STANDARD OPERATING PROCEDURE

FOR

SEMIVOLATILE ORGANICS BY METHOD 8270E

PHILIS SOP L-A-201 Rev. 3

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SOP REVISION FORM

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2.2, 2.3, 2.4, 2.5	Microwave added as an extraction method
2.6	Method number 3546 added
16.8	Microwave method 3546 added to references
Section 17.0	Updated QA-017 form (Figure 1)

For *Review*: Comments

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1.0 Scope and Application, and Components to be Analyzed

1.1 This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

1.2 This procedure can be used to determine presence and concentration of analytes listed in Section 17 Tables 2 and 3 in aqueous, solid, sludge and wipe samples.

1.3 This Standard Operating Procedure (SOP) documents the PHILIS Program application of EPA Method SW846 8270E, "Determination of the Concentration of Semivolatile Organic Compounds in Aqueous and Soil Samples by Gas Chromatography/Mass Spectrometry", which will be used in the PHILIS Mobile Labs.

1.4 This method can be used to detect and quantitate most pH neutral, acidic, and basic organic compounds that are soluble in methylene chloride (or other suitable solvents provided that the desired performance data can be generated) and are capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, halo ethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. In most cases, this method is not appropriate for the quantitation of multi-component analytes, e.g. Aroclors, Toxaphene, Chlordane, etc. This is due to the limited sensitivity for the above mentioned analytes.

Note that the compounds are listed in approximate retention time order. Additional compounds may be added to this list, as long as they are validated prior to sample analysis. This validation would be performed by conducting Method Detection Limit (MDL) and Precision & Accuracy (P&A) studies.

CAUTION: Compounds that are documented as being difficult to analyze using this analytical method are listed in Section 17 Table 4. These compounds may require special treatment when being determined by this method.

Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of gas chromatograph/ mass spectrometers and skilled interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Aqueous samples are extracted with methylene chloride using automated solid phase extraction (SPE), separatory funnel, or by micro-extraction techniques. The extract is typically concentrated to 1mL, and internal standards are added prior to analysis by GC/MS. Other final volumes for extract concentration are allowed based on data requirements.

2.2 Soil or solid samples are extracted using pressurized solvent extraction (PSE), microwave extraction or a micro extraction. Table 1 below is an example of amounts of soil or solid extracted and an approximate expected analyte range that may be used to determine the amount of soil to extract if estimated concentrations of analytes are available.

2.3 For low level soil samples, 30 grams of soil are extracted with 50:50 methylene chloride/acetone using pressurized solvent extraction (PSE) or microwave extraction. The extract is concentrated to 1.0 mL, and internal standards are added prior to analysis by GC/MS. Anticipated analyte concentration range for this process is 0.083 mg/Kg to 5.0 mg/Kg.

2.4 For medium level soil samples, 15 grams of soil is extracted with 50:50 methylene chloride/acetone using pressurized solvent extraction (PSE) or microwave extraction. The extract is concentrated to 10 mL, and internal standards are added prior to analysis by GC/MS. Anticipated analyte concentration range for this process is 1.66 mg/Kg to 100 mg/Kg.

2.5 For high level soil samples, 1 gram of soil is extracted with 50:50 methylene chloride/acetone using pressurized solvent extraction (PSE) or microwave extraction. The extract is concentrated to 10 mL, and internal standards are added prior to analysis by GC/MS. Anticipated analyte concentration range for this process is 24.9 mg/Kg to 1500 mg/Kg.

2.6 Extraction procedures are described in PHILIS specific extraction SOPs and they are based on SW 846 Methods 3510, 3511, 3535A, 3545A, 3546 and 3570. Other extraction procedures are acceptable provided the procedure is validated prior to use on samples.

2.7 Qualitative identification of compounds detected by this method is based on retention times and on comparison of the sample mass spectrum with characteristic ions in a reference mass spectrum. Once a target compound has been identified, quantitation of that compound is based on the integrated area of the primary characteristic ion relative to the integrated area of the primary characteristic ion of the nearest internal standard.

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 Chain of Custody (COC) ‡: Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; the collector, the time of collection, preservation, and requested analyses. See also Legal Chain of Custody Protocols.

Each time the samples are transferred, the document should be signed by the person releasing the samples and by the person receiving the samples. A date and time must also be recorded.

3.3 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000B table 4.1.

3.4 Internal Standards (IS) ‡: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.5 Laboratory Control Sample (LCS) ‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 Matrix Spike (spiked sample of fortified sample)‡: A sample prepared, taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a referenced method, by adding a known amount of target analyte to a specified amount of the sample for which an independent test results of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

3.7 Matrix Spike Duplicate (spiked sample or fortified sample duplicate)‡: A replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

3.8 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Method Blank analytical results are evaluated to determine the presence of contamination in the analytical method process. The method blank should not contain analytes of interest that are ½ the Reporting Limit or greater.

3.9 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.0.

3.10 Required Detection Limit (RDL): Detection limits established by a regulatory authority for certain analytes. The laboratory MDL values must be equal or lower than the RDL. This is also known as the CRQL, the contract-required quantitation limit.

3.11 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.12 Second Source Calibration Verification (SCV): A solution prepared from a source that is different from the calibration standards. The SCV is immediately following the ICS, and is used to verify calibration standard accuracy.

3.13 Selected Ion Monitoring: A mass spectrometry technique that provides lower detection level capability by monitoring fewer mass scans for longer periods of time than is done in full-scan methods.

3.14 Surrogate Standard (SS): Organic compounds which are similar to the target analytes in chemical composition and mimic the behavior of the target analytes throughout the analytical process. Surrogate compounds are not normally found in environmental samples. Each calibration standard, sample, MB, LCS, MS, and MSD is spiked with surrogate standards. Surrogates are used to evaluate analytical efficiency by measuring recovery. See analytical method SOP for a list of specific surrogate compounds that are appropriate for sample-specific analysis.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Positive matrix interferences can be caused by contaminants that are extracted from the sample during the extraction process. Negative matrix interference can occur when samples contain materials that have a strong affinity for the analyte compounds. The amount of matrix interference varies from sample to sample. Cleanup procedures may help eliminate some of the interferences.

4.2 Contaminants in the solvents, reagents, glassware, and other extraction components may lead to matrix interferences. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running MBs with every batch. GC/MS data for every MB, LCS, MS, MSD, and sample must be evaluated for interferences. If interferences are detected, the lab should attempt to determine the source of interference and take corrective action to eliminate it.

4.3 High purity reagents, solvents, and gases must be used to minimize interference problems with the sample analysis.

4.4 Carryover contamination may occur when a sample containing low levels of SVOCs is analyzed immediately following a sample containing high levels of SVOCs. If this situation occurs during a non-monitored analysis, the sample containing the low concentration SVOCs may require reanalysis. If the situation occurs during monitored analysis, a blank should be run after the high level sample to ensure that the system is free of contamination. To reduce carryover, the injection syringe must be rinsed with solvent between samples.

4.5 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis. Sample preparation equipment used for sample preparation shall not be composed of plastic materials.

5.0 Health and Safety Warnings

5.1 This method does not address all safety issues associated with its use. Laboratory personnel are responsible for maintaining a safe work environment and a current awareness of the Chemical Hygiene Plan regarding the safe handling of the chemicals listed in this method.

WARNING: This procedure involves working with hazardous materials. It is the responsibility of the analyst to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous.

5.2 Specific Safety Concerns or Requirements

WARNING: Standard laboratory personal protective equipment (PPE) for routine laboratory functions will include safety glasses with side shields, disposable nitrile gloves, laboratory coat, and closed-toe non-absorbent shoes. Additional PPE may be required as based on increased hazards of the work task performed or abnormal event such as spill clean-up. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and vinyl gloves provide no protection against the organic solvents used in this method, so nitrile or similar material must be used.

WARNING: GC/MS instruments and other equipment may have heated zones which can cause severe burns if contacted. Prior to working on any equipment containing a heated source, the equipment will be cooled to a safe temperature.

WARNING: The MS is under vacuum pressure. It must be vented and brought up to atmospheric pressure and cooler temperatures prior to working on the source.

WARNING: GC/MS instruments have high voltage areas. Instrument power must be turned off and the instrument unplugged prior to performing source maintenance. The power source of the equipment will be lock-out and/or a tag placed at or near the source to prevent inadvertent operation during a maintenance function.

WARNING: The toxicity and/or carcinogenicity of the reagents and analytes used in this method have not been precisely defined; therefore, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

WARNING: All preparation of standards and sample preparation are required to be conducted in an operating fume hood. Acetone and methanol are highly flammable and require handling caution near any heated source and required storage only in a flammable storage cabinet. Methylene chloride is a highly volatile chemical that poses a significant inhalation hazard if spilled. Methanol can be absorbed through the skin and methylene chloride is very corrosive to the skin and eyes, therefore extreme care is needed and strict hygiene practices.

5.3 A Material Safety Data Sheet (MSDS) and PHILIS Chemical Hazard Summary sheet are available for each analyte and reagent used in the mobile laboratory to all employees and are required reading/understanding prior to working with the chemical. Special safety precautions for sample preparation (e.g. solvent extraction equipment and methods) are provided in the sample preparation SOPs.

6.0 Equipment and Supplies

6.1 Glassware

6.1.1 Small glass vials (1mL or 2 mL) are used for storage of sample extracts, calibration standards and stock standards.

6.1.2 4mL, 10 mL, 40 mL, or 60 mL vials are used for storage of standards and spiking solutions.

6.2 Solvents

6.2.1 Acetone—Capillary GC, GC/MS, pesticide or equivalent grade

6.2.2 Methylene Chloride—Capillary GC, GC/MS, pesticide or equivalent grade

6.2.3 Methanol—Capillary GC, GC/MS, pesticide or equivalent grade

6.3 Syringes

6.3.1 Gas-tight micro syringes- various sizes for transferring the concentrated extracts, diluting samples, adding internal standards to extracts, and preparing calibration standards.

6.4 Instrumentation

6.4.1 Gas chromatograph/mass spectrometer system: an analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly interfaced to the source.

6.4.2 Column: PHILIS Castle Rock uses 30m x 0.25mm ID, 0.25-µ m film thickness fused-silica capillary column coated with 5% diphenyl/95% dimethyl polysiloxane (Restek RTX-5MS or equivalent). PHILIS Edison uses RXI-5 Sil MS 30 m x 0.25 mm. Alternate columns are acceptable if they provide acceptable performance.

6.4.3 Mass Spectrometer: Capable of scanning from 35 to 500 amu every one second or less, using 70eV in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for DFTPP that meets all the criteria in Table 7, when 50 ng or less of the tuning standard is injected.

6.4.4 Auto sampler: Gerstel MPS-2 rail system or equivalent.

6.4.5 GC/MS interface: Capillary column direct into the ion source.

6.4.6 Data System: The data system is equipped with the Agilent Chemstation software for data acquisition, Enviroquant for data processing and Gerstel's Maestro for the autosampler. Mass Hunter is used on the newer instruments. Other equivalent software may be used.

6.4.7 Syringe: 10 µL Gerstel syringe, or equivalent.

7.0 Reagents and Standards

7.1 Reagents

Note: Original containers of reagents shall be labeled with expiration dates in accordance with the OSHA Hazard Communication Program. All containers of prepared reagents must bear a name, preparation date, and must be linked to the preparation records.

7.1.1 Reagent water can be Milli-Q water, tap water, distilled water or any other water provided no interferences are noted.

7.1.2 Reagent soil is TCL-free sand and is used for QC samples. Ottawa Sand that has been processed through the Fast PSE may also be used for QC samples.

7.1.3 Helium carrier gas is 99.999% (UHP) or greater such as Research Grade, 99.9999%.

7.1.4 Nitrogen- gas is 99.999% (UHP) grade.

7.2 Standards

A minimum five-point calibration curve is prepared for establishing average response factors or linear regression curve fitting. Six calibration points are required for quadratic (second-order) curve fits. The low point of the calibration curve must be equal to or less than the reporting limit. The high standard defines the calibration range. See Section 17 Tables 8 and 9 for examples of the preparation of the ICAL levels for the Full List and the PAH lists. Other amounts of the standards listed below may be used based on the sensitivity of the instrument.

7.2.1 An internal standard (IS) solution is purchased at a concentration of 2000 µg/mL. The list of internal standards for this method is provided in Section 17 Table 4. Other concentrations of IS may be used provided the amount in the standards and samples remain constant.

7.2.2 Internal standards are added to all standards and extracts, resulting in a final concentration of 40 µg/mL.

7.2.3 Surrogate Standard Spiking Solution is purchased or prepared so that the resulting concentration in samples and quality control is at 40 µg/mL. Surrogate compounds for this method are listed in Section 17 Table 6.

7.2.4 DFTPP GC/MS Tuning Standard is used for determining acceptable instrument performance. The methylene chloride solution contains 50 µg/mL of decafluorotriphenylphosphine (DFTPP). Pentachlorophenol, benzidine, and DDT should also be included in the Tuning Standard at 50 µg/mL. Preparation in alternate solvents may result in degradation of DFTPP. The instrument is only required to pass the tuning standard when a calibration in analyzing.

7.2.5 Laboratory Control Spiking Solution is purchased or prepared so that the resulting concentration is at 40 µg/mL. The LCS shall include all compounds of interest. The LCS may be prepared from a source different than used for the instrument calibration or the same source as the calibration. Other levels could be used as long as the resulting concentration of the LCS is near the midpoint of the calibration curve.

7.2.6 Matrix Spike Solution is the same as the Laboratory Control Spiking Solution.

7.2.7 The levels are defined with a final volume of 1000 µL, although there is actually 1020 µL after the addition of the internal standard mix. Thus, compound concentrations (including internal standards and surrogates) are all 1.96% lower in absolute terms than stated. However, since every extract (standards, samples and QC) contains 1020 µL (2% more than the stated volume) after the addition of the IS mix, the deviation of concentrations from true values is offset by the deviation in final extract volumes from true values. Other final volumes may be used based on reporting requirements.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Samples are collected by field sampling teams in 1000-mL amber bottles or 8-oz amber jars and are put on ice to maintain a temperature of 0-6°C and submitted to the laboratory. See SOP sample login procedures, for sample acceptance criteria. Other containers may be used provided the size is adequate for the reporting limits required, are clean, and do not add any interferences.

8.2 Samples received on the collection day shall be considered acceptable if there is evidence that the chilling process has begun such as arrival on ice. In such cases, sample temperatures that are in excess of 6 °C upon receipt are acceptable.

8.3 Samples are maintained at the temperature of 0-6°C.

8.4 Sample extraction holding time is 7 days for aqueous samples and 14 days for soil samples. The sample extracts must be analyzed within 40 days of extraction.

9.0 Quality Control and Acceptance Criteria

QC requirements include the Initial Demonstration of Capability and ongoing QC requirements that must be met when preparing and analyzing samples.

9.1 Initial Demonstration of Capability (IDOC) is an evaluation that must be successfully performed by an analyst prior to analyzing any field samples and any time major method modifications are made. The following is done to demonstrate laboratory capability to perform this method:

9.1.1 Prior to conducting the IDOC study, the analyst tunes the instrument and generates an acceptable instrument calibration following the procedure outlined in Section 10 of this SOP. A MB is analyzed to demonstrate that the background contamination is low enough to not interfere with analytes.

9.1.2 Method precision and accuracy is demonstrated by analyzing four (4) replicate LCSs fortified at a known concentration (e.g. 40µg/mL) typically around the midpoint of the calibration. Precision and accuracy are calculated.

9.1.3 Recovery limits are established using instrument generated data. The acceptable range will be set using the control charts at three standard deviations and updated every six months or sooner.

9.1.4 MDLs are established by analyzing a minimum of seven replicates of a known concentration and a minimum of seven blanks extracted and analyzed over a three-day period.

9.1.5 MDL verification is performed at the time of initial method development, each time the MDL study is performed, and on an annual basis.

9.1.6 RL's are established by the lowest point in the calibration curve.

9.2 Ongoing QC is applied when performing this method and includes analyzing an acceptable instrument calibration, verification standard, MB, LCS, MS, MSD, with samples. Every batch must contain at least one MB, LCS, MS, and MSD. If there is not enough volume for an MS/MSD pair, then a sample DUP or an LCSD must be performed for precision data Control Limits.

9.2.1 Control limits are determined for surrogates, laboratory control samples, matrix spike samples and precision and accuracy. Limits can be calculated when 15 – 20 data points are available and monitored every 20 – 30 data points thereafter. They should be evaluated at least every 6 months. The recovery limits are the mean recovery ±3 standard deviations for surrogates, MS, and LCS. Precision limits for the MS/MSD or LCS/LCSD pair are the absolute value of the mean relative percent difference (RPD) ±3 standard deviations.

9.2.2 These limits do not apply to dilutions, but the surrogate and matrix spike recoveries will be reported unless the dilution is 4x or more.

All surrogates, LCS, and MS recoveries (except for dilutions) must be entered into Element so that historical control limits can be generated. For multiple dilutions, reported from the same extract, surrogates will be reported for all dilutions of less than 4x.

9.3 MDL Procedure

MDLs and RLs are established by analyzing a minimum of seven replicates of a standard at or near the estimated MDL and seven blank replicates. Tabulation of results and MDL calculations are performed by the method in 40 CFR, Part 136, Method Update Rule Revision 2.

9.3.1 Initial MDLs

9.3.1.1 Initial MDLs are established by analyzing a minimum of seven replicates of the low-level calibration standard and a minimum of seven blanks prepped and analyzed over three separate days. The MDL should be spiked 1 to 5 times the estimated MDL. Extract and analyze the MDL standards and blanks with the same procedure as regular samples.

9.3.1.2 For each compound, calculate the mean and standard deviation of the replicates in micrograms per liter (µg/L). Then calculate the MDL by multiplying the standard deviation by the Student's t value. The one-sided (single-tailed) Student's t values at the 99% confidence levels are used (e.g., t = 3.143 at the 99% confidence level for n = 7). MDL studies are repeated annually and verified each time they are prepared. MDL results are stored in Element each time they are calculated. MDL blanks are calculated using the above formula and then adding the mean of the blank results provided that the analyte is detected in all MDL blank analyses. If the mean of the blank results in a negative number then use 0 in place of the mean. The sum of these two numbers is the blank MDL. The larger of the two values will be used as the MDL. If all MDL blanks show no analyte detection, then the spiked MDL determination is used. If there is a mixture of analyte detections and non-detections, then the largest method blank detection is used as the MDL blank. Again, the larger of the MDL spike and MDL blank is used as the analyte MDL.

9.3.2 Ongoing MDL Data Collection

9.3.2.1 Ongoing MDL's are determined by preparing and analyzing two spiked standards at 1-5 times the estimated md and two blanks once per quarter for a minimum of seven determinations. The blanks and spikes may be analyzed in the same prep batch, but is not required. If the instruments are being used regularly, the MDL spikes may be added to the routine batches and the regular blanks used. All blanks analyzed during the evaluation period should be used.

9.3.2.2 At least once per year re-evaluate the MDL by calculating as above in 12.3.1.2. Use the larger of the spiked determinations and blank determinations for the MDL value. If all blanks are non-detect, then the MDL Blank is not calculated. If all blanks have detection, then the MDL Blank is calculated as a regular MDL. If there are less than 100 blank determinations, and there is a mixture of detects and non-detects, then use the highest value to determine the MDL.

9.4 MDL Verification (MDLV)

9.4.1 At least once every thirteen months, re-calculate the MDL spike and MDL blank from the collected spiked samples and method blank results.

9.4.2 Include data generated within the last twenty four months, but only data with the same spiking level. Only documented instances of gross failures (instrument malfunctions, mislabeled samples, cracked vials, etc.) may be excluded from the calculations.

9.5 Method Blank (MB)

9.5.1 For aqueous samples, the method blank is reagent water, and for soil samples it is Ottawa sand or an analyte-free sand. The method blank is free of the analytes of interest and is spiked with the surrogates. At least one method blank must be prepared with every batch.

9.5.2 Acceptance Criteria: The result for the method blank must be less than one half the RL or less than 10% of the analyte concentration found in the associated samples, whichever is higher, to report definitive results. If the analyte result is not less than ½ the RL then the associated samples must be greater than 10 times the blank to report definitive results.

9.5.3 Corrective Action: If a compound fails to meet these criteria, the lead chemist will be informed. In general, batch samples, other than those that are non-detect for the contaminant compounds will be re-extracted. However, if the analyte in the method blank was not detected in any of the associated samples, the data can still be reported.

9.6 Instrument Blank (IB)

Instruments must be evaluated for contamination during every 12-hour analytical run. This can be accomplished by analysis of a MB. If a MB is unavailable, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated the same way as a method blank.

9.7 Laboratory Control Sample (LCS)

The LCS is prepared using reagent water for aqueous samples or analyte-free sand for soil samples. A laboratory control sample is prepared and analyzed with every batch of samples. The compounds must be spiked at a concentration that falls within the working range of the calibration. See Section 6.0 of this SOP.

9.7.1 Acceptance Criteria: All analytes must be within the control limits to report definitive data. Example control limits are in Table 2. Current control limits are stored in the LIMS and are updated every six months.

9.7.2 Corrective Action: If any analyte in the LCS is outside the established control limits, a corrective action must be performed. A corrective action may consist of a data evaluation to determine the effect on data, to complete reprep and reanalysis. All corrective actions must be documented.

9.7.3 If the batch is not re-extracted or re-analyzed, the reasons for accepting the batch must be clearly presented in the report. An example of acceptable reasons for this might be that the MS/MSD are acceptable and sample surrogate recoveries are within control limits, showing that the problem was just on the LCS. This is also applicable if the analyte that failed is not a target analyte for the project, or if the analyte recovered above the control limit, but was not detected in the associated samples.

9.7.4 If re-extraction and re-analysis of the batch are not possible due to limited sample volume, the LCS is reported, all associated samples are flagged accordingly, and the appropriate comments are made in the report.

9.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The matrix spike is a second aliquot of one of the samples in the batch, and the matrix spike duplicate is a third aliquot of the same sample. The MS/MSD are spiked with the same analytes and concentration as the LCS. The MS and MSD samples are prepared with every batch. See Section 6 of this SOP.

9.8.1 Acceptance Criteria: The percent recovery must be within the control limits. The RPD for the pair must be less than or equal to the control limit.

9.8.2 Corrective Action: If the recovery or RPD of an analyte is outside of its control limits, or if an RPD fails, then a corrective action must be performed. Typically, if the recoveries of the MS/MSD are similar but not within control limits and the recoveries of the LCS are within control limits, then the analysis can continue. This is documented as matrix interference.

9.8.3 If there are recovery failures in the MS/MSD and the LCS, then the batch must be re-extracted and/or re-analyzed. Or, all associated data must be qualified and a reason must be included in the data package detailing the batch was not re-extracted and re-analyzed.

9.8.4 If re-extraction is not possible due to limited sample volume, then a duplicate LCS (LCSD) may be run with the re-extraction batch. The RPD of the LCS/LCSD must be less than or equal to the established control limit.

9.9 Surrogates

9.9.1 Each sample, MB, and QC sample is spiked with the surrogate standards. The surrogates must be spiked within the working range of the ICAL. The surrogates are listed in Table 6. After analysis, if any of the surrogates fail to meet criteria, the sample must be re-extracted or re-analyzed. If the re-extraction fails in the same manner, it can be documented in the report that the failure is due to matrix interference.

9.9.2 If a sample has a surrogate failure and it has an associated MS/MSD, and the surrogate recoveries in the pair also fail, then the sample and the MS/MSD do not require re-extraction. This indicates matrix interference.

9.9.3 If the sample is re-extracted and the surrogates in the re-analysis are acceptable, the re-analysis should be reported. This indicates the failure was within the control of the analyst. However, if the sample is re-extracted outside of the hold time, both sets of results should be reported.

9.9.4 If the re-extraction confirms the surrogate failure, the original results should be reported and the matrix interference should be documented in the report.

9.9.5 Method precision and accuracy are demonstrated by analyzing 4 replicate LCS's fortified at concentration listed in Table 5 according to the procedure described in Section 13 of this SOP. Precision and accuracy are calculated using an EXCEL Spreadsheet.

9.9.5.1 Acceptable precision for RSD is ≤ 30%. Once adequate points are available, laboratory limits will be established.

9.9.5.2 Once adequate points are available, laboratory acceptance limits will be established.

9.9.6 Ongoing QC applied when performing this method includes analyzing acceptable instrument calibration/calibration verification standards, method blanks, LCS, and MS/ MSD. Internal standards and surrogates must be acceptable with all QC samples and with test samples.

9.10 Lower limit of quantitation (LLOQ)

9.10.1 The LLOQ is the lowest concentration at which the laboratory has demonstrated target analytes can be reliably measured and reported with a certain degree of confidence. The LLOQ must be greater than or equal to the lowest point in the calibration curve. The laboratory shall establish the LLOQ at concentrations where both quantitative and qualitative requirements can consistently be met. The laboratory shall verify the LLOQ at least annually, and whenever significant changes are made to the preparation and/or analytical procedure, to demonstrate quantitation capability at lower analyte concentration levels. The verification is performed by the extraction and/or analysis of an LCS (or matrix spike) at 0.5 - 2 times the established LLOQ. Additional LLOQ verifications may be useful on a project-specific basis if a matrix is expected to contain significant interferences at the LLOQ. The verification may be accomplished with either clean control material (e.g., reagent water, solvent blank, Ottawa sand, diatomaceous earth) or a representative sample matrix, free of target compounds.

9.10.2 The LLOQ verification is prepared by spiking a clean control material with the analyte(s) of interest at 0.5 - 2 times the LLOQ concentration level(s). Alternatively, a representative sample matrix free of targets may be spiked with the analytes of interest at 0.5 - 2 times the LLOQ concentration levels. The LLOQ check is carried through the same preparation and analytical procedures as environmental samples and other QC samples. It is recommended to analyze the LLOQ verification on every instrument where data is reported; however, at a minimum, the lab should rotate the verification among similar analytical instruments such that all are included within three years.

9.10.3 Recovery of target analytes in the LLOQ verification should be within established in-house limits or within other such project-specific acceptance limits to demonstrate acceptable method performance at the LLOQ. Until the laboratory has sufficient data to determine acceptance limits, the LCS criteria ± 20% (i.e., lower limit minus 20% and upper limit plus 20%) may be used for the LLOQ acceptance criteria. This practice acknowledges the potential for greater uncertainty at the low end of the calibration curve. Practical, historically based LLOQ acceptance criteria should be determined once sufficient data points have been acquired.

10.0 Calibration and Standardization

Instruments are tuned to meet DFTPP acceptance criteria, calibrated with an ICAL of at least four levels, and confirmed every twelve-hour shift with a continuing calibration verification standard (CCV). Recommended instrument conditions are listed in Table 10.

Allow all standards and sample extracts to warm to room temperature prior to injection.

10.1 DFTPP Tune Checks

10.1.1 Instruments must be checked to verify that the acceptance criteria are met for DFTPP (decafluorotriphenylphosphine) prior to the ICAL. See Table 7 for DFTPP acceptance criteria. The mass spectrum is acquired with three scans (the peak apex scan and the scans immediately preceding and following the apex) and averaged. Background subtraction is required and must be accomplished using a single scan acquired within 20 scans of the elution of DFTPP. The background subtraction should be designated only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or any other discrete peak that does not co-elute with DFTPP.

10.1.2 Inject 50 ng of the tuning standard. Collect the mass spectra of the DFTPP (background-corrected) and confirm that all of the m/z criteria, listed in Table 7, are met. If the tune check does not meet the criteria, the analyst may need to perform maintenance on the instrument and retune the mass spectrometer. The DFTPP tune must pass all criteria before any standards, samples, or blanks are analyzed.

10.1.3 The analysis of the tune check solution is also used to evaluate the inertness of the chromatographic system. If the peak tailing factor for benzidine and/or pentachlorophenol is >2.0 or the degradation for DDT is >20%, it indicates that the chromatographic system needs maintenance to improve the inertness of the system. Degradation and tailing factor checks are performed to verify injection port inertness and are important when the target list includes a broad range of analyte chemistries, especially reactive phenols and pesticides. These checks are optional when the analytes of interest are not subject to the same chromatography or reactivity problems.

10.2 Initial Calibration (ICAL)

10.2.1 Compounds are typically assigned to the internal standard that has the closest retention time to that analyte. Consistent internal standard references across the different instruments should be utilized.

10.2.2 Setting Retention Times, Retention Time Windows and Integration Parameters

Once the purge and trap and GC cycle have finished for the midpoint or other calibration standard, load the quantitation file. Review each peak to make sure that the processing software identified the correct peak. If not, manually integrate the peak. Save all of the retention times. Quantify the calibration file and go through each ion profile of the target list, take note of the ion ratios, verify that the spectrum and profile match the standard spectrum.

The relative retention time (RRT) of the target analytes in every calibration level should be within 0.06 RRT units.

10.2.3 A minimum five-point calibration curve is prepared. This is valid for average response factors or linear regression curve fitting. A minimum of six calibration points is required for quadratic curve fits. The low point of the calibration curve must be at or below the reporting limit. The high standard defines the range of the calibration. See Tables 8 and 9 for the preparation of the ICAL levels.

10.2.4 Acceptance criteria for the Instrument Calibration and CCVs, and the required frequency of their analysis are summarized in Table 10.

10.2.5 Rejection of Calibration Points

10.2.5.1 It is not generally acceptable to remove internal points from a calibration curve. Typically, instrument maintenance and the accuracy of the calibration standards should be examined if the calibration acceptance criteria are not met.

10.2.5.2 If no problems are found, then a point can be rejected as long as it meets the following criteria:

The rejected point is the highest or lowest point in the ICAL. This may be done by analyte. An internal calibration point may also be removed if the reason is obvious. Examples are; a bad injection, internal standards left out, gross contamination, etc. In these cases, the entire point, including all analytes, must be removed and the reason documented.

10.2.6 The lowest remaining calibration point is still at or below the reporting limit. If the calibration point is higher, then the reporting limit must be raised.

10.2.7 The highest remaining calibration point defines the upper concentration of the working range, and all samples above this concentration must be diluted and re-analyzed.

10.2.8 The calibration must still have the minimum number of calibration levels required by the method. [Five levels for average response factors and linear curve-fits, six levels for quadratic (second-order) curve-fits].

10.2.9 The internal standard is added to produce a 40µg/mL (40 ng on column – 1µL inj.) final concentration.

10.2.10 Analyze each calibration level. Calculate the response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in the calculation section of this SOP. Samples may not be analyzed unless the ICAL meets the following criteria:

10.2.11 The RSD must be <20% for each compound of interest.

10.2.12 If the RSD for a compound in the initial calibration is >20%, then the calibration points may be fit to a linear or a nonlinear curve, such as a second-order polynomial. A curve fit should not be employed in lieu of the average RF to compensate for instrumentation problems or needed maintenance.

10.2.13 Linear curve-fits may be used if there are five (5) or more ICAL levels. Quadratic (second-order) curve-fits may be used if there are 6 or more ICAL levels. The use of a weighted linear regression is recommended to improve accuracy of quantitation at the low end of the curve. Curve-fits can be used if it is determined that the curve will generate accurate results across the calibration range. If a curve-fit is used, a re-quantitation of the low point of the ICAL against the ICAL must show acceptable accuracy.

10.2.14 If a linear curve-fit is used, the coefficient of determination (r^2) must be greater than 0.990. For quadratic curve-fits, the intercept and degree of curvature should be examined to be sure that the results will be reliable throughout the working range and the coefficient of determination is greater than 0.990. There must not be two levels that would produce the same value. Quadratic curve-fits should not be used to compensate for detector saturation or to avoid proper instrument maintenance.

10.2.15 The second source calibration verification (SCV) standard, made from a different source than the ICAL (an alternate vendor or a unique lot from the same vendor) must be analyzed immediately after the calibration. The value determined from the second source check should be within 30% of the expected concentration. An alternative recovery limit may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding that these results could be used for screening purposes and would be considered estimated values.

10.2.16 If more than 10% of the compounds in the ICAL are greater than 20%RSD and do not meet the coefficient of determination criteria for curve-fits, then the instrument is not acceptable to analyze samples. Maintenance must be performed and the instrument ICAL must be performed again.

10.2.17 The minimum response factor for the most common target analytes should be met. See Table 11.

10.2.18 Weighting of Calibration Data Points.

In a linear regression curve-fit, the lower points of the ICAL have a significant bias over the higher points in determining the generated curve. This is not seen in quadratic regression. However, in environmental analysis, accuracy at the low end is very important. For this reason, use 1/Concentration^2or 1/Concentration weighting. This will improve accuracy at the low end of the ICAL and should be used for curve-fits. All compounds should be recalculated using the final calibration curve. The recalculated concentration of the low calibration point should be within +/- 50% of the standard's true concentration, and the concentration of the middle point standard should be within +/- 30%.

Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.

10.2.19 The Relative Error of the calibration curve is determined by processing the lowest point and the midpoint of the calibration against the curve. The % difference in true value is the Relative Error.

10.3 Continuing Calibration Verification (CCV)

10.3.1 The CCV standard must contain all target analytes and surrogates to be reported. The level for the CCV is approximately in the middle of the ICAL. Daily analysis of the GC/MS tune check solution is no longer required as part of the CCV. The analyst should, however, closely monitor chromatography as well as target and IS responses in the CCV for deterioration in the system.

10.3.2 The percent difference/drift for each analyte must be less than or equal to 20%. Due to the long list of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the criterion. If the criterion is not met for more than 20% (13 compounds for Full List, 3 compounds for PAH) of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

10.3.3 The IS responses for the CCV must be within a factor of 2 (50-200%) of the responses in the mid-point of the corresponding ICAL.

10.3.4 If any IS retention time in the CCV changes by more than 30 seconds from the retention time of the mid-point of the corresponding ICAL, the chromatographic system must be inspected for malfunctions and corrections must be made.

10.3.5 Sample analysis may begin if the CCV passes the above criteria. If the CCV does not pass the criteria, perform an evaluation of the system, are there any obvious problems, was the correct method used, or do routine maintenance. Re-inject the CCV and if this solves the problem, then continue with the sequence. If not, more extensive maintenance may be required or analyze a new calibration curve.

10.3.6 A CCV may be omitted if samples are analyzed within 12 hours of ICAL, and the injection of the last ICAL standard may be used as the starting time reference for evaluation.

10.3.7 The minimum response factors for the most common target analytes should be met in the CCV. If they are not met, maintenance must be performed before sample analysis can begin. Possible problems that would cause this are: standard mix degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

11.0 Procedure

11.1 Sample extraction

See specific extraction SOPs.

11.2 Sample Preparation

11.2.1 Remove samples from the laboratory refrigerator.

11.2.2 Verify that the samples have been logged into LIMS, and are within holding time. If the sample exceeds holding time, notify the Lead Chemist and follow the corrective action plan.

11.2.3 Batch up to 20 environmental samples for extraction.

11.2.4 For samples to be analyzed as MS/MSD follow the procedure below:

The client must provide enough volume for a parent sample and the MS/MSD. If performing a 1L extraction, this means the client must provide 3L of sample.

11.2.5 For the MS/MSD samples, transfer the samples into their appropriately marked containers (1L bottles, 40mL VOA vials, Microwave extraction vessels or PSE metal tubes).

11.2.6 Spike the MS/MSD with the appropriate amount of surrogates and spikes.

11.2.7 Refer to the extraction SOPs for the preparation procedures.

11.3 Standard Preparation

Follow the example procedure listed in Tables 8 and 9.

11.4 Sample Analysis

11.4.1 Analysis is performed using an automated injection GC/MS instrument.

11.4.2 In Chemstation (or Gerstel software), load the sequence from the previous run and enter in the sequence information for the day. A typical sequence will have one or two rinses, the DFTPP tune, the CCV, an instrument blank, the QC from the batch, then the samples. A tune is only required with a calibration but may be analyzed if desired. If the samples being analyzed are suspicious or possibly high in non-target analytes, running a rinse pattern of H_2O, MeOH, and $MeCl_2$ at the end of the sequence will help maintain the quality of your instrument.

11.5 Calibrate the instrument as described in Section 13.

11.5.1 All samples must be analyzed using the same mass spectrometric conditions as the preceding DFTPP analysis. Add internal standard to the sample extract to result in a 40µg concentration (for example, 100µL of IS solution (at 400µg/mL) in a 1000µL extract). Mix thoroughly before injection into the instrument.

11.5.2 Inject 1µL of the extract using the sample injection technique as used for the standards.

11.5.3 The data system will determine the concentration of each analyte in the extract using calculations in Section 15. Quantitation is based on the initial calibration, not the continuing calibration verification.

11.5.4 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst. The minimum documentation required is a copy of the original data peak integration and a copy showing the manual integration with the analyst initials and date and explanation of the reason for the manual integration.

11.5.5 Tentatively Identified Compounds (TICs) may be requested by the client. Perform a library search on the unknown peaks present in the chromatogram if TICs are requested.

11.5.6 The internal standard response in the sample must be between 50-200% of the response of the internal standard in the daily CCV.

11.6 Identification of Analytes

11.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. See Table 15 for a listing of characteristic ions that may be used for compound identification. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

11.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.6.1.2 Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

11.6.1.3 The Relative Retention Time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

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

11.6.1.5 Use professional judgment in interpretation where interferences are observed.

11.6.2 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo[b]fluoranthene and benzo[k]fluoranthene). The above calculations are only for laboratory standards. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

11.6.3 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.6.4 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

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

11.6.4.2 The relative intensities of the major ions should agree within ± 30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)

11.6.4.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

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

Samples that are diluted must have the internal standard concentration replenished to the level originally in the sample. This may be accomplished by diluting the sample with a solution of methylene chloride containing the proper amount of IS, or by diluting with methylene chloride and then adding the proper amount of IS.

Once surrogates are diluted to a level where accurate quantitation is not possible then surrogates should be reported as diluted out.

11.6.5 If the response for any compound exceeds the current calibration range, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initially diluted extract has no hits or hits below 20% of the calibration range and the matrix allows for an analysis at a lesser dilution, the sample should be re-analyzed at a dilution to bring the most abundant analyte above 50% of the calibration range.

11.6.6 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are significantly less than two times the height of the internal standards, the sample should be reanalyzed at a lesser dilution. This requirement is approximate and subject to analyst judgment. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid damaging the column.

11.6.7 Reporting Dilutions

The least dilute sample with no target analytes above the calibration range will be reported. Other dilutions will be reported only at the client's request.

11.6.8 Retention Time Criteria for Samples

The retention times of the internal standards in the CCV must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 0.5 minutes from that in the midpoint of the ICAL, then the chromatographic system must be inspected for malfunctions and corrections must be made. Re-analysis of the samples analyzed while the system was malfunctioning is required.

If the retention time of any internal standard in any sample varies by more than 0.5 minutes from the preceding CCV, the data must be carefully evaluated to ensure that no analytes have shifted outside of their retention time windows.

11.7 Percent Moisture

Analytical results of soil or solid samples may be reported as a dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as a dry weight.

One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented by the analyst and included in the final report.

12.0 Data Analysis and Calculations

12.1 The concentration of each analyte is calculated using Agilent MSD Chemstation software using the multipoint average response factor method established in Section 13 of this SOP. Response factors and analyte concentrations are calculated by the equations below:

12.2 Relative response factor (RRF):

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

where:
Ax = Area of the quantitation ion for the surrogate or compound being measured.
Ais = Area of the quantitation ion for the specific internal standard.
Cis = Concentration of the specific internal standard.
Cx = Concentration of the surrogate or compound being measured.

12.3 Average RRF:

Average RRF $(\overline{RRF})$: $\overline{RRF} = \frac{\sum_1^n RRF}{n}$

where
n = number of initial calibration standards

12.4 Percent relative standard deviation (%RSD):

$$\%RSD = (^{S}/_{\overline{x}})100$$

where:
$\overline{x} = \overline{RRF}$: $\overline{RRF} = \frac{\sum_1^n RRF}{n}$
where:
s = standard deviation: $= \sqrt{\frac{(\sum_{i=1}^{n}(x_i - \overline{x})^2)}{n-1}}$

12.5 Sample concentration using RRF:

$$\text{Conc.}\left(\frac{\mu g}{L}\right) = \frac{(A_x)(I_x)(D)}{(\overline{RRF})(V_o)(A_{IS})}$$

where :
A_x = area of quantitation ion for compound being measured
I_x = amount of internal standard injected (ng)
A_{is} = area of quantitation ion for the internal standard
$\overline{RRF}$ = mean relative response factor for compound being measured
V_o = volume of water extracted (mL) accounting for dilutions
D = Dilution Factor

12.6 Percent recovery for CCV, SCV, LCS, and MS are performed using the following equation:

$$\%R = \left[\frac{(C_{spk-}\ C_x)}{C_t}\right] \times 100$$

where:
C_{spk} = the concentration of the analyte in the spiked sample
C_x = the concentration of the analyte in the reference (parent) sample; (C_x = 0 for CCV, LCS and SCV.)
C_t = the theoretical spike concentration.

12.7 Relative percent difference for duplicate is calculated using the following equation:

$$RPD = \left[\frac{|C_1 - C_2|}{(C_1 + C_2)/_2}\right] 100$$

where:
C_1 = concentration of the first sample C_2 = concentration of the second sample

13.0 Method Performance

13.1 Data Assessment and Acceptance Criteria for Quality Control Measures

Instrument generated data goes through a series of reviews prior to being submitted to the client. First the analyst reviews the data to ensure method and client requirements are met. Then the instrument data goes through a peer review covering the same items as the analyst. Both reviews are documented on the attached Form QA-017, which is provided in Figure 1. The Quality Assurance Manager also reviews a minimum of 10 % of data to evaluate the QA process.

13.2 Analytical data generated by the instrument software is reviewed and evaluated by the analyst as follows: DFTPP, instrument calibration, calibration verifications, IS/SS, QC measures are evaluated and the results documented on the separate forms:

13.2.1 Generating the tune evaluation of DFTPP.

13.2.2 Generating the instrument calibration relative response factors and percent relative standard deviations.

13.2.3 Generating QA-QC check report for internal standard area counts and percent recoveries for the surrogates.

13.2.4 Calculating analyte percent recoveries CCV, LCS, SCV, MS, and RPD for MSD.

13.3 In order for the analytical data to be acceptable, the calibration standards and quality control measures must meet the criteria listed in this SOP.

13.4 Anytime that an analyst alters an instrument generated quantitation report, the hardcopies of both reports (original and analyst's corrected) must be retained (e.g., manual integration). The altered report must be initialed and dated by the analyst with the reason for altering. The corrected report must also be reviewed, initialed, and dated by a peer or supervisor.

13.5 All false positives are Q-Deleted, with an explanation of the Q-deletion included in the raw data and all positively identified target analytes are reported to LIMS. Include the spectra in the data package.

13.5.1 Manual integration is applied in cases when the instrument data processing software produces integrated areas that are not valid. The manual adjustments to the chromatographic peak must be performed in a consistent manner for the calibration standards, QC and field samples. Please see the Manual Integration SOP.

13.5.2 Chromatograms of all field samples are examined to detect additional peaks, which were not identified as target analytes. If such peaks are present, generate a Library Search Report and report a tentatively identified compound (TIC) if the percent match is greater than 50%. The Lead Chemist should be notified immediately in that case. This is only done if TICs are requested by the client. TICS are usually requested by next 10 largest, etc.

13.5.3 Discrepancies in the analytical run are described in "Data Review Form QA-017 and discussed with the Lead Chemist.

13.6 Reviewed data is entered into LIMS, hard copies of the LIMS report is printed and compared to the original data. All records derived from the analytical process are assembled in the analytical data files. Files can be electronic on the servers or hard copy in file cabinets. Each data file consists of:

13.6.1 Analytical run sheet (sequence log)

13.6.2 DFTPP tune evaluation report

13.6.3 QA-QC check report

13.6.4 Quantitation Report for each Sample

13.6.5 Evaluation reports for CCV, SCV, LCS, MS, and MSD.

13.6.6 Initial calibration form

13.7 Data files are placed in boxes or file cabinets marked EPA Method 8270E and stored in the PHILIS document storage area. Electronic data, including reports are maintained on servers in multiple locations.

13.8 Demonstration of laboratory accuracy, precision, and MDLs are presented in Tables 2 and 3.

13.9 Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

13.10 Corrective Action for Out of Control

In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable and the analyst does the following:

13.10.1 When tuning and instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with tuning and calibration.

13.10.2 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

13.10.3 The analyst shall report to the Lead Chemist and indicate of the "Data Review Form QA-017" any out control event. Such events include:

13.10.3.1 Damage to the sample.

13.10.3.2 Holding time exceeded.

13.10.3.3 Inadequate sample preservation.

13.10.3.4 Sample results exceeds the Agency's action limit

13.10.3.5 Samples do not reflect historical data.

13.10.3.6 Upward trending or sample results approaching interval warning limits.

13.10.3.7 Any non-target analyte peak present on the instrument generated chromatograms that interfere with regular analysis. Tentative identification compounds (TICs) may also be requested by the client.

13.11 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document (SOP A-C-101).

13.12 When tuning and instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with tuning and calibration.

13.13 See Table 14 for a summary of corrective action taken when QC samples or client sample QC does not meet acceptance criteria.

13.14 Contingencies for Handling Out of Control or Unacceptable Data

See the QAPP that the samples were analyzed under for guidance.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. The EPA places pollution prevention as the management option of first choice with regard to laboratory waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The Environmental Protection Agency requires that laboratory waste management practices be compliant with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the PHILIS Chemical Hygiene Plan.

14.3 The waste produced from EPA Method 8270E consist of waste collected from the extraction process, extracts, excess sample, standards (stock mixes, PDS, WS), methylene chloride, and methanol.

14.4 Excess reagents are disposed in accordance with MSDS and laboratory waste management plan requirements.

14.5 Glass pipettes are disposed in the glassware waste container.

14.6 Refer to EPA Method 8270E, sections 14.0 and 15.0 for additional guidance

14.7 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036.

15.0 Waste Management

Waste management procedures are specified in the Hazardous Waste Management Plan.

16.0 References

16.1 EPA Method 8270E Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 6, June 2018; U.S. EPA Office of Solid Waste.

16.2 40 CFR 136, Appendix B, Revision 2. Definition and Procedure for the Determination of the Method Detection Limit – December, 2016.

16.3 U.S. EPA Contract Laboratory Program Statement of Work OLM 04.2.

16.4 U.S. EPA National Functional Guidelines, Superfund Organic Methods Data Review, June, 2008.

16.5 2003, 2009, and 2016 NELAP manuals.

16.6 EPA Method 3500C, Organic Extraction and Sample Preparation, Revision 3, May 2003; U.S. EPA Office of Solid Waste.

16.7 EPA Method 3545A Pressurized Fluid Extraction (PFE), Revision 1, February 2007; U.S. EPA Office of Solid Waste.

16.8 EPA Method 3546 Microwave Extraction, Revision 1, February 2007; U.S. EPA Office of Solid Waste

17.0 Tables, Diagrams, Flowcharts and Validation Data

Table 1. Example Extraction and Analyte Range

Soil Sample Type	Analytical Range	RL Range, mg/Kg	Sample Mass	Final Extract Volume
Trace analysis of clean soil sample; clean conformational analysis	Low Level	0.083 – 5.0	30 grams	1.0 mL
Moderate soil contamination; extent of contamination evaluation project	Medium Level	1.66 - 100	15 grams	10 mL
Heavy contamination of soil, waste characterization	High Level	24.9 - 1500	1 gram	10 mL

Table 2. Example Analytes Determined by EPA Method 8270E
Method Detection Limits (MDLs) and Precision & Accuracy (P&A)

8270 Method List		MDL	MDL	MDL	MDL	RPD	Control Limits	RPD	Control Limits
Compound	CAS No.	Water (SPE) (ug/L)	25 mL Water (Micro-extract) (ug/L)	100 mL Water (Sep Funnels) (ug/L)	Soil (ug/Kg)	SPE (%)	SPE (% Recovery)	Micro (%)	Micro Ext (% Recovery)
N-Nitrosodimethylamine	62-75-9	11	34.1	7.6	40	20	1 - 63	20	1 - 97
Phenol	108-95-2	1.7	30.5	4.3	29	20	1 - 91	20	1 - 63
Aniline	62-53-3	0.4	97.9	17.0	25	20	1 - 97	20	23 - 92
Bis(2-chloroethyl) ether	111-44-4	1.4	80.6	12.8	37	20	1 - 114	20	43 - 91
2-Chlorophenol	95-57-8	1.8	83.6	11.4	42	20	8 - 93	20	15 - 96
1,3-Dichlorobenzene	541-73-1	1.1	63.5	12.4	39	20	1 - 84	20	35 - 90
1,4-Dichlorobenzene	106-46-7	1.1	68.0	12.4	38	20	1 - 89	20	38 - 84
Benzyl alcohol	100-51-6	2.5	40.8	9.8	40	20	1 - 86	20	1 - 130
1,2-Dichlorobenzene	95-50-1	2.1	68.3	12.9	40	20	1 - 90	20	38 - 87
2-Methylphenol	95-48-7	2.1	47.2	9.2	38	20	4 - 107	20	12 - 89
Bis(2-chloroisopropyl) ether	39638-32-9	1.2	76.3	12.8	41	20	3 - 139	20	36 - 123
3/4-Methylphenol	106-44-5	0.9	39.8	9.2	40	20	14 - 82	20	1 - 93
N-Nitrosodi-n-propylamine	621-64-7	2.2	66.0	13.1	35	20	1 - 136	20	46 - 99
Hexachloroethane	67-72-1	1.4	62.1	10.6	36	20	1 - 81	20	29 - 85
Nitrobenzene	98-95-3	1.7	62.4	8.4	35	25	1 - 145	25	37 - 99
Isophorone	78-59-1	2.0	57.5	8.6	34	20	1 - 121	20	41 - 96
2-Nitrophenol	88-75-5	2.0	69.7	7.2	31	20	1 - 79	20	7 - 113
2,4-Dimethylphenol	105-67-9	2.3	60.2	22.4	26	20	4 - 105	20	39 - 82
Bis(2-chloroethoxy)methane	111-91-1	2.0	72.0	11.6	40	20	1 - 125	20	39 - 99
2,4-Dichlorophenol	120-83-2	2.4	80.6	6.7	34	20	8 - 91	20	1 - 123
1,2,4-Trichlorobenzene	120-82-1	1.3	63.8	24.6	36	20	5 - 97	20	44 - 90
Naphthalene	91-20-3	1.4	67.6	10.2	37	20	3 - 97	20	40 - 94
4-Chloroaniline	106-47-8	1.2	79.1	11.6	34	20	1 - 74	20	32 - 104
Hexachlorobutadiene	87-68-3	1.1	58.8	11.2	40	20	5 - 84	20	26 - 93
4-Chloro-3-methylphenol	59-50-7	1.8	47.6	5.1	22	20	1 - 136	20	1 - 125
2-Methylnaphthalene	91-57-6	1.7	65.0	7.3	35	20	3 - 110	20	40 - 100
Hexachlorocyclopentadiene	77-47-4	1.8	31.7	5.6	42	20	1 - 71	20	21 - 97
2,4,6-Trichlorophenol	88-06-2	1.8	108	7.1	39	20	1 - 76	20	7 - 131
2,4,5-Trichlorophenol	95-95-4	2.1	91.7	7.4	36	20	1 - 74	20	18 - 132
2-Chloronaphthalene	91-58-7	1.9	64.2	10.2	32	20	1 - 100	20	48 - 94
2-Nitroaniline	88-74-4	1.8	44.6	5.7	32	20	1 - 54	20	45 - 119
Dimethyl phthalate	131-11-3	1.8	68.5	34.7	33	20	1 - 112	20	57 - 113
2,6-Dinitrotoluene	606-20-2	2.0	43.3	6.0	35	20	1 - 115	20	54 - 114
Acenaphthylene	208-96-8	2.2	65.0	8.5	28	20	1 - 76	20	54 - 102
Acenaphthene	83-32-9	1.7	71.1	6.7	35	20	9 - 83	20	53 - 102
3-Nitroaniline	99-09-2	1.4	60.5	6.9	32	20	1 - 58	20	55 - 112
2,4-Dinitrophenol	51-28-5	5.5	53.0	12.1	83	20	1 - 49	20	6 - 133
4-Nitrophenol	100-02-7	1.6	54.1	8.8	27	20	8 - 81	20	1 - 250
Dibenzofuran	132-64-9	1.7	68.4	7.5	29	20	1 - 106	20	59 - 102
2,4-Dinitrotoluene	121-14-2	1.6	3.0	4.5	31	20	1 - 99	20	31 - 126
Diethyl phthalate	84-66-2	1.4	65.7	7.6	36	20	6 - 111	20	54 - 118
4-Chlorophenyl phenyl ether	7005-72-3	1.6	66.3	8.6	31	20	2 - 104	20	45 - 117
Fluorene	86-73-7	1.4	71.3	7.0	30	20	2 - 105	20	53 - 112
4-Nitroaniline	100-01-6	1.7	48.1	3.4	39	20	1 - 62	20	65 - 114
4,6-Dinitro-2-methylphenol	534-52-1	1.5	35.5	4.3	16	20	1 - 44	20	12 - 147
4-Bromophenyl phenyl ether	101-55-3	1.5	70.7	6.4	30	20	1 - 500	20	52 - 116
Hexachlorobenzene	118-74-1	1.0	71.8	7.7	38	20	1 - 101	20	55 - 120
Pentachlorophenol	87-86-5	1.3	51.0	4.0	37	20	1 - 56	20	14 - 132
Phenanthrene	85-01-8	0.8	72.8	6.5	30	20	2 - 105	20	63 - 115
Anthracene	120-12-7	1.0	64.7	4.6	20	20	1 - 85	20	63 - 115
Malathion	121-75-5								

Table 3. Analytes Determined by EPA Method 8270E with Example Detection Limits and Precision & Accuracy (P&A) -PAHs only

PAH by 8270		MDL	MDL	MDL	MDL		RPD	Control Limits
Compound	CAS No.	Water ug/L	Soil ug/Kg	Water, Low-Level SIM Method ug/L	Soil, ug/Kg		(%) Water	(% Recovery) Soil
Acenaphthylene	208-96-8	1.0	4.8	0.2	1.8		20	31 - 120
1-Methylnaphthalene	90-12-0	1.5	14	0.2	2.1		20	45 - 115
2-Methylnaphthalene	91-57-6	1.7	11	0.2	2.2		20	41 - 118
Pyrene	129-00-0	1.8	18	0.4	2.1		20	55 - 119
Benz[a]anthracene	56-55-3	1.7	13	0.2	1.8		20	29 - 125
Benzo[a]pyrene	50-32-8	1.4	16	0.4	4.3		20	21 - 109
Fluoranthene	206-44-0	1.5	23	0.2	1.4		20	60 - 115
Benzo[b]fluoranthene	205-99-2	0.7	14	0.3	2.1		20	15 - 96
Fluorene	86-73-7	1.4	5.0	0.3	1.7		20	45 - 119
Dibenzo[a,h]anthracene	53-70-3	3.2	22	0.2	2.6		20	7 - 108
Anthracene	120-12-7	1.3	11	0.2	1.2		20	52 - 113
Acenaphthene	83-32-9	1.5	6.0	0.2	1.8		20	57 - 111
Chrysene	218-01-9	1.5	18	0.3	1.6		20	68 - 109
Phenanthrene	85-01-8	1.2	12	0.3	1.0		20	67 - 111
Indeno[1,2,3-cd]pyrene	193-39-5	1.0	11	0.2	3.7		20	44 - 111
Benzo[g,h,i]perylene	191-24-2	0.9	9.0	0.2	2.0		20	33 - 116
Benzo[k]fluoranthene	207-08-9	0.9	27	0.5	2.3		20	48 - 126
Naphthalene	91-20-3	1.4	9.0	0.2	2.0		20	50 - 114

Table 4. Difficult Compounds to Analyze

Compound	Analysis Problem and Treatment
Hexachlorocyclopentadiene	Subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
N-Nitrosodiphenylamine	Decomposes in the gas chromatograph inlet and cannot be distinguished from diphenylamine.
Pentachlorophenol 2,4-dinitrophenol 4-nitrophenol 4,6-dinitro-2-methylphenol 4-chloro-3-methylphenol 2-nitroaniline 3-nitroaniline 4-chloroaniline benzyl alcohol	Subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
3-methylphenol & 4-methylphenol	Due to inadequate chromatographic resolution compounds are reported as 3&4-methylphenol.
1,2-diphenylhydrazine	Compound is reported as azobenzene, which is formed by decomposition.
N-Nitrosodimethylamine	Difficult to separate from the solvent under the chromatographic conditions used.
Pyridine	Compound degrades at the GC injection port temperatures in this method. Lowering the injection port temperature may affect other compounds in this method adversely; therefore, a different method should be considered if pyridine is required. Pyridine may be evaporated off during sample concentration.

Table 5. Internal Standards used for EPA Method 8270E

Compound	Applicable Methods for IS	Example Spiking Level in ng
Acenapthene-d_{10}	Full List, PAH	40
Chrysene-d_{12}	Full List, PAH	40
1,4-Dichlorobenzene-d_4	Full List	40
Napthalene-d_8	Full List, PAH	40
Perylene-d_{12}	Full List	40
Phenanthrene-d_{10}	Full List, PAH	40

Table 6. Surrogate Standards Used for EPA Method 8270E

Compound	Applicable Methods	Example Spiking Level in ng
Nitrobenzene-d_5	Full List, PAH	40
2-Fluorobiphenyl	Full List, PAH	40
Terphenyl-d_{14}	Full List, PAH	40
Phenol-d_5	Full List	40
2-Fluorophenol	Full List	40
2,4,6-Tribromophenol	Full List	40

Table 7. DFTPP Key Ions and Ion Abundance Criteria

m/z	8270E Ion Abundance Criteria
68	<2% of mass 69
69	Present
70	<2% of mass 69
197	<2% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
365	>1% of mass 198
441	< 150 % of mass 443
442	Base peak or present
443	15-24% of mass 442

Alternate tuning criteria may be employed (e.g., CLP or Method 625), provided that method performance is not adversely affected.

Table 8. 8270E Calibration Levels

Example Full List 8270 Calibration Levels - 1000/2000µg/mL Stocks										
	Level (ng)									
Stock Concentration (ng/µL)	2.5	5	10	20	50	80	120	160	SCV - 50	2.5
B/N Surrogates (µL)	2.5	5	10	20	50	80	120	160	50	2.5
Acid Surrogates (µL)	1.25	2.5	5	10	20	40	60	80	20	1.25
MegaMix (µL)	2.5	5	10	20	50	80	120	160	0	2.5
SCV Stock (µL)	0	0	0	0	0	0	0	0	50	0
Total (µL)	6.25	12.5	25	50	120	200	300	400	120	6.25
MeCl2	993.75 µL	987.5µL	975 µL	950 µL	880 µL	800 µL	700 µL	600 µL	880 µL	993.75 µL
Internal Standard	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL
Final Volume	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL

Table 9. Example PAH 8270 Calibration Levels

PAH Only 8270 Calibration Levels - 1000/2000µg/mL Stocks										
	Level (ng)									
Stock Concentration (ng/µL)	2.5	5	10	20	40	80	120	160	SCV - 40	2.5
B/N Surrogates (µL)	2.5	5	10	20	40	80	120	160	40	2.5
PAH Standard (µL)	1.25	2.5	5	10	20	40	60	80	0	1.25
MegaMix (µL)	0	0	0	0	0	0	0	0	40	0
Total (µL)	3.75	7.5	15	30	60	120	180	240	80	3.75
MeCl2	996.25 µL	992.5µL	985 µL	970 µL	940 µL	880 µL	820 µL	760 µL	920 µL	996.25 µL
Internal Standard	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL	20 µL
Final Volume	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL	1000 µL
Stock Concentration (ng/µL)	2.5	5	10	20	40	80	120	160	SCV - 40	2.5

Table 10. Example EPA Method 8270E Analysis Sequence with QC and Instrument Calibration Frequency and Acceptance Criteria

Analysis #	Sample Name	QC and Instrument Calibration Acceptance Criteria	QC and Instrument Calibration Frequency
1	DFTPP	1. DFTPP see Table 6	Analyzed prior to instrument calibration.only
2	Cal 1	1. Instrument Calibration must have %RSD ≤ 20%. If greater than 10% of analytes cannot meet the RSD or regression curve criteria (RSD < 20% or r^2 > 0.99), then instrument may need maintenance or curve evaluation (dropping upper or lower points), trying different curve fits, etc. 2. Should meet 8270E recommended minimum RRF or be able to see standard at the reporting limit. 3. Must have relative retention time = 0.06 RR	Calibration Analyzed anytime CCV fails criteria for analytes of interest. And system evaluation, minor maintenance, etc. will not produce an acceptable CCV.
3	Cal 2		
4	Cal 3		
5	Cal 4		
6	Cal 5		
7	Cal 6		
8	Cal 7		
9	MB	Must be free from contamination that could prevent determination of target analytes at the RL. Must be <1/2 RL.	Find problem and reanalyze all associated samples and QC.
10	SCV	1. Determination of target analytes 2. Concentration of target analytes must be within +/- 30% of true value. 3. IS Response 50 – 150% of Cal 3 or Cal midpoint 4. IS RT's ± 30 seconds	Analyzed immediately after Cal curve
		Daily sequences require a CCV and should have a method or instrument blank. After that, any or all of the items that were included in the preparation batchs may be analyzed as long as the 12 hour CCV window is not exceeded. Sample number is not limited. Below is an example sequence that includes all the preparation batch components.	
11	DFTPP	1. Same as Above	1. Same as above

Analysis #	Sample Name	QC and Instrument Calibration Acceptance Criteria	QC and Instrument Calibration Frequency
12	CCV	1. Percent Recovery of Target Analytes ± 20% 2. SS Percent Recovery--meet in-house limits. 3. Should meet 8270E recommended minimum RRF or evaluate to determine if the reporting limit can be achieved.	1. Analyzed initially with each batch of samples or QC within 12 hour period.
13	MB	1. Same as Above	1. Same as above. Prepared with each batch of samples. This can also be an instrument blank.
14	LCS	1. Percent Recovery of Target--meet in-house limits or data flagged.2. SS Percent Recovery --meet in-house limits or data flagged. 3. IS Response 50 - +100% of CCV	1. Prepared with each batch of samples.
15	Sample 1	1. IS/SS see at the bottom of this table	
16	MS	1. Percent Recovery of Target Analytes--meet in-house limits or data flagged 2. SS Percent Recovery--meet in-house limits or data flagged 3. IS Response 50 - +100% of CCV	1. Prepared with each batch of samples.
18	MSD	1 - 3 same as above %RSD (section 12) --meet in-house limits or data flagged	1. Prepared with each batch of samples.
19	Sample 2	See statements below for IS and SS.	Reanalyze at a dilution
20	Sample 3		
20	Sample 4		
21	Samples 5-20		
Internal Standard (IS) and Surrogate Standard (SS) in all samples and QCs must meet the following acceptance criteria: 1 IS Response 50 - 200 % of the midpoint of the most recent calibration or the daily CCV. 2 SS must meet in-house limits or data flagged			

Table 11. Example GC/MS Instrument Conditions PHILIS-Castle Rock, CO

GC Conditions	
Inlet	Split at 280°C,
Capillary Column	Restek RX-5MS, 30M length, 0.25mm ID, 0.5um film thickness
Column Mode	Constant flow, 3.4mL/min
Temperature Program	Initial temp = 50°C, Initial time = 1.50 min
	25°C/min ramp to 170°C
	12°C/min ramp to 320°C and hold for about one minute past the elution of the last compound.
Run Time	About 20 minutes with a new column,
Carrier Gas	Helium
	Pulsed split 20.0mL/min, 3.00 min
	Total flow ≈ 34mL/min
Injection Volume	1.0µL
Split Ratio	3:1
Split Flow	≈ 24mL/min
Transfer line	280°C
MS Conditions	
MS Source	230°C or 240°C
MS Quadrupole	200°C

NOTE: The conditions listed above are subject to final fine adjustments to maximize instrument sensitivity. Changes to the above conditions are acceptable as long as method criteria are met.

Table 12. Example GC/MS Instrument Conditions PHILIS-Edison, NJ

GC Conditions	
Inlet	280°C,
Capillary Column	Restek RX-5silMS, 30M length, 0.25mm ID, 0.25um film thickness
Column Mode	Constant flow, 1.2 mL/min
Temperature Program	Initial temp = 40°C, Initial time = 1.0 min
	25°C/min ramp to 280°C, hold 0 min.
	35°C/min ramp to 320°C and hold 2.0 minutes to end of run.
Run Time	About 28 minutes injection to injection.
Carrier Gas	Helium
	Pulsed split = 20 psi to 0.20 minutes
	Total flow ≈ 24mL/min
Injection Volume	1.0µL
Split Ratio	5:1
Split Flow	≈ 6 mL/min
Transfer line	300°C
MS Conditions	
MS Source	230°C
MS Quadrupole	150°C

Table 13. Recommended Minimum Response Factor Criteria for Initial and Continuing Calibration Verification Using the Suggested Primary Quant Ions

Suggested Semivolatile Compounds Minimum Response Factor (RF)			
Compound	**RF**	**Compound**	**RF**
Benzaldehyde	0.010	2,4-Dinitrophenol	0010
Phenol	0.800	4-Nitrophenol	0.010
Bis(2-chloroethyl)ether	0.700	Dibenzofuran	0.800
2-Chlorophenol	0.800	2,4-Dinitrotoluene	0.200
2-Methylphenol	0.700	Diethyl phthalate	0.010
2,2'-Oxybis-(1-chloropropane)	0.010	1,2,4,5-Tetrachlorobenzene	0.010
Acetophenone	0.010	4-Chlorophenyl-phenyl ether	0.400
4-Methylphenol	0.600	Fluorene	0.900
N-Nitroso-di-n-propylamine	0.500	4-Nitroaniline	0.010
Hexachloroethane	0.300	4,6-Dinitro-2-methylphenol	0.010
Nitrobenzene	0.200	4-Bromophenyl-phenyl ether	0.100
Isophorone	0.400	N-Nitrosodiphenylamine	0.010
2-Nitrophenol	0.100	Hexachlorobenzene	0.100
2,4-Dimethylphenol	0.200	Pentachlorophenol	0.050
Bis(2-chloroethoxy)methane	0.300	Phenanthrene	0.700
2,4-Dichlorophenol	0.200	Anthracene	0.700
Naphthalene 0.700	0.700	Carbazole	0.010
4-Chloroaniline	0.010	Di-n-butyl phthalate	0.010
Hexachlorobutadiene	0.010	Fluoranthene	0.600
Caprolactam	0.010	Pyrene	0.600
4-Chloro-3-methylphenol	0.200	Butyl benzyl phthalate	0.010
2-Methylnaphthalene	0.400	3,3'-Dichlorobenzidine	0.010
Hexachlorocyclopentadiene	0.050	Benzo(a)anthracene	0.800
2,4,6-Trichlorophenol	0.200	Chrysene	0.700
2,4,5-Trichlorophenol	0.200	Bis-(2-ethylhexyl)phthalate	0.010
1,1'-Biphenyl	0.010	Di-n-octyl phthalate	0.010
2-Chloronaphthalene	0.800	Benzo(b)fluoranthene	0.700
2-Nitroaniline	0.010	Benzo(k)fluoranthene	0.700
Dimethyl phthalate	0.010	Benzo(a)pyrene	0.700
2,6-Dinitrotoluene	0.200	Indeno(1,2,3-cd)pyrene	0.500
Acenaphthylene	0.900	Dibenz(a,h)anthracene	0.400
3-Nitroaniline	0.010	Benzo(g,h,i)perylene	0.500
Acenaphthene	0.900	2,3,4,6-Tetrachlorophenol	0.010

Table 14. 8270E Method Criteria

Item	Measure	Action
Instrument Tune	Outside 8270E Acceptance Criteria	Re-Tune-- Repeated failure indicates a need for system adjustment or maintenance. Perform system maintenance and re-tune the instrument. No analysis should be performed until the system is tuned correctly.
Instrument Tailing or Breakdown	Pentachlorophenol or Benzidine tailing above 2 or DDT Breakdown above 20 %.	**Advisory Only--**Evaluate the need for system maintenance/perform maintenance if needed and re-tune.
Internal Standard(s)—(IS)	50-200% of the mid-point of the initial calibration standard or daily CCV.	If the problem is a calibration sample, evaluate the system (repair) and reanalyze. Remake the standard if an error is suspected. If the problem is a prepped QC sample or field sample, re-analyze. If the re-analysis is within limits, report the results within limits. If the problem is a prepped QC sample, evaluate, the batch may need to be reprepped. If the reanalysis of a field sample is outside limits, dilute and reanalyze. Report the diluted results. Flag data that does not meet acceptance criteria.
Response Factors	See Table 11 for a list of recommended minimum response factors.	If the response factor is below acceptance criteria, then the system must be evaluated to make sure the analyte can be seen at the reporting limit. Recalibrate and reanalyze affected samples.
Initial Calibration (ICAL)	Average Response Factor >20.0 % RSD.	Evaluate points in the curve for use of linear or quadratic regression (r2 must be ≥0.990). Also evaluate upper and lower points for removal..Internal calibration points may be removed if there is an obvious reason, then the entire calibration point must be removed. Criteria still not met, recalibrate if compound is an analyte of interest.
ICAL Point Eval. all compounds and all levels	Not within ±50% of True Value for low point and ±30% for all others	Recalibrate if % deviation or drift is not met and compound is an analyte of interest.
Initial Calibration Verification	Not within ±30% of true value for deviation or drift.	Recalibrate if % deviation is not met and the compound is an analyte of interest.
Continuing Calibration Verification (CCV)—Analyzed if ICAL is not analyzed.	Not within ±20% of true value for deviation	If the CCV is not within ±20 % of the true value, then perform routine maintenance, such as verify all instrument settings, method used, front end maintenance, etc. Reinject a CCV and if passes, continue sequence. If not further maintenance or a new ICAL is required. Further maintenance would also require two passing CCV's to show the problem is solved.
Method Blank	Analyte(s) of interest at or above ½ reporting limit.	If the associated samples are non-detect, no action is required. If the analyte(s) is/are detected in the sample, flag with a "b" or reanalyze. If the analyte level in the sample is 10 time greater than the blank contamination, the results are not affected. Locate the source of the contamination.
Laboratory Control Spike (LCS)	% recovery outside laboratory acceptance criteria	If the LCS % recovery is high and the sample is non-detect, no action is required. If the LCS is high and the sample(s) have detects, reanalyze the sample. If the LCS is low, the samples should be reanalyzed. Flag data that does not meet laboratory acceptance criteria
Laboratory Control Spike Duplicate (LCSD)	% Recovery outside laboratory acceptance criteria. RPD acceptance criteria is 20%.	% recovery same as the LCS. If the RPD value is above the acceptance criteria in the LIMS, then evaluate the system for possible problems. Reprep and reanalyze samples as necessary and if possible. Flag data that does not meet laboratory acceptance criteria
Matrix Spike (MS)	% Recovery outside laboratory acceptance criteria.	If the % Recovery is outside laboratory acceptance criteria, evaluate the LCS. If the LCS is in control, then there is the possibility of matrix effect. The sample should be flagged appropriately.
Matrix Spike Duplicate (MSD)	% Recovery outside laboratory acceptance criteria. RPD acceptance criteria is 20%.	% recovery same as the MS. If the RPD value is above the acceptance criteria in the LIMS, then evaluate the system for possible problems. Reanalyze samples if possible or flag results.
Surrogate(S)	% Recovery outside laboratory acceptance criteria.	If the % recovery is outside laboratory acceptance criteria on a QC sample, evaluate the system. Surrogate recalibration may be necessary. If the % recovery is on a client sample, reprep and reanalyze if possible. If the % recovery is within criteria, report the sample within limits. If % recovery is outside criteria and is confirmed, then there is a matrix effect. Flag the results as estimated and report the initial result.

Table 15. Example Characteristic Quantitation Ions for SVOA*

Compound	Primary Quant Ion	Secondary Quant Ions
Phenol	94	65,66
Aniline	93	66,65
Bis(2-chloroethyl) ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
Benzyl alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 111
2-Methylphenol	108	107, 77, 79, 90
Bis(2-chloroisopropyl)ether	45	77, 121
3/4-Methylphenol	107	108, 77, 79, 90
N-Nitrosodi-di-n-propylamine	70	42, 101, 130
Hexachloroethane	201	117, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	109, 65
2,4-Dimethylphenol	122	107, 121
Bis(2-chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129, 65, 92
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	142	107, 144
2-Methylnaphthalene	142	141
1-Methylnaphthalene	142	141, 115
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 97, 132, 99
2-Chloronaphthalene	162	127, 164
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
2,6-Dinitrotoluene	165	63, 89
Acenaphthylene	152	151, 153

Compound	Primary Quant Ion	Secondary Quant Ions
Acenaphthene	153	154, 152
3-Nitroaniline	138	108, 92
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	65	139, 109
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 89
Diethylphthalate	149	177, 150
4-Chlorophenyl phenyl ether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	65, 108, 92, 80, 39
Azobenzene	77	182, 51, 105
2-Methyl-4,6-dinitrophenol	198	51, 105
Diphenylamine	169	168, 167
4-Bromophenyl phenyl e...	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	176, 179
Carbazole	167	166, 139
Di-n-butyl phthalate	149	150, 104
Fluoranthene	202	101, 203
Pyrene	202	200, 203
Butyl benzyl phthalate	149	91, 206
Benzo[a]anthracene	228	229, 226
Chrysene	228	226, 229
Bis(2-ethylhexyl)phthalate	149	167, 279
Di-n-octyl phthalate	149	167, 43
Benzo[b]fluoranthene	252	253, 125
Benzo[k]fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 277
Dibenzo(a,h)anthracene	278	139, 279
Benzo(ghi)perylene	276	138, 277

* Other semivolatile compounds may be analyzed using Method 8270E

Figure 1. Example GC/MS Data Review Form

PHILIS Program

CSS

DATA REVIEW FORM – GC/MS

Instrument and Date: _____ **Sequence #:** _____

Analysis: *(Select One)* ☐ Semivolatiles ☐ Volatiles ☐ Other

	Yes	No	Peer Rvw	QA Rvw	Comments
Analyst Report					
PHILIS narrative is complete	☐	☐	☐	☐	
Reported data matches the raw data	☐	☐	☐	☐	
Reporting limits and qualifiers are correct	☐	☐	☐	☐	
Sample Receiving					
Samples received in acceptable condition and compliant with COC	☐	☐	☐	☐	
Samples properly preserved	☐	☐	☐	☐	
Sample receipt checklist filled out	☐	☐	☐	☐	
Instrument Tune and Calibration					
Instrument met tuning criteria, where required, and analyses were completed within the 12 hour clock	☐	☐	☐	☐	
ICAL average response factor % RSD is <20 or applied curve fit meets criteria	☐	☐	☐	☐	
The ICAL has an adequate number of points	☐	☐	☐	☐	
Response factors meet minimum criteria for ICAL and CCV	☐	☐	☐	☐	
ICAL low point is within 50% of known value and the mid-point is within 30% of the known value or SOP listed levels	☐	☐	☐	☐	
SCV is within 30 % of true values for deviation or drift	☐	☐	☐	☐	
CCV compounds meet acceptance criteria	☐	☐	☐	☐	
Method Blank					
Analytes detected at or above their reporting limits are flagged	☐	☐	☐	☐	
Samples					
Samples prepared and extracts analyzed within holding time limits	☐	☐	☐	☐	
Target compound report included and chromatograms provided	☐	☐	☐	☐	
Manual integration/Q-Deletion is initialed and dated by analyst and reviewer on ion profiles	☐	☐	☐	☐	
All target quantitation ion integrations and spectral identifications are included	☐	☐	☐	☐	
Calculations have been verified—see calculations sheet.	☐	☐	☐	☐	
Internal standard summary					
Is area between 50%-200% of the ICAL midpoint or daily CCV	☐	☐	☐	☐	
Retention times are within 0.5 minutes of the midpoint of the ICAL	☐	☐	☐	☐	
Surrogate recovery report					
Surrogate recovery meets acceptance criteria	☐	☐	☐	☐	
Sample results are properly flagged	☐	☐	☐	☐	
Preparation batch summary					
All samples are accounted for	☐	☐	☐	☐	
Results reflect sample mass/volume prepared	☐	☐	☐	☐	
Solid results are provided dry weight basis	☐	☐	☐	☐	
Matrix spike/matrix spike duplicate					
MS/MSD percent recoveries are within limits	☐	☐	☐	☐	
Relative percent differences are within limits	☐	☐	☐	☐	
Sample results been flagged appropriately	☐	☐	☐	☐	
Laboratory control spike/laboratory control spike duplicate					
LCS/LCSD recoveries are within limits	☐	☐	☐	☐	
Relative percent differences are within limits	☐	☐	☐	☐	
Have sample results been flagged appropriately	☐	☐	☐	☐	

Analyst review signature Date | Peer review signature Date | QA review signature Date

PHILIS2 Form ID#: QA-017 / Release Date: 09/18/2023

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