 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.

9.5 Surrogate

Use of surrogates is optional.

Surrogates standards may be required when analyzing samples that are not fortified at the laboratory. Recoveries should be within 100%±30% to be used without technical justification. Surrogates may be fortified into each sample during the preparation to fully evaluate matrix effects.

9.6 Lab Control Spike

Lab Control Spike samples (LCSs) are mandatory.

A laboratory control spike (LCS) is a mandatory QC element in which known quantities of the target analytes, internal standards and surrogates (when applicable), are added to a surrogate matrix or blank sampling media in the laboratory at the time when samples are prepared and brought through the same preparatory and analytical steps as other samples. LCS results are used to evaluate the method accuracy and precision in samples and evaluate for possible interferences by the sample matrix. When a sufficient amount of surrogate matrix or blank sample media is available, at least three levels (two levels for surrogates) in triplicate are included, 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. Acceptance criteria are RSD≤25% (or RPD, if duplicates prepared) and 100%±30% accuracy to be used without technical justification.

The use of LCSs, and their acceptance criteria should be specified in the GPO or protocol prior to the start of the study. 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±30% of their respective nominal value (33% of the QC samples, not all replicates at the same concentration, may be outside 70%-130% of nominal value), the average recovery will be flagged as outside method acceptance criteria.

If more than 33% of the LCS samples fail to meet method acceptance criteria, the data will not be reported, and the samples will need to be re-prepared and/or analyzed.

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 9.7 Lab Matrix Spike).

9.7 Lab Matrix Spike

Lab Matrix Spike samples (LMSs) are optional.

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. LMS concentrations should be prepared as directed by the project GPO or study protocol. 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.

9.8 Field Matrix Spikes (FMS)

Field Matrix Spike samples (FMSs) are optional.

The use of FMSs, including spiking concentrations, and their acceptance criteria should be specified in the GPO or protocol prior to the start of the project/study. In lieu of that, FMSs 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.

9.9 Trip Blanks Matrix Spikes (TBMS)

Trip Blank Matrix Spikes are optional.

The use of TBMSs, including spiking concentrations, and their acceptance criteria should be specified in the GPO or protocol prior to the start of the project/study. TBMS recoveries should be within 100%±30% 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.

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. The curve is calculated from the plot of individual calibration points using MassHunter software or equivalent chromatography and/or 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 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 average relative response factor may be used for quantitation if the relative standard deviation (RSD) of the relative response factors (RRF) is <20% for any analyte as it is assumed that the RRF is constant over the calibration range. If the RSD of any target analyte is greater than 20%, a linear or quadratic curve fit with or without weighting should be considered. 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 study 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 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 (e.g. a study for physical/chemical properties) 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.

10.4 System Suitability Utilizing Multiple Injections

Additional system suitability requirements such as injecting a minimum of three system suitability standards prior to each analytical run may be used, but is not specifically required.

It is suggested that the system suitability injections have area counts (or area ratios when using IS calibration), with a target RSD of ≤10% and a target retention time RSD of ≤2%. There is no defined acceptability limit on these results. Ultimately, any effects on these parameters for the System Suitability standards will also be evident on all standards and QC samples analyzed as part of the analysis batch. Any effect of system suitability is incorporated within QC acceptance criteria. Non-compliant system suitability samples should be noted in the final report; however, a method deviation is not required. Repeated non-compliance of the system suitability samples should not be disregarded, since it may be an indication that the instrument is not operating properly.

11 Procedures

GC/MS 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 control samples must be analyzed using the same settings. If changes are made after analysis has been initiated, recalibration is necessary. The following analytical conditions and settings may be used as a guide.

Example GC/MS Parameters

Analytical Column: J & W DB-624, 0.25mm, 30m, 1.4µm df; column flow 1.1 mL/min

Column split flow: 10:1

Example GC temperature program profile: 50 ºC for 4 minutes, ramp 15 ºC / min to 230 ºC, and hold for 3 minutes for an 19 minute run time. (Sub-ambient starting temperatures require the use of a cryogen, such as liquid nitrogen.)

MS Quadrupole Temp: 150ºC

MS Source Temp: 300 ºC (5975C and 5977 only)

Multiplier Voltage: Typically set by the software as the result of a tune. This may be increased to meet sensitivity requirements, especially in the SIM mode. The addition of 100 to 400 electron volts, EV, to the set point is common.

Full Scan Mode: 35 to 500 atomic mass units (amu). This may be adjusted depending on the molecular weight of the analytes.

Selected Ion Mode (SIM): Typical dwell times for ions are 35 to 100 msec so that there are a minimum of 10 to 15 scans across each chromatographic peak of interest.

12 Data Analysis and Calculations

Each dataset should be processed using chromatography software (e.g. Agilent MassHunter). 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 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:

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

13 Analyte Identification

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 Compounds Utilizing a Calibration Curve

The relative intensities of the characteristic ions (i.e. three ions of greatest relative intensity, or any ions over approximately 30% relative intensity, if less than three such ions occur in the reference spectrum) in the sample agree to within approximately 30% of the relative intensities of these ions in the reference spectrum. For example, if an ion has an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum may range between 20% and 80%. When interferences or co-eluting components are observed, use professional judgement when interpreting the spectrum.

The relative retention time (RRT) of the detected sample above the LLOQ is within ± 0.06 RRT units of the RRT of the corresponding calibration standards.

13.2 Tentatively Identified Compounds (TICs)

Depending on the GPO or protocol objectives, 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:

The relative intensities of major ions (i.e. ions greater than 10% of the most abundant ion) should be present in the sample spectrum and agree to within ±30%.

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.

If the GPO or protocol requires the estimation of TICs, 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)

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

17 References

EPA Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 5, July 2014

18 Affected Documents

None

19 Revisions

Revision Number	Summary of Changes