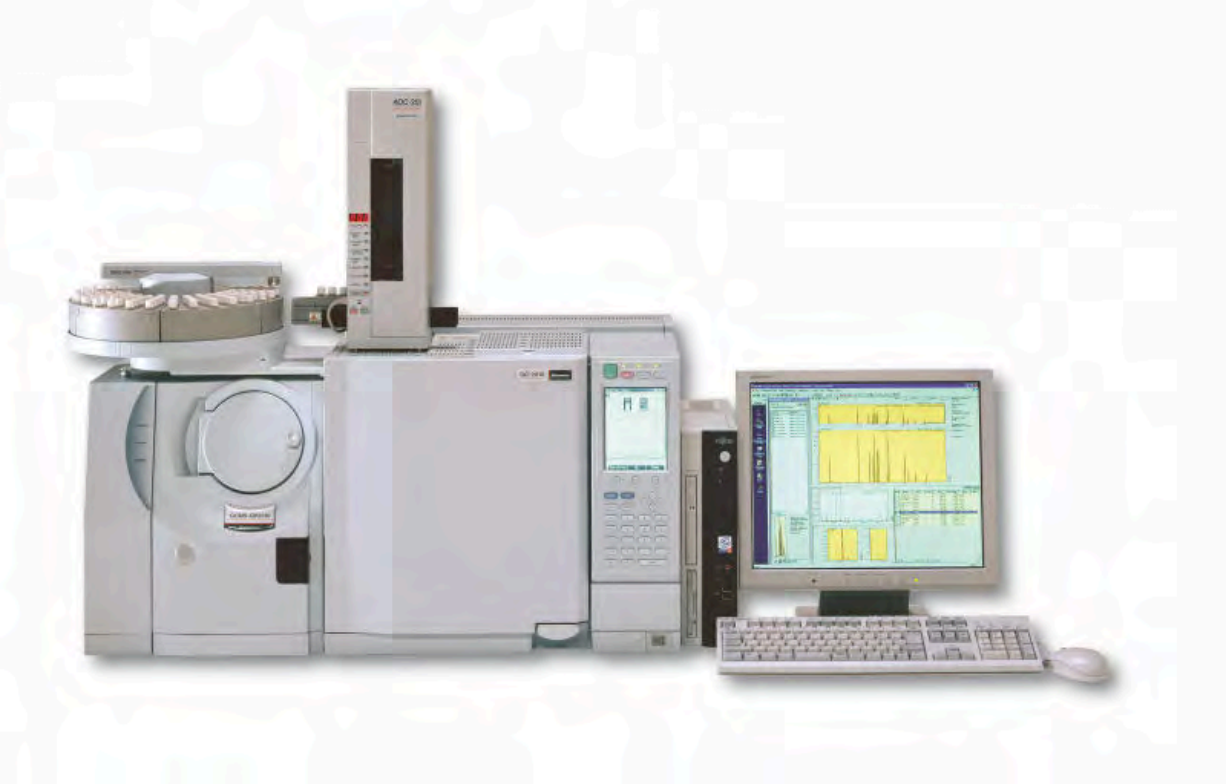
STANDARD OPERATING PROCEDURE

For

Method 8270C/D/E SIM

SEMIVOLATILE ORGANIC COMPOUNDS
BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) IN SELECTIVE ION MODE (SIM)



SOP Revision Log for AEL SOP SVOC-028

Revision Number	Revision Date	Reason for Revision	Section(s) and Page(s) Revised
Revision 00	3/10/05	Initial Creation	All sections affected
Revision 01	2/17/07	Revisions throughout, update language and definitions.	All sections affected
Revision 02	7/9/10	Revisions and re-writes throughout. Added revision log, section 22 maintenance, renumbered sections 22, and 23.	All sections affected
Revision 03	2/7/11	Added section 1.3 and 11.4 to add allowance for acid as well as base-neutral extraction so that PAHs can be extracted in conjunction with FL-PRO samples, revised 6.24 for PQL definition, Added to section 24.1 new personnel for method validation.	Sections 1.3, 6.24, 11.4, 24.1
Revision 04	9/30/14	Revisions throughout, update language and definitions. Update equipment list. Allows for reduced volume extractions. Update control limits. Update validating analysts section 24.	All sections affected
Revision 05	2/25/15	Instrument J7H added to Jacksonville instrumentation list. Sec 9.3.6. Stock standards are purchased from an approved vendor. Reference to Crescent and CPI standards removed. Section 10. Add GC/MS instrument operating conditions for QP2010Plus. Section 13.1.2, Update validating analyst Sec 24	Section 9.3.6, 10, 13.1.2, 24
Revision 06	4/30/15	SIMS operating condition added as table 5.	Section 24
Revision 07	4/14/17	Update method to include requirements of tuning with DFTPP, specific surrogates, and checking DDT breakdown, when performing for DoD clients under DoD QSM 5.1 criteria. Update setting of RRT. Update method validating analyst. Update references and tables to latest editions (DoD QSM 5.1)	Sections 1.2, 4.1, 10.16, 10.8.2, 12.3, 12.7.1 13.2, 13.3, 13.5.6, 23, 24.1, 24.2 tables 2 - 5
Revision 08	4/09/18	Revision, re-writes throughout and addition of 1,4-Dioxane.	All sections affected.
Revision 09	2/28/19	Updated target reference ions. Update to include criteria for 8270E. Update to DoD QSM 5.2 criteria.	24.3 Table 1
Revision 10	4/20/2020	Re-writes throughout, update to DoD QSM 5.3 criteria, and removal of 1,4-Dioxane soils.	All sections affected.
Revision 11	11/06/2020	Revise to edit surrogate level 1 concentration from 0.1 ug/ml to the correct value of 1.0ug/ml	10.7.2.1 Initial Cal. Standards Table
Revision 12	12/22/2020	Include rules for relative error and its calculation. Add procedure for processing Appendix 9 compounds (1,4-Dioxane)	Section 13.5, 14.2.6.3

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1.0 Identification of Test Method

1.1 METHODS 8270C, D, & E; SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) IN SELECTIVE ION ACQUISITION MODE (SIM) (as opposed to full scan acquisition mode).

1.2 This SOP deviates from the EPA 8270 referenced method in the following areas:

NOTE: These deviations from the referenced test method are the best conditions for our instrumentation and represent improved performance over the referenced test method conditions.

1.2.1 The mass spectrometer uses a scan range of 40 to 450 amu at a rate of 0.38 seconds per scan versus the referenced test method range of 35 to 500 amu and a scan rate of 1 second per scan. The scan range and scan rate of this SOP give better fits for the compounds normally analyzed under both 8270 test methods.

1.2.2 Standards are all purchased from certified vendors and are not made from stock reference materials.

1.2.3 Instrument chromatographic conditions have been optimized for the column and analytes of interest and do not match exactly those recommended in the method. These deviations from the referenced test method are the best conditions for our instrumentation and represent improved performance over the referenced test method conditions.

1.2.4 Tuning when in SIMs mode only is not required (except when performing under DoD criteria for DoD client work).

1.3 In house studies have shown that Polyaromatic Hydrocarbons do not require pH adjustment for extraction; therefore, PAH samples can be extracted under acid as well as base or neutral conditions. This allows for the extracts, when silica gel treated, to be used for both PAH analysis and FL-PRO analysis as long as QC is extracted that meet both method's acceptance criteria and all QC passes through all the processes that samples pass through. Also allowed per method is a volume less than 1 liter. New MDLs at this lesser volume are comparable to those of 1-liter volumes and will be in use for these lower volume extractions.

2.0 Applicable Matrix or matrices

2.1 This method is applicable to nearly all types of samples, regardless of water content, including ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, solid materials, and sediments.

3.0 Detection Limit

3.1 The method detection limit is determined in accordance with AEL SOP ADMIN-012, referencing 40CFR136, appendix B.

3.2 For the current MDLs, see the electronic version specific for the method, instrument, and matrix in the "AEL-QA" folder on the lab server.

4.0 Scope and Application, including components to be analyzed:

4.1 Analytes:

PARAMETER	CAS NUMBER
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benz(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(g,h,i)perylene	191-24-2
Benzo(a)pyrene	50-32-8
Carbazole	86-74-8
Chrysene	218-01-9
Dibenz(a,h)anthracene	53-70-3
53-	
Dibenzofuran	132-64-9
Fluoranthene	206-44-0
Fluorene	86-73-7
Indeno(1,2,3-cd)pyrene	193-39-5
2-Methylnaphthalene	91-57-6
1-Methylnaphthalene	90-12-0
Naphthalene	91-20-3
Phenanthrene	85-01-8
Pyrene	129-00-0
1,4-Dioxane	123-91-1

4.2 Method 8270 C, D, & E can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

4.3 See Table 1 in section 24.3 for a list of compounds and their characteristic ions that have been evaluated.

4.4 This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed in Section 4.0 in municipal and industrial discharges as provided under 40 CFR Part 136.1.

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

5.0 Summary of Method

5.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (SVOC-001; 3510C, SVOC-002; 3550B, and SVOC-003; 3580A).

5.2 The semi volatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

5.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

6.0 Definitions

See also AEL ADMIN SOP-039 Laboratory Definitions

6.1 Extraction Batch – A group of field samples with similar matrices, which are prepared at the same time in the same location using the same procedure and processed as a unit. A Method Blank, a Laboratory Control Sample, a Matrix Spike, and a Duplicate Matrix Spike must accompany each extraction batch of 20 or fewer field samples.

6.2 Continuing Calibration Verification (CCV) – A known interference free matrix spiked with a known concentration (near the mid-point of the Initial Calibration) of the target analytes. The CCV is analyzed at the beginning of a 12-hour analytical run and is used to verify that the instrument calibration is in control before and after sample analysis. A CCV, with a criterion of 50-150% is required at the end of the 12-hour analytical run ONLY for DOD samples.

6.3 DoD (DOD): Acronym for Department of Defense.

6.4 Initial Calibration (ICAL) – Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method.

6.5 Calibration Curve – A calibration or standard curve is a curve that plots known standard concentrations of an analyte versus the instrument response for that analyte.

6.6 Initial Calibration Verification (ICV) – A known interference free matrix spiked with a known concentration (near the mid-point of the Initial Calibration) of the target analytes. ICV standards are made from a stock solution that is different from the stock used to prepare calibration standards. This standard is analyzed immediately after the calibration to confirm the usability of the calibration.

6.7 Instrument Blank (IB) – An instrument blank is an aliquot of the method solvent, containing no analytes of interest. The purpose of an IB is to ensure that the analytical system is free from contamination associated with the instrument analysis. An IB also provides one way of determining the level of noise and baseline rise attributable solely to the analytical system, in the absence of any other analytes or non-analytical related contaminants. The blank should contain the internal standard.

6.8 Internal Standard (IS) – An internal standard is pure analytes added to a sample, extract, or standard solution in a known amount. The IS is used to measure the relative responses of other method analytes that are components of the same sample of solution. The internal standard must be an analyte that is not a sample component.

6.9 Method Blank (MB); also referred to as Laboratory Reagent Blank (LRB) – An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

6.10 Laboratory Control Sample (LCS); also referred to as Laboratory Fortified Blank (LFB) – A known interference free matrix spiked prior to sample extraction with a known concentration of standard. The LCS is analyzed exactly like a sample; the purpose of the LCS is to monitor analytical control for the batch. Percent recoveries are calculated for each of the analytes.

6.11 Laboratory Control Sample Duplicate (LCSD) – A second known interference free matrix spiked prior to sample extraction with a known concentration of standard. Analyses of duplicates indicate precision associated specifically with the laboratory procedures, removing any associated variables that might occur during sample collection, preservation, or storage procedures.

6.12 Matrix Spike/Matrix Spike Duplicate (MS/MSD); also referred to as Laboratory Fortified Matrix (LFM) – An aliquot of a client supplied sample that is chosen at random, to which known quantities of the method analytes are added in the laboratory. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the values in the MS corrected for the background concentration. Matrix Spikes are analyzed with every batch or per 20 samples.

6.13 Matrix – The substrate (e.g. water, soil, etc.), which may contain the analyte of interest.

6.14 Liquid Sample - A sample classified as a groundwater, surface water, wastewater or other water-soluble liquid.

6.15 Representative Sample: A well-mixed aliquot of sample that constitutes an accurate representation of contents within the container. Methods used to achieve a representative sub-sample are described below:

6.15.1 Aqueous/Liquid samples.

6.15.1.1 Sample is shaken until homogeneous and then poured or pipetted into appropriate container.

6.15.2 Soil Samples.

6.15.2.1 If container size is sufficient, sample is mixed within until homogeneous. If container size is insufficient, the entire sample is transferred to an appropriate container and mixed.

6.15.2.2 Miscellaneous Solid Samples. Sample is crushed, pulverized, shaken and stirred as appropriate to ensure the aliquot used for analysis represents the entire contents of the original sample container as accurately as possible.

6.16 Sample Duplicate (DUP) - A second aliquot of a client supplied sample. The sample duplicate is analyzed exactly as the client supplied sample and is used to determine whether the laboratory is capable of obtaining reproducible results.

6.17 Stock Standards Solution – A concentrated solution of one or more target analytes at a known concentration, purchased from a reputable commercial vendor, and having Certificates of Analysis. Stock standard solutions are used to prepare working calibration standards. Stock standards once opened must be replaced after 1 year or sooner if routine QC indicates a problem.

6.18 Working Calibration Standard (WS) – A solution of all the target analytes at a known concentration prepared either from one or more intermediate calibration standards and/or from one or more stock standard solutions. Working standards once made must be replaced after 6 months or sooner if routine QC indicates a problem.

6.19 Analysis Window – Samples are analyzed in a time frame referred to as a “window.” The window is initiated with the analysis of the continuing calibration verification (CCV) standard. If the CCV passes the specific criteria, then samples are analyzed until the 12-hour time limit expires. Before more samples can be analyzed, a new window must be opened.

6.20 DOD Analysis Window – Samples are analyzed in a time frame referred to as a “window.” The window is initiated with the analysis of the DFTPP Tune standard. If the Tune passes specific criteria, a 12-hour analysis window is opened at the time of the injection of the DFTPP. Next, a continuing calibration verification (CCV) standard is analyzed. If both of

these analyses pass their specific criteria, then samples are analyzed until the 12-hour time limit expires. Before more samples can be analyzed, a new window must be opened.

6.21 Decafluorotriphenylphosphine (DFTPP) Tune Standard – Used to verify mass spectral instrument performance (mass and ion abundance criteria) for semi volatile analysis.

6.22 Surrogate Analyte (Surr) – A surrogate analyte is an organic compound that is similar to the analytes of interest in chemical composition, extraction characteristics, and chromatography, but is not normally found in environmental samples. The purpose of the surrogate analyte is to evaluate the preparation and analysis of the samples. These compounds are spiked into blanks, standards, samples, and matrix spiked samples prior to analysis. Percent recoveries are calculated for each surrogate and are used to evaluate the method performance.

6.23 GC/MS - used as an abbreviation for gas chromatograph/mass spectrometer. When MS abbreviated alone, always defined as matrix spike, when MS used in conjunction with GC as in GC/MS, always defined as mass spectrometer.

6.24 Selective Ion Monitoring (SIM) – Mass spectrometry technique where ions resulting from fragmentation are selectively monitored, therefore excluding other ions. The technique enhances sensitivity as compared to full scan analysis. Because the analysis results in significantly less mass spectral information, this gain in sensitivity is made at the expense of analyte selectivity. Therefore, the use of SIM results in significantly lower instrument detection limits, but increases the uncertainty associated with the analysis.

6.25 Case Narrative (CN) – A case narrative is simply a means of describing exactly what transpired with the samples during the analytical process. Case narratives are required for variances that occur within a project.

6.26 Non-Conformity Form (NCF) – A form which will be completed and processed for each QC failure or deviation from normal protocol that occurs outside the scope of normal operation as defined by the AEL QM Section 10, AEL SOP Admin-016, and Method SOP.

6.27 Semi-volatile department abbreviations used in sample preparation logbooks, data printouts and other Semi-volatile areas:

6.27.1 RR/RA – Rerun/Reanalyze

6.27.2 CF – Confirmation

6.27.3 NR – Not a Real Hit

6.27.4 NAP – Not a Peak

6.27.5 DNC – Does Not Confirm

6.27.6 STR – Straight/No Dilution

6.27.7 NT – Not Target

6.27.8 WRT – Wrong Retention Time

6.27.9 DNR – Do Not Report

6.27.10 BDL –Below Detection Limit

6.27.11 FH – Fails High

6.27.12 FL – Fails Low

6.27.13 DF – Dilution Factor

6.27.14 DIL – Dilution

6.27.15 STD – Standard

6.27.16 IS – Internal Standard

6.27.17 Surr – Surrogate

6.27.18 OOT – Out of Tune/CCV Window

6.27.19 WS – Working Standard

6.28 Safety Data Sheets (SDS) Safety Data Sheets (SDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data, including storage, spill, and handling precautions.

6.29 Limit of Detection (LOD) – The LOD is **not** synonymous with the MDL. The LOD is an estimate of the minimum amount of a substance that an analytical process can reliably detect with a high level of confidence (99% Confidence; that is a false negative rate of 1%). The LOD is at the level of the MDL. The LOD must go through all the same processes that a sample will go through and be detected above instrument noise level.

6.30 Limits of Quantitation (LOQ) – The minimum levels, concentrations, or quantities of a target variable (e.g. target analyte) that can be reported with a specific degree of confidence. It is also the lowest concentration that produces a quantitative result within specified limits of precision and bias. For DOD work the LOQ will be set at or above the concentration of the lowest initial calibration standard. For DOD work the LOQ will be the concentration at which the PQL is verified. The LOQ can equal the PQL, but is not synonymous with the PQL.

6.31 Limits of Quantitation (LOQ) Verification – LOQ verifications are a spiked clean matrix sample that must go through all the same processes which regular samples will go through, and be within the precision and bias acceptance criteria of the method. The LOQ verifications are spiked at the concentrations of the LOQ.

6.32 Method Detection Limit (MDL) – The MDL is an estimate of the minimum amount of a substance that an analytical process can readily detect. The MDL is the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined most often as 3.14 times the standard deviation of a low level, seven replicate study; however, it can be determined for some methods as the lowest increment measurable with confidence. MDLs are determined for each analyte, matrix, prep method, cleanup method, analysis method, and instrument. (See each method's requirements). The MDL is one way to establish a Detection Limit, not a Limit of Detection.

6.33 Method Detection Limit **(**MDL) Verification – MDL verifications are spiked clean matrix samples that must go through all the same processes that a regular sample will go through and be detected above instrument noise level. For labs accredited under DOD ELAP, the MDL verifications must be performed immediately after the initial MDL study and on a quarterly basis thereafter. For labs accredited under NELAC (TNI) Standards only, MDL verifications are to be performed immediately after the initial MDL study and on a yearly basis thereafter..

6.34 Practical Quantitation Level (PQL); also know as the Method Reporting Limit (MRL or RL) – the lowest calibration standard or lowest quantitation level for the method and matrix. The concentration below which data is to be qualified as having less certainty. PQLs are at a concentration greater than that of the MDL.

6.35 Qualifier Codes (For Florida and FDEP work)

6.35.1 A - Value reported is the mean (average) of two or more determinations. This code shall be used if the results of two or more discrete and separate samples are averaged. These samples shall have been processed and analyzed (e.g. laboratory replicate samples, field duplicates, etc.) independently. Do not use this code if the data is the result of replicate analyses on the same sample aliquot, extract or digestate. Under most conditions, replicate values shall be reported as individual analyses.

6.35.2 I - The reported Value is between the laboratory method detection limit (MDL) and the laboratory practical quantitation limit (PQL).

6.35.3 K- Off scale low.

6.35.4 L- Off scale high. Use if reporting above the acceptable level of quantitation.

6.35.5 U- Indicates that a compound was analyzed for but not detected. The value associated with the qualifier will be the MDL.

6.35.6 V- Indicates that the analyte was detected in both the sample and the associated method blank. NOTE: The method blank value **cannot** be subtracted from the associated sample to give a result. The sample result will be reported as is with the "V" qualifier.

6.35.7 H - Value based on field kit determination; results may not be accurate. This code shall be used if a field-screening test (i.e. field gas chromatograph data, immunoassay, vendor-supplied field kit, etc.) was used to generate the value and the field kit or method has not been recognized by the Department as equivalent to laboratory methods.

6.35.8 O - Sampled, but analysis lost or not performed. NOTE: if reporting data to STORET, a numerical value must be entered. Such values are not meaningful and shall not be used.

6.35.9 Q - Sample held beyond the accepted holding time. This code shall be used if the value is derived from a sample that was prepared and/or analyzed AFTER the approved holding time restrictions for sample preparation and analysis.

6.35.10 Y - The laboratory analysis was from an unpreserved or improperly preserved sample. The data may not be accurate.

6.35.11 REJ - Data is rejected and should not be used. Some or all of the quality control data for the analyte were outside criteria, and the presence or absence of the analyte cannot be determined from the data.

6.35.12 NAI - Not analyzed due to interference.

6.35.13 J - Estimated value; value not accurate.

6.35.13.1 This code shall be used in the following instances:

6.35.13.1.1 "1" Surrogate recovery limits have been exceeded;

6.35.13.1.2 "2" No known quality control criteria exists for the component;

6.35.13.1.3 "3" The reported value failed to meet the established quality control criteria for either precision or accuracy;

6.35.13.1.4 "4" The sample matrix interfered with the ability to make any accurate determination; or

6.35.13.1.5 "5" The data is questionable because of improper laboratory or field protocols (e.g. composite sample was collected instead of a grab sample).

6.35.13.2 A "J" value shall be accompanied by justification for its use (ex. J(4)).

6.35.13.3 A "J" value shall not be used if another code applies (ex. K, L, M, T, V, Y, PQL).

6.35.14 If more than one code applies, and the data is to be entered into STORET, only one code shall be reported. The code shall be selected based on the following hierarchy: REJ, NAI, O, Y, V, H, J, B, K, L, M, PQL, T, Z, A.

7.0 Interferences

Note: All references to other methods are in reference to EPA SW-846 methods

7.1 Refer to Methods 3500 (Sec. 3.0, in particular) and 8000, for a discussion of interferences.

7.2 Sources of interference in this method can be grouped into three broad categories.

7.2.1 Contaminated solvents, reagents, or sample processing hardware.

7.2.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

7.2.3 Compounds extracted from the sample matrix to which the detector will respond.

7.3 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks. Reagents of sufficient quality are used to reduce this possibility and purchased in accordance with ADMIN-013.

7.4 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinsing with tap water, followed by organic-free reagent water. Drain the glassware and dry it in an oven at 130^{o}C for several hours, or rinse with methanol or acetone and drain. Store dry glassware in a clean environment.

7.5 The chromatographic conditions described allow for a unique resolution of the specific PAH compounds covered by this method. Other PAH compounds, in addition to matrix artifacts, may interfere.

7.6 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

7.7 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe is rinsed automatically with solvent between sample injections. Whenever an unusually concentrated sample (10 times the upper limit of the curve) is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

8.0 Safety

8.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure

should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

8.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Safety Data Sheets (SDS) should be made available to all personnel involved in the chemical analysis. These are stored in the common areas of the labs.

8.3 Refer to the AEL Chemical Hygiene Plan and Safety Manual for safety precautions and for the Hygiene Plan and Emergency Response Plan.

8.4 See Standard Methods, 22nd / Online Edition, Section 1090 Laboratory Occupational Health and Safety.

9.0 Equipment and Supplies

9.1 See SOP SVOC-001; 3510C, SVOC-002; 3550B, and SVOC-003; 3580A.

9.2 Gas Chromatograph (GC)/Mass Spectrometer (MS) system:

Note: For all labs, see the Quality Manual, Section 7, for the current listing by room location and letter designation for each piece of major equipment (by make, model, and serial number) and a full inventory of all major pieces of equipment in each lab.

9.2.1 Gas Chromatograph (Shimadzu model: GC-2010 or GC-2010 Plus and Agilent model 6890N) – An analytical system complete with gas chromatograph; suitable for sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. Each Shimadzu GC shall be mounted with the Shimadzu Auto sampler; Model # AOC-20i and the Agilent GC shall be mounted with the Agilent 7683 for direct injection into the injector and onto the column.

9.2.1.1 Jacksonville: Shimadzu: GC model 2010 (serial number 6091951425), GC model 2010-Plus (serial number 10681550 and C7062400216). Agilent GC model 6890N (serial number US10623036).

9.2.2 Auto sampler Syringe – 10uL.

9.2.3 Chromatographic Column – Phenomenex Zebron ZB-Semi Volatiles 30m x 0.25mm x 0.25um, or equivalent.

9.2.4 Detector - Mass Spectrometer (MS) (Shimadzu QP2010SE, or QP2010 and Agilent 5973).

9.2.5 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Decafluorotriphenylphosphine (DFTPP), which meets the criteria in Table 2

Section 24 when 2uL of the GC/MS tuning standard is injected through the GC (50ng of DFTPP).

9.2.6 GC/MS interface (Direct) – Any GC-to-MS interface that gives acceptable calibration points at 50ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

9.3 Data System (Shimadzu Lab Solutions – version GCMS solution 4.2 and 4.3. Agilent – Environmental Chemstation/MSD Chemstation version E.02.02.1431) – A data system used for measuring and storing peak heights and peak areas. The computer system should be interfaced to the mass spectrometer. The system allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer software searches any GC/MS data file for ions of a specific mass and can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). The software allows integrating the abundances in any EICP between specified time and scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library is available.

9.4 Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers, for preparation of standards.

9.5 Auto sampler Vials – 2.0 mL glass with polytetrafluoroethylene (PTFE) - lined screw caps.

9.6 Standard Solution Storage Containers – 10-20mL amber glass vials with Teflon lined screw caps.

9.7 Pasteur Pipettes – Glass, disposable.

9.8 Micro-Syringes –10µL, 25µL, 50µL, 100µL, 250µL, 500µL, and 1000µL.

10.0 Reagents and Standards

Note: Although sources of the reagents and standards noted in this SOP may be provided, they may also change based on availability, quality, and cost. The use of a different source or concentration is acceptable without modification of the procedures, provided the products are equivalent. Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Note: All reagents and standards must be labeled with their unique ID, the name of the material, the concentration, the date prepared, and the expiration date.

Note: Stock standard solutions are ordered from NELAC (TNI) approved vendors. Stock standards are received from the vendor in sealed amber ampoules. Once opened, store the stock standard

solutions in amber vials with Teflon screw tops. All stock standards are stored at -10ºC to -20ºC or 0ºC to 6ºC and protected from light (unless otherwise instructed by the manufacturer). Check stock standards frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards. Opened stock standards should be replaced after 6 months or sooner, if comparison with check standards indicates a problem.

Note: Prior to making any laboratory prepared standards, allow the stock standard to warm to room temperature. Store intermediate and working standards in screw-top vials at -10ºC to -20ºC or 0ºC to 6ºC and protect from light. Working standards should have an expiration date of six months (unless the manufacturer's expiration date is sooner). Allow working standards to warm to room temperature prior to use.

10.1 Reagents and Standards are ordered and tracked internally in accordance with SOPs ADMIN-013 and ADMIN-031.

10.2 The mixing of reagents shall be tracked in a reagent logbook kept in the Extractions room. The mixing of intermediate and/or working standards shall be tracked in a standard logbook kept in the Semi-Volatiles room. Both logbooks will contain the following information:

10.2.1 For parent material:

10.2.1.1 The manufacturer lot number.

10.2.1.2 The manufacturer name.

10.2.1.3 The chemical name and/or chemical description.

10.2.1.4 The expiration date.

10.2.1.5 The AEL receiving lot number.

10.2.2 For any laboratory prepared reagents and/or standards:

10.2.2.1 The recipe (the amount of parent material used and how the standard was mixed) is included in the logbook.

10.2.2.2 The creation date.

10.2.2.3 The expiration date.

10.2.2.4 The standard concentration.

10.3 Reagents:

10.3.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society,

where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

10.3.2 Methylene chloride, hexane, acetone, purge and trap methanol – pesticide grade or better in accordance with ADMIN-013.

10.3.3 Pentafluortributylamine (PFTBA) – Calibration gas supplied with the MS, using in tuning the MS.

10.4 Stock standards - Stock solutions purchased as certified solutions. Opened stock standards must be replaced after 1 year or sooner; if comparison with check standards indicates a problem (common problems occur from degradation or evaporation of the standard). Certificates of analysis are stored in the SVOC lab in accordance with Quality Manual 5.0. Store purchased standards according to manufacturer specifications. All purchased stock standards solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard.

Note: Alternative standards from the ones listed below may be used, provided they are from a certified vendor.

10.4.1 Primary Stock Standards

10.4.1.1 2000ug/mL 8270 Calibration Mix 5 (Restek C/N 31995)

10.4.1.2 2000ug/mL Carbazole Solutions (O_2SI C/N 010239-03)

10.4.1.3 1000ug/mL Dibenzofuran Solution (O_2SI C/N 010067-01)

10.4.2 1,4-Dioxane Primary Stock Standards

10.4.2.1 40,000ug/mL 1,4-Dioxane (Phenova C/N ALO-130054)

10.4.3 Secondary Stock Standards

10.4.3.1 2000ug/mL Custom PAH Plus Mix (Phenova C/N ALO-130250)

10.4.3.2 1000ug/mL Custom SV Mix (Phenova C/N ALO-130250)

10.4.4 1,4-Dioxane Secondary Stock Standards

10.4.4.1 2000ug/mL 1,4-Dioxane Standard (Restek C/N 30287)

10.4.5 Surrogate Stock Standards

10.4.5.1 5000ug/mL B/N Surrogate Mix (Restek C/N 31086)

10.4.5.2 2000ug/mL SoM01.1 Deuterated Monitoring Compound Mix Sim

Compounds (DMCs) (Restek C/N 33913) – DoD samples only

10.4.6 Internal Stock Standard

10.4.6.1 4000ug/mL SV Internal Standard Mix (Restek C/N 31006)

10.4.7 1,4-Dioxane Internal Stock Standard

10.4.7.1 1,4-Dioxane-d8 Standard (Restek C/N 30614)

10.4.8 DFTTP Stock Standards (DOD requirement only)

10.4.8.1 1000ug/mL GC/MS Tuning Mixture (Restek C/N 31615)

10.5 Laboratory Prepared Standards

10.5.1 All laboratory prepared standard solutions must be replaced after 1 year or sooner if routine QC indicates a problem or the method requires a shorter expiration date. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation.

10.5.2 Extraction Spiking Standards

10.5.2.1 Surrogate Spike – Prepared by diluting 200uL of the 5000ug/mL B/N Surrogate Mix to a final volume of 100mL in Acetone. The surrogate spike concentration is 10.0ug/mL. 1.0mL of the surrogate spike will be added to each sample and QC sample before the extraction.

10.5.2.2 DoD Surrogate Spike - Prepared by diluting 100uL of the 5000ug/mL B/N Surrogate Mix and 250uL of the 2000ug/mL Deuterated Monitoring Compound Mix Sim Compounds to a final volume of 50mL in Acetone. The surrogate spike concentration is 10.0ug/mL. 1.0mL of the surrogate spike will be added to each sample and QC sample before the extraction.

10.5.2.3 LCS/MS/MSD Spike – Prepared by diluting 125uL of 2000ug/mL PAH Plus Methylnaphthalenes and 250uL 1000mg/L Custom SV Mix Solution up to 50mL with Acetone. The LCS/MS/MSD Spike concentration is 5.0ug/mL. 1.0mL of the spike will be added to each QC sample before the extraction.

10.5.2.4 1,4-DX LCS/MS/MSD Spike – Prepared by diluting 125uL of 2000ug/mL 1,4-Dioxane Standard up to 50mL with Methanol. The 1,4-DX spike concentration is 5.0ug/mL. 1.0mL of the 1,4-DX spike will be added to each QC samples before the extraction.

10.5.2.5 1,4-DX Isotope IS – Prepared by diluting 125uL of 2000ug/mL 1,4-dioxane-d8 standard up to 50mL with Methanol. The 1,4-DX Isotope IS

concentration is 5ug/mL. 1.0mL of the 1,4-DX Isotope IS will be added to each sample and QC sample before extraction.

10.5.3 Tune Standard (DOD requirement only) – Prepared by diluting 50uL of the 1000ug/mL GC/MS Tuning Mixture and 50uL of the 2mg/mL 4,4—DDT & Endrin Standard to a final volume of 1.0mL DCM. Final concentration of the tune standard is 50ug/mL.

10.5.4 PAH Internal Standard (PAH IS) – Prepared by diluting 200uL of 4000ug/mL SV Internal Standard Mix up to 2.0mL with DCM. The IS concentration is 400ug/mL. 10uL of the IS will be added to each sample and QC sample before analysis.

10.5.5 1,4-Dioxane Isotope Internal Standard (1,4-DX IS) - Prepared by diluting 250uL of 2000ug/mL 1,4-dioxane-d8 standard up to 1.0mL with DCM. The 1,4-DX Isotope IS concentration is 500ug/mL. 10uL of the 1,4-DX IS will be added to each sample and QC sample before analysis.

10.6 Working Standard – Using stock standard, prepare a working standard, as needed, which contains the compounds of interest, either singly or mixed together. The working standard should be replaced at least every 6 months.

10.6.1 PAH Primary Working Standard (1º WS) – Prepared by diluting the following to a final volume of 5.0mL in DCM. The final concentration of the PAH 1º WS is 100ug/mL:

10.6.1.1 250uL of the 2000ug/mL 8270 Calibration Mix #5,

10.6.1.2 250uL of the 2000ug/mL Carbazole Solution,

10.6.1.3 250uL of the 2000ug/mL SOM01.1 Deuterated Monitoring Compound Mix Sim Compounds,

10.6.1.4 500uL of the 1000ug/mL Dibenzofuran Solution,

10.6.1.5 100uL of the 5000ug/mL B/N Surrogate Mix.

10.6.2 PAH Secondary Working Standard (2º WS) – Prepared by diluting the following to a final volume of 5.0mL in DCM. The final concentration of the PAH 2º WS is 100ug/mL:

10.6.2.1 250uL of the 2000ug/mL Custom PAH Plus Mix,

10.6.2.2 250uL of the 2000ug/mL SOM01.1 Deuterated Monitoring Compound Mix Sim Compounds,

10.6.2.3 100uL of the 5000ug/mL B/N Surrogate Mix,

10.6.2.4 500uL of the 1000ug/mL Custom SV Mix.

10.6.3 1,4-DX Primary Working Standard (1º WS) – Prepared by diluting the following to a final volume of 10.0mL in DCM. The final concentration of the 1,4-DX 1º WS is 20ug/mL 1,4-DX;100ug/mL B/N Surrogate:

10.6.3.1 5uL of the 40,000ug/mL 1,4-Dioxane,

10.6.3.2 200uL of the 5000ug/mL B/N Surrogate.

10.6.4 1,4-DX Secondary Working Standard (2º WS) – Prepared by diluting the following to a final volume of 10.0mL in DCM. The final concentration of the 1,4-DX 1º WS is 20ug/mL 1,4-DX;100ug/mL B/N Surrogate:

10.6.4.1 100uL of the 2000ug/mL 1,4-Dioxane Standard,

10.6.4.2 200uL of the 5000ug/mL B/N Surrogate.

10.7 Initial Calibration (ICAL) Standards

10.7.1 8270 PAH Calibration Standards – Prepared as described below in DCM.

10.7.1.1 Typical 8270 PAH Initial Calibration Standards

ICAL Level µg/mL	Volume of 8270 PAH 1º WS used	Final Volume (mL)	Amount of PAH IS to Use*	Concentration of the IS
ICAL 1 0.025µg/mL***	50 µL of ICAL 4**	1.0mL DCM	10 µL	4µg/mL
ICAL 2 0.05µg/mL	100 µL of ICAL 4**	1.0mL DCM	10 µL	4µg/mL
ICAL 3 0.2µg/mL	2 µL	1.0mL DCM	10 µL	4µg/mL
ICAL 4 0.5µg/mL	5 µL	1.0mL DCM	10 µL	4µg/mL
ICAL 5 1.0µg/mL	10 µL	1.0mL DCM	10 µL	4µg/mL
ICAL 6 2.0µg/mL	20 µL	1.0mL DCM	10 µL	4µg/mL
ICAL 7 5.0µg/mL	50 µL	1.0mL DCM	10 µL	4µg/mL
ICAL 8 50µg/mL	500 µL	1.0mL DCM	10 µL	4µg/mL
ICAL 8 100µg/mL	1000 µL	1.0mL DCM	10 µL	4µg/mL

***IS is added to the 1.0mL final volume**
****A second ICAL 4 is prepared for the ICAL levels 1 & 2; do not add internal standard to this ICAL 4 vial.**
*****ICAL level 1 reports only Benzo(b)Fluoranthene**
******ICAL levels 1 and 2 are the PQLs for water samples. ICAL level 3 is the PQL for soil samples.**

10.7.2 8270 1,4-Dioxane Calibration Standards – Prepared as described below in DCM.

10.7.2.1 Typical 8270 1,4-Dioxane Initial Calibration Standards

ICAL Level µg/mL	Surrogate Final Conc. µg/mL	Volume of 8270 1,4-DX 1º WS used	Final Volume (mL)	Amount of PAH IS and 1,4-DX Isotope IS to Use*	Concentration of the IS	Concentration of the 1,4-DX Isotope IS
ICAL 1 0.2µg/mL	1.0 µg/mL	10 µL	1.0mL DCM	10 µL	4µg/mL	5µg/mL
ICAL 2 0.5µg/mL	2.5 µg/mL	25 µL	1.0mL DCM	10 µL	4µg/mL	5µg/mL
ICAL 3 1.0µg/mL	5.0 µg/mL	50 µL	1.0mL DCM	10 µL	4µg/mL	5µg/mL
ICAL 4 2.0µg/mL	10 µg/mL	100 µL	1.0mL DCM	10 µL	4µg/mL	5µg/mL
ICAL 5 5.0µg/mL	25 µg/mL	250 µL	1.0mL DCM	10 µL	4µg/mL	5µg/mL
ICAL 6 10µg/mL	50 µg/mL	500 µL	1.0mL DCM	10 µL	4µg/mL	5µg/mL
ICAL 7 20µg/mL	100 µg/mL	1000 µL	1.0mL DCM	10 µL	4µg/mL	5µg/mL

***IS is added to the 1.0mL final volume**

10.8 8270C/D/E PAH Initial Calibration Verification (ICV) Standard – Prepared by diluting 200uL of the PAH Secondary Working Standard (Section 10.6.2) to a final volume of 1.0mL DCM. Add 10uL of the 400ug/mL PAH Internal Standard (Section 10.5.4) to the 1.0mL final volume. The final concentration of the target analytes is 20ug/mL.

10.9 8270C/D/E 1,4-DX Initial Calibration Verification (ICV) Standard – Prepared by diluting 100uL of the 1,4-DX Secondary Working Standard (Section 10.6.4) to a final volume of 1.0mL DCM. Add 10uL of the 4000ug/mL Internal Standard (Section 10.5.4) and 10uL of the 5000ug/mL 1,4-DX Isotope Internal Standard (Section 10.5.5) to the 1.0mL final volume. The final concentration of the target analytes is 2.0ug/mL. The final concentration of the surrogate is 10ug/mL.

10.10 8270C/D/E Continuing Calibration Verification (CCV) Standards – Prepared at the same concentration as Initial PAH Calibration Standard 7 or 8 (Table 10.7.1.1) or the same concentration as the ICV (Section 10.8).

10.11 8270C/D/E 1,4-DX Continuing Calibration Verification (CCV) Standards – Prepared at the same concentration as Initial 1,4-DX Calibration Standard 4 (Table 10.7.2.1).

11.0 Sample collection, preservation, shipment and storage

11.1 See AEL Admin-005 and Admin-023.

11.2 See AEL Quality Manual section 6.0 for sample acceptance policy.

11.3 See FDEP SOP FS1000 for preservation requirements, shipping conditions, and holding time requirements.

11.3.1 PAH/PRO combo samples - Samples for PAH analysis do not require; other than thermal preservation to follow FDEP SOP preservation tables. (If chlorinated samples expected, FDEP requires dechlorinating). FL-Pro extracts do require pH adjustment to <2 with either H_2SO_4 or HCL. In house studies have shown that PAH extraction recoveries are not affected by variations in pH; therefore PAH sample can be extracted under these acid conditions. This allows for the extracts, when silica gel treated, to be used for both PAH analysis and FL-Pro analysis as long as QC is extracted that meet both method's acceptance criteria and all QC passes through all the processes that samples pass through.

11.4 Aqueous samples must be extracted within 7 days of collection and analyzed within 40 days of extraction.

11.5 Soil/sediment samples must be extracted within 14 days of collection and analyzed within 40 days of extraction.

12.0 Quality Control

12.1 The GC/MS system must be tuned to meet the DFTPP criteria – see Table 2 Section 24.4.

12.2 There must be an initial calibration of the GC/MS system – see Section 13.

12.3 The GC/MS system must meet the calibration verification acceptance criteria – see Section 13.

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

12.5 Initial Demonstration of Capability – each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff is trained or significant changes in instrumentation are made. This will consist at a minimum of a method blank and 4 replicates spiked with a standard from a different source than that used to create the analytical curve.

12.5.1 Recovery levels for IDOC analytes shall fall within the lab generated QC limits for laboratory control spikes (see Table 12 of Section 24.14 and Table 13 of Section 24.15). These limits are taken directly from the tables of limits in the DOD Quality Systems Manual rev 5.3. These limits are based on an extensive collection of limits from DOD labs across the country and are consistent

with those charted from AEL data. The analytes that are not listed in the DOD tables will use the laboratory generated control limits. If laboratory generated limits are not available, the following range is used for QC acceptance criteria: 33-132%.

12.5.2 The Demonstration of Capability is not considered complete until the analyst has documentation saying that they have read, understood, and agreed to follow the AEL-SOP for this method and the associated EPA and/or Standard Methods on which the AEL-SOP was based.

12.5.3 Initial DOC's must be successfully performed by each analyst in accordance with the Quality Manual and ADMIN-030.

12.6 Method Detection Limit (MDL) - MDLs must be established for all analytes, following the procedures outlined in ADMIN SOP-012, which conforms to EPA CFR 40 part 136.6 appendix B, updated October 2017. Below is a summary of the steps for performing MDLs. Please refer to the ADMIN SOP-012 for the full procedures.

12.6.1 New MDL Study: Most MDL determinations are for already established analyte, matrix, and instrument combinations. In those cases where a new analyte is to be introduced, an initial MDL study will have to be implemented. Select a spiking level, typically 2 to 10 times the estimated MDL. Process a minimum of seven spiked samples and seven method blank samples through all steps of the method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates.

12.6.2 New Instrument: To bring on a new instrument for an already established method a full set of seven low-level replicates is not needed. Only two spiked samples and two method blank samples prepared and analyzed on different calendar dates are required for the new instrument. The resulting values shall be compared against existing MDLs for validity. If both method blank results are below the existing MDL, then the existing MDL_b is validated. Combine the new spiked sample results to the existing spiked sample results and recalculate the MDLs. If the recalculated MDL_s is within 0.5 to 2.0 times the existing MDL and fewer than 3% of the MB have results above the existing MDL, the existing MDL can be left unchanged and the new instrument is validated.

12.6.3 Existing Instrument, Major Maintenance: Follow the procedures for bringing on a new instrument.

12.6.4 Ongoing Data Collection: During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked samples on each instrument, in separate batches (separate prep batches and separate analytical batches), using the same spiking concentration used with established MDLs. If any analytes are repeatedly not detected in the quarterly spiked sample analyses, or do not meet the qualitative identification criteria of the method then this is an indication that the spiking level is not high enough and should be adjusted upward. Note that it is not necessary to analyze additional method blanks

together with the spiked samples; the method blank population should include all of the routine method blanks analyzed with each batch during the course of sample analysis.

12.6.4.1 At least once per year, re-evaluate the spiking level. If more than 5% of the spiked samples do not return positive numerical results that meet all method qualitative identification criteria, then the spiking level must be increased and the initial MDL re-determined following the procedure for establishing a new MDL.

12.6.5 Ongoing Annual Verification: At least once every thirteen months, re-calculate MDLs and MDL_b from the collected spiked samples and method blank results using the equations in the ADMIN SOP-012. These calculations shall be performed by the QA department along with updating and maintaining all chart and LIMs entry of any MDL changes.

12.7 Sample Quality Control for Preparation and Analysis

Note from QMS 5.3: The lab may use the same extract for full scan and SIM analysis if the SIM-specific Deuterated Monitoring Compounds (DMCs) are added prior to extraction.

12.7.1 The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank (MB), a matrix spike (MS), a duplicate (MSD, DUP, or LCSD), a laboratory control sample (LCS), and the addition of surrogates to each field sample and QC sample.

12.7.1.1 Each sample, MB, LCS, LCSD, MS, and MSD must be spiked with the surrogate spike.

12.7.2 Every twelve-hour analytical shift, prior to sample analysis, the laboratory must analyze an Instrument Blank (IB).

12.7.2.1 The IB contains only the surrogates and internal standards in DCM.

12.7.2.2 The IB must not contain any analyte of interest above the Method Detection Limit (MDL), or else the instrument system is contaminated.

12.7.3 Every twelve-hour analytical shift, prior to sample analysis, the laboratory must analyze a DFTPP standard (DoD criteria only). See Section 10.5.3 for the recipe for the Tune Standard. If the DFTPP fails criteria (see Section 24 Table 2) take corrective action before proceeding with calibration and/or analysis.

12.7.4 Every twelve-hour analytical shift, prior to sample analysis, the laboratory must analyze a CCV (see Section 13.3 for acceptance criteria).

12.7.5 With every batch of 20 samples (or less) the laboratory must analyze the following:

12.7.5.1MB -1 per batch of 20 or less.

12.7.5.1.1 Any analyte of interest must not be detected above the MDL.

12.7.5.2LCS – 1 per batch of 20 or less.

12.7.5.2.1 A Laboratory Control Sample (LCS) should be included with each analytical batch and once every twenty samples. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike.

12.7.5.2.2 The spike recoveries must be within the upper and lower control limits. See Table 7 of Section 24.7 and Table 8 of Section 24.10 for the control limits.

12.7.5.3MS/MSD – May be analyzed with every batch of 20 samples or less per matrix.

12.7.5.3.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate un-spiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an un-spiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. A matrix spike is required for every twenty samples and every extraction batch.

12.7.5.3.2 The spike recoveries must be within the upper and lower control limits. See Table 7 of Section 24.7 and Table 8 of Section 24.10 for the control limits.

12.7.5.3.3 The RPD for all analytes shall be within the limits specified in Table 7 of Section 24.7 and Table 8 of Section 24.10.

12.7.6 The laboratory must maintain performance records to document the quality of data that is generated.

12.7.7 Surrogate recoveries: The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory.

12.7.8 Deuterated surrogate recoveries (DoD samples only): The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. (Note: QSM 5.3 Appendix C limits do not exist for these surrogates, so in-house limits do not need to be reviewed against QSM 5.3 Appendix C table limits.)

12.7.9 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. If the peaks look normal, if the response obtained is comparable to the response from previous calibrations, etc., the instrument is considered still in calibration.

12.7.10 Assessing the Internal Standard – The peak areas or heights of the internal standards in the calibration verification standard must be within 50% to 200% (1/2 to 2x) of their respective peak areas or heights in the mid-point calibration standard.

12.7.10.1 If the IS response is above the QC acceptance criteria, there is an implied negative bias associated with the sample data.

12.7.10.2 If the IS response is below the QC acceptance criteria, there is an implied positive bias associated with the sample data.

12.7.10.3 See Section 20.0 for the contingencies for handling out-of-control IS responses.

13.0 Calibration and Standardization

Note: See also Section 10 for initial calibration curve standard preparation and curve concentration levels.

Note: See also AEL SOP ADMIN-038 for Calibration, Manual Integrations, and Rules for Chromatography, which outlines the procedures for choosing curve type, calculations performed, integrations allowed, and associated statistics.

13.1 Initial Calibration

13.1.1 The GC/MS operating conditions –

13.1.1.1 The GC operating conditions listed in Table 3 section 24.5 serve as guidelines only. Changes to the chromatographic conditions can be made by the analyst in order to improve the speed of analysis, lower the cost of analysis, and/or improve the separation or lower the detection

limit as long as the changes meet the initial and continuing calibration criteria and quality assurance criteria listed in this SOP.

13.1.1.2 Once these operating conditions are established they will be used to calibrate the instrument. All samples, blanks and quality assurance samples must be analyzed with the same operating conditions.

13.1.2 Mass spectrometer tuning and GC performance requirements

13.1.2.1 Before injecting calibration standards, the IB should be analyzed at the beginning of a run to confirm that the analytical system is free from contamination. The IB is used to determine the level of noise and baseline rise attributable solely to the analytical system, in the absence of any other analytes or non-analytical related contaminants. The IB is considered to be passing if the results for all target compounds are below the method detection limit (MDL).

13.1.2.2 Use of the DFTPP mass intensity criteria as tuning acceptance criteria has been dropped for sample analysis when for local and state regulatory reporting. <u>On work for DoD clients and for any work performed under DoD QSM 5.3 Standards, tuning shall still be required.</u>

Note: As of the 9/30/14 SOP revision, it will no longer be required to analyze a tune with DFTPP when performing SIM only analysis for sample analysis (when for local and state regulatory reporting), as we are citing the language in CLP requirements (see reference in section 23.7). Auto-tuning of the MS is still required after major instrument maintenance and before a new calibration (ICAL). A tune with DFTPP **<u>MUST</u>** be performed for all SIM DoD samples (this includes the ICAL associated to the samples and iDOCs).

13.1.2.3 For local and state regulatory work - Before injecting calibration standards and after the IB, the CCV or ICV should be analyzed at the beginning of a run. The CCV or ICV must pass all criteria before any standards and samples can be run. The CCV or ICV standard is the start of the 12-hour analysis window.

13.1.2.4 For DOD work - Before injecting calibration standards and after the IB, the tune should be analyzed at the beginning of a run. The tune must pass all criteria before any standards and samples can be run. The tune standard is the start of the 12-hour analysis window.

13.1.2.4.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP. Analyses must not begin until the tuning criteria are met. The tuning acceptance criteria are listed in Table 2 section 24.4.

13.1.2.4.2 Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be

accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

13.1.2.4.3 Use the DFTPP mass intensity criteria in Table 2 section 24.4 as tuning acceptance criteria.

Note: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

13.1.2.4.3.1 For DoD work - A DDT degradation standard should be analyzed with DDT breakdown to be less than or equal to 20%. See Section 15.0 for the DDT breakdown calculation.

13.1.2.4.3.2 If degradation is excessive and/or poor chromatography is noted, the injection liner shall be changed. If, after changing the injection linter, poor chromatography is still noted, the injection port may require cleaning. It may also be necessary to cut off the first 6-12 in. of the capillary column

13.1.3 Initial Calibration Curve (ICAL) – The internal calibration technique is used for this method. The internal standard approach assumes that variations in instrument sensitivity, amount injected, etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. Nine standards are used to calibrate the instrument for the PAH analysis; a minimum of five standards must be used. Seven standards are used to calibrate the instrument for the 1,4-Dioxane analysis; a minimum of five standards must be used. The lowest concentration standard (Practical Quantitation Limit (PQL)) is at the MRL; the highest concentration is at the end of the linear range (Upper Quantitation Limit (UQL)). See Section 10 for appropriate dilutions to prepare the calibration curve.

13.1.3.1 Analyze the 8270C/D/E PAH and 1,4-Dioxane Calibration Standards following the same GC operating procedures as the client samples (recommended procedures are listed in Table 3 Section 24.5).

13.1.3.2 When using an average response factor (RF) calibration (using a calibration factor (CF) fit), for the curve evaluation, a %RSD of $\leq$15% (8270C) and a %RSD of $\leq$20% (8270D/E), for the CF's over the working range verifies acceptance of the calibration curve. A minimum of five calibration points are required for an average RF calibration model. AEL evaluates the calibration curve using the tightest criteria in order to analyze method 8270C samples with samples for 8270D & E.

13.1.3.3 When using a linear regression model, a minimum of 5 calibration points are required, and the coefficient of determination (r^2) must be equal to or greater than 0.990 (or the correlation coefficient (r) must be equal to or greater than 0.995).

13.1.3.4 When using a quadratic regression model, a minimum of 6 calibration points are required, and the coefficient of determination (r^2) must be equal to or greater than 0.990 (or the correlation coefficient (r) must be equal to or greater than 0.995).

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

13.1.4 System Performance Check Compounds (DoD only)

13.1.4.1 The minimum acceptable RRF for Fluoranthene-d10 and 2-methylnaphthalene-d10 criteria is 0.4. Therefore, they must meet the minimum requirement when the system is calibrated.

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

13.2 Initial Calibration Verification (ICV) – Before sample analysis can begin, the integrity of the standard used to prepare the calibration curve must be verified by the analysis of a second source (see section 10.13, 10.14 and 10.15).

13.2.1 For the ICV to be valid, the recovery for all analytes must be between 70-130%.

13.2.2 For DOD samples the ICV recovery for all analytes must be between 80-120%.

13.3 Continuing Calibration Verification (CCV) – Analyzed prior to sample analysis, after the IB, Tune (DoD criteria only), and ICAL/ICV (if a calibration was performed). A CCV must be run at the beginning of every 12-hour analysis window, after the tune standard. For DOD samples, a CCV must be run at the start of the 12-hour analysis window as well as at the end of the 12-hour analysis window and be of the same source as that which made the curve.

13.3.1 8270C/D/E CCV criteria – All target analytes must be between 80-120%.

13.3.2 8270C/D/E Ending CCV criteria - All target analytes must be between 50-150% (DoD criteria only).

13.3.3 CCV resolution criteria - The height of the valley between benzo(b)fluoranthene and benzo(k)fluoranthene must be less than 50% of the average of the two peak heights.

Note: DOD QSM 5.2 requires that ICV's meet 80-120% drift or %difference.

13.4 Retention Times

13.4.1 CCV retention times - The retention times of the CCV components are checked so that the relative retention time (RRT) of the CCV is within ± 0.06 RRT units of the RRT of the initial calibration. For example, for a 34 minute run, the methods allow the earlier eluting compounds a ± 9 second window and late eluting compounds a ± 122 second window. RRTs may be updated based on the daily CCV.

NOTE: Experience with the instruments may dictate a tighter window, especially for later eluting compounds. If a small shift is seen, adjust the retention times at this time. A small shift is one that can be seen as a result of trimming the column and should be relative in size to that trimming. Any shift that is adjusted for shall have an associated reasonable explanation for that shift. An unknown shift shall require an investigation into the cause of the shift; if warranted, a new calibration curve should be performed.

13.4.2 Internal retention times - The retention times of the internal standards in the CCV must be evaluated immediately after or during the data acquisition. If the retention time for any internal standard changes by more than ±10 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, re-analysis of the QC and samples analyzed while the system was malfunctioning is required. On days when the ICAL is not performed, the initial CCV is used.

13.5 From the 2016 TNI Standards, the laboratory is required to use and document a measure of relative error in the calibration. By employing relative error acceptance criteria, concentrations calculated from the low end of the curve shall have the same confidence in their accuracy as those taken from any other point on the curve. Acceptance criteria must be met.

13.5.1 For calibrations evaluated using an average response factor, the determination of the relative standard deviation (RSD) is the measure of the relative error. If the average response factor acceptance criteria have been met, then acceptance is also met for the relative error.

13.5.2 For calibrations evaluated using correlation coefficient or coefficient of determination, the laboratory shall evaluate relative error by either the measurement of the Relative Error (%RE) or the measurement of the Relative Standard Error (%RSE)

Measurement of the Relative Error (%RE)

Relative error is calculated using the following equation:

$$\%\ Relative\ Error = \frac{x'_i - x_i}{x_i} \times 100$$

xi = True value for the calibration standard
x'i = Measured concentration of the calibration standard

13.5.3 This calculation shall be performed for two (2) calibration levels: the standard at or near the mid-point of the initial calibration and the standard at the lowest level.

13.5.4 The ICV can be used to satisfy the midpoint verification using the acceptance criteria already in place. The low level of the curve can be either recalculated for recovery as if run as an LCS, or a low level standard is to be analyzed. The acceptance criteria for the low level are the same as those used for LCS.

14.0 Procedure

14.1 Sample Preparation:

14.1.1 Water Extraction: see SOP SVOC-001 for waters and aqueous sample.

14.1.2 Soil Extraction: see SOP SVOC-002 for soils and sludges.

14.1.3 Waste Dilutions: see SOP SVOC-003 for wastes requiring a waste dilution.

14.2 GC/MS analysis of samples:

14.2.1 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL of the internal standard solution (section 10.5.4 or 10.5.5) to the 1-mL concentrated sample extract obtained from sample preparation.

14.2.2 Inject a 2 µL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Section 24.5 Table 3). The injection volume must be the same volume used for the calibration standards.

14.2.3 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and re-analyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (4 mg/mL).

14.2.4 The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry.

14.2.5 Qualitative analysis:

See also ADMIN SOP-038: Calibration, Manual Integration, and Rules for Chromatography.
See also TECH SOP-009 Multi-peak Compound Identification for Organics.
See also TECH SOP-010 Establishing and Maintaining Retention Time Windows.
(These three SOPs are required reading for any analyst performing this method).

14.2.5.1 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. The reference mass spectrum must be generated by the laboratory using the GC/MS operating 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.

14.2.5.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

14.2.5.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

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

14.2.5.2 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 sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Diastereomeric pairs (e.g., Benzo(b)fluoranthene and Benzo(k)fluoranthene) that may be separable by the GC should be identified, quantified and reported as the sum of both compounds by the GC.

14.2.5.3 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.

14.2.5.4 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes co-elute (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 co-eluting compound.

14.2.6 Quantitative analysis

See also ADMIN SOP-038 Calibration, Manual Integration, and Rules for Chromatography

14.2.6.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

14.2.6.2 Quantitation is automatically calculated with GCMS Solutions software.

14.2.6.3 The analytical method selected to process (often referred to as “crunch”) the raw data will be the one with the most recent calibration for the analytes to be quantitated. The normal PAH SIMs list will be processed with the PAH curve and will generate a single quant report. If the Appendix 9 (namely 1,4-Dioxane) analytes are to also be processed, a separate analytical method for Appendix 9 (1,4-Dioxane) compounds will be loaded and the raw data run will be quantitated under that processing method as well. This will generate a second quant report. The curve and QC must also be evaluated as passing for those analytes under that extra processing step as well in order to report. The original PAH report and the Appendix 9 report will both then constitute the full processed report.

15.0 Calculations

15.1 Multiply all concentrations by any external dilutions as well as any dilutions incurred during extraction to obtain the final result.

15.2 Relative Retention Time (expressed as a unitless quantity):

$$RRT = \frac{\text{Retention Time of the analyte}}{\text{Retention Time of the IS}}$$

15.3 DDT Breakdown

$$\%\ Breakdown\ 4'4\text{-}DDT = \frac{area\ 4,4'\text{-}DDE + area\ 4,4'\text{-}DDD}{area\ 4,4'\text{-}DDE + area\ 4,4'\text{-}DDD + area\ 4,4'\text{-}DDT} * 100$$

15.4 Average (% RSD) Calibration Calculations:

15.4.1 Calculate the Response factors (RF) or Relative response factor (RRF); for each compound:

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

Where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

15.4.2 Calculate the mean response factor (RF) for each compound:

$$\overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where: n = The number of standards analyzed.

15.4.3 The processing software will calculate the standard deviation (SD) and the RSD of the calibration factors for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left[RF_i - \overline{RF}\right]^2}{(n-1)}} \qquad RSD = \frac{SD}{\overline{RF}} * 100$$

Where: n = The number of standards analyzed.

15.4.4 Calculation of the percent difference (%D) for all analytes in the ICV and/or CCV:

$$\%D = \frac{C_{expected} - C_{found}}{C_{expected}} * 100 = \frac{RF_{ccv} - \overline{RF}}{\overline{RF}} * 100$$

Where:

$C_{expected}$ = the true value of the analyte or surrogate.
C_{found} = the on-column analyte or surrogate result

15.4.5 Determine the concentration of individual compounds in the sample using the following equation:

$$\text{Concentration (ug/L)} = \frac{(As)\,(Is)}{(Ais)\,(\overline{RF})}$$

Where:

A_s = response of the analyte in the sample
I_s = concentration of internal standard present (in ug/L).
A_{is} = response of the internal standard
$\overline{RF}$ = Average Response Factor (unitless)

15.5 Linear Calibration Calculations (using a least squares regression (first-order) calibration fit):

15.5.1 Option 1: X_s is the concentration of the analyte in the calibration standard aliquot introduced into the instrument and Y_s is the ratio of response of the analyte to the response of internal standard times the mass of the internal standard in the calibration standard aliquot introduced into the instrument.

$X_s = C_s$ and $Y_s = A_s \times \frac{C_{is}}{A_{is}}$

Where:

Cs = concentration of analyte in the volume of calibration standard introduced into the instrument.
Cis = concentration of internal standard in the volume of calibration standard injected into the instrument.
As = Peak response of analyte.
Ais = Peak response of internal standard.

15.5.2 Option 2: *x* is the ratio of the analyte concentration in the calibration standard aliquot introduced into the instrument to the internal standard concentration in the calibration standard aliquot introduced into the instrument and *y* is the ratio of response of the analyte to the response of internal standard.

$x = \frac{C_s}{C_{is}}$ and $y = \frac{A_s}{A_{is}}$

Where:

Cs = concentration of analyte in the volume of calibration standard introduced into the instrument.
Cis = concentration of internal standard in the volume of calibration standard injected into the instrument.
As = Peak response of analyte.

Ais = Peak response of internal standard.

15.5.3 The linear least squares regression equation is:

$$y = ax + b$$

Where:
a = The slope of the linear regression.
b = The intercept of the linear regression.

15.5.4 The processing software will calculate the coefficient of determination (r^2) for each analyte by squaring the correlation coefficient as:

$$r^2 = \left[r = \frac{n\sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\sqrt{\left(n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2\right)\left(n\sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i\right)^2\right)}} \right]^2$$

15.5.5 Calculation of the Percent Drift for all analytes in the ICV and/or CCV:

$$\% \text{ Drift} = (\text{Analyte Result} / \text{True Value}) * 100$$

15.5.6 Calculations of sample amounts when using a linear regression calibration fit:

$$\textit{Option 1} \qquad X_s = \frac{\left(\frac{(A_s \times C_{is})}{A_{is}}\right) - b}{a}$$

$$\textit{Option 2} \qquad X_s = \frac{\left(\left(\frac{A_s}{A_{is}}\right) - b\right) \times C_{is}}{a}$$

Where:
X_s = calculated concentration of the analyte or surrogate in the sample aliquot introduced into the instrument
A_s = peak response of the analyte or surrogate in the sample
A_{is} = peak response of the internal standard in the sample
C_{is} = concentration of the internal standard in the sample aliquot introduced into the instrument.
a = The slope of the linear regression.
b = The intercept of the linear regression.

15.6 Percent Recovery for standards and LCS/LCSD

$$\% \text{ Recovery} = (\text{LCS Result} / \text{True Value}) * 100$$

15.7 Percent Recovery for MS and MSD samples

% Recovery = [(MS/D Result - Parent Sample Result) / Spike True Value] * 100

15.8 Dry weight determination:

$$\text{mg/dry kg PH} = \frac{\text{Cs}}{1\text{- (\%moisture/100)}}$$

Where:
Cs = Concentration of Pesticides (in mg/L or mg/kg)

15.9 Relative Percent Difference (RPD)

$$\text{\% RPD} = \frac{|\text{Difference b/w Dups}|}{\text{Average of Dups}} * 100$$

15.10 Method Detection Limit: The MDL is typically calculated as 3.143 times the standard deviation (SD).

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n}\left[X_i - \overline{X}\right]^2}{(n-1)}} \qquad \text{MDL} = \text{SD} \times 3.143$$

Where: n = The number of standards analyzed.
X = One of the seven replicate MDL values.

16.0 Method Performance (See Sections 12.0 Quality Control and 18.0 Data Assessment and acceptance criteria for quality control measures).

17.0 Pollution Prevention

17.1 See Standard Methods section 1100, 22nd Edition / On-Line edition – Waste Minimization and Disposal.

17.2 See SOP Admin-018 and the AEL Safety Manual.

18.0 Data Assessment and acceptance criteria for quality control measures

18.1 It is the responsibility of the analyst to assess all data for quality control acceptance criteria.

18.2 It is the responsibility of the analyst to review all data/data entry for adherence to quality control criteria and any transcription or typographical errors prior to peer or supervisor review.

18.3 It is the responsibility of the analyst and/or supervisor to initiate and/or recommend correction action for out of control data.

18.4 All out of control data will be qualified according to SOP Admin-008.

18.5 See AEL QM Section 10.0.

18.6 All calibration will have a minimum of a five-point curve (Note: a minimum six-point curve is required for a quadratic calibration fit). Points at the ends of the curve may be dropped if they are non-linear. If a data point is not usable or unacceptable within the curve, it will be re-analyzed. A data point for the ICAL can be dropped only if it can be documented as a non-repeatable error.

18.7 Each analytical batch at a minimum will follow the "12 hour rule," where, at the beginning of each 12-hour period, an IB, TUNE (DoD requirement only), and CCV must be analyzed.

18.7.1 The instrument must be free of analytes as exhibited by an instrument blank at the beginning of each analysis window.

18.7.2 The Tune (DoD requirement), where applicable must pass the method criteria for any following data to be reported.

18.7.3 The CCV must meet method acceptance criteria to report unqualified data.

18.7.3.1 If any analyte fails with a low recovery, no data results can be reported for that analyte.

18.7.3.2 If any analyte fails with a high recovery, non-detects can be reported if qualified or properly noted in the case narrative. Corrective action (ex: remixing standard, cleaning injection liner, etc.) will be taken before the next analysis window (or next analytical sequence if the instrument is running multiple analysis windows in one night).

18.8 Method Blank (MB) – The MB must pass the surrogate recovery acceptance limits and be clean of analytes of interest. If there are hits in the method blank, these hits must be below the method detection limit.

18.8.1 If the hits are above the method reporting level, and the samples themselves are clean of those hits (below the MDL), the sample results are fine to report.

18.8.2 If the MB results are above the MDL, and samples have the same hits, then sample results will not be accurate and the MB and samples must be re-analyzed and/or re-extracted to prove that the hits were not contamination.

18.9 Laboratory Control Spikes (LCS) – The LCS must fall within control chart limits for percent recoveries of both analytes for valid data reporting. If the LCS fails, first check the instrument for possible problems. Document any issues, and then re-analyze the LCS. If the LCS still fails, then all samples in the extraction batch must be re-extracted or re-analyzed.

18.10 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Failure to meet control limits for analyte and surrogate recoveries does not in itself require data to be rejected. Data can be flagged (J(4)) for matrix interference.

18.11 At any point in the analytical batch, an analyst may use his/her discretion to fail or reject data he/she feels to be suspicious or in error. At this point, the analyst should seek the help of a supervisor or the QC officer.

18.12 Data should be rejected for individual sample runs if the chromatogram looks odd, retention times shift outside retention time windows, or surrogates fail due to reasons other than matrix interferences.

18.13 Any and all QC failures must be reported to a supervisor and the QC officer.

18.14 Extraction personnel should be informed of any failures immediately. They should also be informed of any trends that develop in sample recoveries.

19.0 Corrective action for out of control data

19.1 See Section 20.0 for out of control or unacceptable data.

19.2 See SOP ADMIN-016 and ADMIN-028.

20.0 Contingencies for handling out of control or unacceptable data

20.1 If a blank failure occurs, any sample containing that analyte will get a ‘V’ qualifier and an NCF is required.

20.1.1 If the MB exhibits contamination, but the samples are BDL for the analytes in question, there is no need for any qualifier nor does an NCF need to be written.

20.2 If the surrogate(s) happen to fall outside of the limits mentioned in Table 5 and Table 6 of section 24, they will be qualified with a “J(1)” or “J(4)” qualifier, depending on whether or not there is matrix interference involved.

20.3 LCS failure

20.3.1 If the LCS fails the lower criteria and there is insufficient sample to re-extract, the sample will be reported as is; however, every analyte that failed will get a “J(3)” qualifier and an NCF is required.

20.3.2 If the LCS fails the upper criteria and the sample is BDL for the analyte in question, the failure will be case narrated. The sample will not be qualified nor does an NCF need to be written.

20.3.3 If the LCS fails the upper criteria and the sample contains a hit for the analyte in question and there is insufficient sample to re-extract, the sample will be reported as is; however, the analyte in question will get a "J(3)" qualifier and an NCF is required.

20.4 If the MS/MSD requires a dilution greater than 1:5, the recovery is suspect and will not be calculated. The MS/MSD failure will be case narrated and the sample will not be qualified.

20.5 If the native sample that is used for the MS/MSD has a target analyte detected at a concentration greater than 4 times the spike value, the spike recovery in the MS and MSD will not be calculated. The MS/MSD failure will be case narrated and the sample will not be qualified.

20.6 See ADMIN-016 for the NCF writing process.

20.7 See ADMIN-028 for the Case Narrative writing process.

20.8 Internal Standard (IS) – The peak areas or heights of the internal standards in the calibration verification standard must be within 50% to 200% (1/2 to 2x) of their respective peak areas or heights in the mid-point calibration standard.

20.8.1 If the IS response is above the QC acceptance criteria, then there is an implied negative bias associated with the sample data:

20.8.1.1 If a deviation of greater than 200% occurs with an individual extract, but the surrogate yield is within the acceptance criteria, then the data can be reported. The acceptable surrogate yield proves that the elevated IS response did not affect the quantitation of extraction efficiency. The elevated IS should be noted on the coversheet for the data pack and in the case narration for the batch.

20.8.1.2 If a deviation of greater than 200% occurs with an individual extract, and the surrogate yield is NOT within the acceptance criteria, optimize instrument performance and inject a second aliquot. The elevated IS response may be impacting the data quantitation.

20.8.1.2.1 If the re-injected aliquot produces an acceptable internal standard response, report the results for the re-analysis.

20.8.1.2.2 If a deviation of greater than 200% is obtained for the re-injected extract, then sample matrix interference may be causing issues with the Internal Standard recoveries. Re-

analysis of the sample should be repeated at a dilution beginning with Section 14.0, provided the sample is still available. Otherwise, report the results obtained from the re-injected extract, but annotate as suspect.

20.8.1.2.2.1 If the dilution re-analysis produces an acceptable internal standard response, report results and note in the case narration that a dilution was required due to sample matrix interferences.

20.8.1.2.2.2 If the dilution re-analysis does not produce an acceptable internal standard response, report results and note in the case narration that the internal standard recoveries were not within QC criteria due to sample matrix interferences.

20.8.2 If the IS response is below the QC acceptance criteria, then there is an implied positive bias associated with the sample data:

20.8.2.1 If a deviation of less than 50% occurs with an individual extract, and the sample does NOT contain target analytes above the Method Detection Limit (MDL), then the data can be reported.

20.8.2.1.1 The positive bias implied by the elevated IS recovery has no effect on a result below the detection limit. The data will be "U" qualified automatically in the report as non-detected. The low IS should be noted on the coversheet for the data pack and in the case narration for the batch.

20.8.2.2 If a deviation of less than 50% occurs with an individual extract, and the sample does contain target analytes above the Method Detection Limit (MDL), but the surrogate yield is within the acceptance criteria, then the data can be reported.

20.8.2.2.1 The acceptable surrogate yield proves that the elevated IS response did not affect the quantitation of extraction efficiency. The low IS should be noted on the coversheet for the data pack and in the case narration for the batch.

20.8.2.3 If a deviation of less than 50% occurs with an individual extract, and the sample does contain target analytes above the Method Detection Limit (MDL), and the surrogate yield is NOT within the acceptance criteria, optimize instrument performance and inject a second aliquot. The elevated IS response may be impacting the data quantitation.

20.8.2.3.1 If the re-injected aliquot produces an acceptable internal standard response, report results for the re-analysis.

20.8.2.3.2 If a deviation of less than 50% is obtained for the re-injected extract, then sample matrix interference may be causing issues with the Internal Standard recoveries. Re-analysis of the sample should be repeated at a dilution beginning with Section 14.0, provided the sample is still available. Otherwise, report the results obtained from the re-injected extract, but annotate as suspect.

20.8.2.3.2.1 If the dilution re-analysis produces an acceptable internal standard response, report results and note in the case narration that a dilution was required due to sample matrix interferences.

20.8.2.3.2.2 If the dilution re-analysis does not produce an acceptable internal standard response, report results and note in the case narration that the internal standard recoveries were not within QC criteria due to sample matrix interferences.

21.0 Waste Management

21.1 Refer to SOP for Waste Management (ADMIN-018) for any other questions.

21.2 See Standards Method section 1090, 22nd Edition / On-Line edition– Waste Minimization and Disposal.

22.0 Cautions/Preventative Maintenance

22.1 Routine, preventative instrument maintenance must be performed and documented in a maintenance logbook to assure optimum instrument performance. All maintenance is documented in the maintenance log in accordance with Quality Manual 8.0.

22.2 System Carryover – Highly concentrated calibration standards and client samples containing high concentrations of target analytes can be retained in the GC systems and bleed out (carryover) into subsequent QC and client samples. Blanks must be analyzed after the initial calibration and "hot" client samples to prove the system is free of such contamination before more batches QC (MB, etc.) are analyzed. It is not acceptable to delete carryover from batch QC or client samples. Client samples must be rerun to confirm suspected hits from carryover.

22.3 Gas Chromatograph

22.3.1 A regular schedule of maintenance is dictated more by the instrument checks and a visual check of the chromatography more than by any set schedule. Most maintenance is done in response to a failure of one of the QC checks done during the course of normal operation or poor chromatographic performance. These checks ensure that the instrument is working at top performance and is proof that the instrument is in good working order.

22.3.2 Injector liners, inlet seals, and other injection port consumables must be cleaned or changed if any related problems occur (i.e. increase baseline, noise, integration, or signal deviations).

22.3.3 Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and "clean" (uniform, without fragmentation) by using the proper column-cutting tool.

22.3.4 Over time, the column will exhibit poorer overall performance. This is due to repeated temperature cycling and the number of heavily contaminated samples being analyzed. The length of time for this to occur varies. The most obvious evidence is calibration difficulties (e.g., more compounds requiring linear or non-linear calibration models) poor resolution, excessive column, bleed, peak tailing and/or the peaks are seen to broaden and flatten. When a noticeable decrease in column performance is evident, and other maintenance options do not result in improvement, the analytical column should be replaced. On average, a column will require replacement once every 6 months to 12 months, but that time can be much sooner dependent on sample matrices and sample load.

22.3.5 "Hot" or "dirty" samples or the cumulative effect of many samples can cause the chromatography to degrade as well. Performing routine maintenance can bring performance back to normal operation. However, in some cases when the chromatography is not improved with this maintenance, the column will require replacement.

22.3.6 A new analytical column must be conditioned according to manufacturer specifications. This typically involves a slow temperature ramp over a period of hours with moderate carrier gas flow through the column. Heating the column without carrier gas flow will irreparably damage the column. The columns should not be heated past the manufacturer's maximum temperature recommendation.

22.3.7 A dirty detector can result with use over time. If the baseline is seen as becoming erratic or the signal response is seen to degrade, this may indicate that the detector needs cleaning. Cleaning the source will most times restore full signal response.

22.4 When any maintenance is performed, the system should be carefully inspected for leaks prior to beginning analysis. Any parts of the instrument that have been recently taken apart and re-assembled are the most likely places for a leak to develop. It is also important to periodically check for leaks at the detectors where the columns are inserted.

22.5 Typical Instrument Preventative Maintenance Schedule – GC/MS

22.5.1 Daily:

22.5.1.1 Keep wash/rinse vials filled with appropriate solvent.

22.5.1.2 Check CCV results to see if a liner or septa change is needed. If the CCV indicates instrument issues, perform inlet maintenance.

22.5.1.3 Check the Helium tank pressure, replace tank as needed.

22.5.2 Monthly:

22.5.2.1 Clean auto-samplers and check that needles are clean and in working condition (clean or replace the syringes if needed.

22.5.2.2 Clean any accumulated dust and dirt off of the instrumentation.

22.5.2.3 Check the fore line pump oil level. Add pump fluid as needed until the oil level in the window is near, but not above, the upper fill line.

22.5.3 Semi-Annual:

22.5.3.1 Run a new Calibration Curve.

22.5.3.2 Clean MS (includes filament replacement and cleaning of ion source, pre-rods, and lenses) when needed.

22.5.4 Yearly:

22.5.4.1 Replace oil in rotary pump.

22.5.4.2 Replace column (or earlier if needed).

23.0 References

23.1 *Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Capillary Column Technique*, Method 8270C, Revision 3, December 1996 in Test Method for Evaluating Solid Waste, Physical/Chemical Methods, U.S. EPA, SW-846.

23.2 *Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Capillary Column Technique*, Method 8270D, Revision 5, July 2014 in Test Method for Evaluating Solid Waste, Physical/Chemical Methods, U.S. EPA, SW-846.

23.3 *Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Capillary Column Technique*, Method 8270E, Revision 6, June 2018 in Test Method for Evaluating Solid Waste, Physical/Chemical Methods, U.S. EPA, SW-846.

23.4 *Determinative Chromatographic Separations*, Method 8000C, Revision 3 in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. EPA, SW-846.

23.5 *Determinative Chromatographic Separations*, Method 8000D, Revision 4 May-2018 in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. EPA, SW-846.

23.6 Standard Methods 22nd Edition / On-Line edition.

23.7 EPA CFR 40 Part 136.6, Appendix B.

23.8 TNI Standards 2016

23.9 ISO 17025: 2005 & 2017 Standards

23.10 DOD Quality Systems Manual

23.10.1 DoD ELAP QSM rev. 5.2, December 2018

23.10.2 DoD ELAP QSM rev 5.3, May 2019.

23.11 AEL Health and Safety Manual.

23.12 AEL Policy and Procedures Manual.

23.13 AEL Quality Manual, latest revision.

23.14 AEL Admin SOPS.

24.0 Tables, Diagrams, flowcharts, and validation data

24.1 PAH Validation Data. See the employee file for the following individuals for an acceptable initial demonstration of capability, which serves as validation data for this method at AEL:

24.1.1 Jacksonville: Carl Martin and Joe Kurtz.

24.1.2 Tampa: Lauren Paladino and Kathryn Ecker.

24.1.3 Miami: Adolfo Fernandez, Ludwing Valentin and Kenneth Vessels.

24.2 1,4-Dioxane Validation Data. See the employee file for the following individuals for an acceptable initial demonstration of capability, which serves as validation data for this method at AEL:

24.2.1 Jacksonville: Joe Kurtz and Josh Mueller.

24.3 Table 1 – Characteristic Ions of Target Analytes, Retention Time, Internal Standard Group, Sim Window

Characteristic Ions of Target Analytes PAH

Compound	Retention Time (min)	Primary Ion	Secondary Ion	Tertiary Ion	Quaternary Ion	Internal Standard Group	Sim Window
Nitrobenzene-d5	2.543	82	54	128		1	1
Naphthalene-d8	3.666	136	54	108		1	1
Naphthalene	3.71	128	129	127		1	1
2-Methylnaphthalene-d10	5.243	152	150	122		1	2
2-Methylnaphthalene	5.335	142	141	115		1	2
1-Methylnaphthalene	5.56	142	141	115		1	2
2-Fluorobiphenyl	6.208	172	170	85		2	2
Acenaphthylene	7.274	152	151	153		2	3
Acenaphthene-d10	7.572	164	162	80		2	3
Acenaphthene	7.635	154	152	153		2	3
Dibenzofuran	7.987	168	139	84		2	3
Fluorene	8.639	166	165	167		2	4
Phenanthrene-d10	10.303	188	80	187	184	3	5
Phenanthrene	10.341	178	179	176		3	5
Anthracene	10.429	178	179	176		3	5
Carbazole	10.74	167	166	139		3	5
Fluoranthene-d10	12.292	212	106	104		3	6
Fluoranthene	12.328	202	101	203		3	6
Pyrene	12.687	202	203	200		4	6
p-Terphenyl-d14	13.016	244	245	122		4	6
Benzo[a]anthracene	14.642	228	229	226		4	7
Chrysene-d12	14.657	240	241	120		4	7
Chrysene	14.698	228	229	226		4	7
Benzo[b]fluoranthene	16.364	252	253	125		5	8
Benzo[k]fluoranthene	16.407	252	253	125		5	8
Benzo[a]pyrene	16.874	252	253	125		5	8
Perylene-d12	16.972	264	132	130	260	5	8
Indeno(1,2,3-cd)pyrene	19.059	276	138	277		5	9
Dibenzo(a,h)anthracene	19.134	278	139	279		5	9
Benzo(g,h,i)perylene	19.672	276	138	277		5	9

Characteristic Ions of Target Analytes 1-4 Dioxane Curve

Compound	Retention Time (min)	Primary Ion	Secondary Ion	Internal Standard Group	Sim Window
1,4-Dioxane-d8	2.12	98	64	1	1
1,4-Dioxane	2.16	88	58	1	1
1,4-Dichlorobenzene-d4	5.33	150	115	2	2
Nitrobenzene-d5	5.89	82	54	2	2

24.4 Table 2 – DFTPP Criteria (DoD only)

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

24.5 Table 3 - Recommended 8270 and DFTPP GC/MS Operating Conditions

Typical 8270 PAH GC Operating Conditions

System	Condition
Injection Volume	2uL
Column Oven Temp	120°C
Injection Temp	240°C
Injection Mode	Split
Flow Control Mode	Pressure
Pressure	97.3 kPa
Total Flow	19.0mL/min
Column Flow	1.19mL/min
Linear Velocity	40.9cm/sec
Purge Flow	0.0mL/min
Split Ratio	15.0
Temperature Program	120°C hold 4min 15mL/min to 270°C hold 0min 12mL/min to 300°C hold 7min
GC Run program time	23.50min

Typical 8270 1,4-Dioxane GC Operating Conditions

System	Condition
Injection Volume	2uL
Column Oven Temp	40°C
Injection Temp	240°C
Injection Mode	Split
Flow Control Mode	Pressure
Pressure	112.0 kPa
Total Flow	64.6 mL/min
Column Flow	2.0 mL/min
Linear Velocity	51.0 cm/sec
Purge Flow	0.0mL/min
Split Ratio	31.3
Temperature Program	40°C hold 2.0min 25mL/min to 250°C hold 0min 40mL/min to 300°C hold 0min
GC Run program time	11.65min

Typical 8270 PAH MS Operating Conditions

System	Condition
Ion Source Temp	260°C
Interface Temp	300°C
Solvent Cut Time*	1.8min
Event time	0.2 sec

*The solvent cut time is a recommended start time. It can be adjusted after the column has been clipped and/or a new column has been installed.

Typical 8270 1,4-Dioxane MS Operating Conditions

System	Condition
Ion Source Temp	260°C
Interface Temp	300°C
Solvent Cut Time*	1.5min
Event time	0.3 sec

Typical DFTPP GC Operating Conditions

System	Condition
Injection Volume	2uL
Column Oven Temp	125°C
Injection Temp	240°C
Injection Mode	Split
Flow Control Mode	Pressure
Pressure	123.1kPa
Total Flow	11.9mL/min
Column Flow	1.49mL/min
Linear Velocity	45.9cm/sec
Purge Flow	0mL/min
Split Ratio	7.0
Temperature Program	125°C hold 2min 25mL/min to 300°C hold 4min
GC Run program time	14.0 min

Typical DFTPP MS Operating Conditions

System	Condition
Ion Source Temp	260°C
Interface Temp	300°C
Solvent Cut Time*	2.9min
Mass Range	40-450m/z (amu)
Scan Time	0.22scan/sec
Scan speed	2000

24.6 Table 4 - Water Surrogate Acceptable Recoveries (from Laboratory Control Charts)

Surrogate Acceptance Range for Waters for Method SIM 8270

Surrogate	**Acceptable % Recovery**
Nitrobenzene d_5	55-111
2-Methylnaphthalene-d10	50-150
2-Fluorobiphenyl	53-106
Fluoranthene-d10	50-150
p-Terphenyl-d_{14}	58-132

24.7 Table 5 - Soil Surrogate Acceptable Recoveries (from Laboratory Control Charts)

Surrogate Acceptance Range for Soils for Method SIM 8270

Surrogate	**Acceptable % Recovery**
Nitrobenzene d_5	37-122
2-Methylnaphthalene-d10	50-150
2-Fluorobiphenyl	46-115
Fluoranthene-d10	50-150
p-Terphenyl-d_{14}	54-127

24.8 Table 6- Typical PAH Analytical Sequence

Calibration Curve Analytical Sequence	Daily Analytical Sequence
DCM Rinse	DCM Rinse
IB	IB
Tune (DOD only)	Tune (DOD only)
ICAL (1 through 9)	CCV
ICV	QC and client samples (12-hour window = 24 injections after tune or CCV)
QC and client samples (12-hour window = 24 injections after tune or CCV)	

**DOD samples require a closing CCV with the criteria of 50-150%. The opening CCV of the second window can be used as the closing CCV for the first analysis window.

24.9 Table 7 –Typical 1,4-Dioxane Analytical Sequence

Calibration Curve Analytical Sequence	Daily Analytical Sequence
DCM Rinse	DCM Rinse
IB	IB
Tune (DOD only)	Tune (DOD only)
ICAL (1 through 7)	CCV
ICV	QC and client samples (12-hour window = 30 injections after tune or CCV)

QC and client samples (12-hour window = 30 injections after tune or CCV)

**DOD samples require a closing CCV with the criteria of 50-150%. The opening CCV of the second window can be used as the closing CCV for the first analysis window.

24.10 Table 8 – Method Required Quality Control for 8270C/D/E

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Blank (IB)	At the beginning of each analytical sequence	No analytes detected above the MDL	Correct problem then re-analyze
Continuing Calibration Blank (CCB)	Analyzed after "hot" client samples	No analytes detected above the MDL	Correct problem then re-analyze
DFTPP Tune (DOD only)	Analyzed after the IB prior to any QC and project samples and every 12 hours	DFTPP criteria – Table 2 DDT breakdown <20%	Correct problem and re-analyze all QC and project
Resolution Check	Performed benzo(b) and benzo(k)fluoranthene on the mid-point calibration standard and on the CCV of every analytical run.	Resolution Criteria - The height of the valley between the 2 isomers must be less 50% of the average height of the 2 peak heights. Correct problem and re-analyze all QC and project	
Minimum five-point initial calibration for %RSD and linear regression (minimum six-point if quadratic regression used)	Prior to sample analysis	8270C: %RSD $\leq$ 15%; linear regression or quadratic regression coefficient of determination $r^2 \geq 0.995$ or correlation coefficient (r) $\geq$ 0.990. 8270D/E: %RSD $\leq$ 20%; linear regression or quadratic regression coefficient of determination $r^2 \geq 0.995$ or correlation coefficient (r) $\geq$ 0.990.	Correct problem then repeat initial calibration
Initial Calibration Verification (ICV)	Analyzed after the ICAL; prior to sample analysis	70% - 130% DOD samples 80% - 120%	Correct problem then repeat initial calibration
Continuing Calibration Verification (CCV)	At the beginning of each analytical sequence and every 12-hours. Run after the DFTPP tune standard.	8270C/D/E: CCC: 80-120% & DMC surrogates RF > 0.4 (DOD only) Closing bracketing CCV required for DOD samples 50-150%	Correct the problem. If the CCV fails high re-analyze all samples that contained hits above the MDL. If the CCV fails low re-analyze all samples bracketed

			by the CCV failure
Initial Demonstration of Capability (IDOC) and Continuing Demonstration of Capability (CDOC)	MB, and 4 replicate second source analyses, prior to analysis of samples; once per year to maintain CDOC's	See Table 13 & Table 14 in Section 24 for control limits, RPD less than 30%	Correct problem and re-analyze or re-extract for analytes that did not meet criteria
Initial Method Detection Limit (MDL) Study	7 replicate LCS (MDL_s) at a concentration at the RL and 7 Method Blanks (MDL_b)	Calculate the MDL_s and the MDL_b. Choose the greater of the two as the initial MDL.	None
Ongoing MDL Data Collection	Every quarter, prepare and analyze 2 spiked samples at the RL on each instrument, in separate batches	Evaluate the spiked samples against the control limits in Table 9 & Table 10 in Section 24.	None
Method Blank (MB)	One per analytical batch of 20 samples or less	No analytes detected above the MDL	Correct problem and re-analyze all samples that contain target analytes above the MDL
LCS and LCSD	One LCS/LCSD per analytical batch of 20 samples or less	See Table 9 and Table10 in section 24 for control limits, RPD less than 30%	Correct problem and re-analyze all samples affected by failure
MS and MSD	One MS/MSD per analytical batch of 20 samples or less	See Table 9 and Table 10 in section 24 for control limits, RPD less than 30%	Flag the data if matrix interference is evident
Surrogate Recoveries	Spiked into every sample including all QC samples	See Table 5 and Table 6 in section 24 for control limits.	Reanalyze, or re-extract and re-analyze, or flag the data

24.11 Table 9 - DOD QSM 5.3 QC Requirements Table B-22

Table B-22. Organic Semi-Volatile Analysis by GC/MS in SIM Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Tune Check	Prior to ICAL and prior to each 12-hour period of sample analysis.	Specific ion abundance criteria of DFTPP from method 8270. Tune check can be acquired as a full scan.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune. In addition to the full scan tune check, optimization for the analytes of interest is recommended.
Deuterated Monitoring Compounds (DMCs) (surrogates)	All field and QC samples.	PAH analysis: DMCs required for polyaromatic hydrocarbon (PAH) target analytes: fluoranthene-d_{10} and 2-methylnaphthalene-d_{10}. Minimum RRF for PAH DMCs: 0.40. All DMCs: Requires 50-150% recovery until in-house limits can be established.	Correct problem, and then reprep and reanalyze all samples with failing DMCs if sufficient sample material is available. If obvious chromatographic interference is present, reanalysis may not be necessary, but the client must be notified prior to reporting data and the failures must be discussed in the Case Narrative.	Apply Q-flag to all associated samples and analytes if acceptance criteria are not met and explain in the Case Narrative.	For non-PAH target analytes, other DMCs with similar chemistry must be assigned. Laboratories may use the same extract for full scan and SIM analysis if the SIM-specific DMCs are added prior to extraction.

Table B-22. Organic Semi-Volatile Analysis by GC/MS in SIM Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Performance Checks	At the beginning of each 12-hour period, prior to analysis of samples.	Degradation ≤ 20% for DDT.	Correct problem, then repeat performance checks.	Flagging is not appropriate.	No samples shall be analyzed until the performance checks are within criteria. DDT breakdown and tailing factors are considered overall measures of port inertness and column performance and are required checks for SIM operation. DDT breakdown and tailing factor checks can be acquired as a full scan.

Table B-22. Organic Semi-Volatile Analysis by GC/MS in SIM Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration (ICAL) for all analytes	At instrument set-up, prior to sample analysis.	Each analyte must meet one of the following options: RSD for each analyte ≤ 20% [If pentachlorophenol is a target analyte, an RSD of ≤ 40% allowed] or Linear least squares regression for each analyte: $r^2 \geq 0.99$.	Correct problem then repeat ICAL.	Flagging is not appropriate.	Minimum 5 levels required for ICAL with one calibration point at the same concentration as the daily CCV. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte.

Table B-22. Organic Semi-Volatile Analysis by GC/MS in SIM Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Evaluation of Relative Retention Times (RRT)	With each sample.	RRT of each reported analyte within ± 0.06 RRT units of the mean RRT of the calibration standards. RRTs may be updated based on the daily CCV.	Correct problem, then rerun ICAL.	NA.	RRTs shall be compared with the most recently updated RRTs. Characteristic ions must maximize in the same scan or within one scan of each other. After any maintenance is performed which could affect retention times, RRTs may be updated based on the daily CCV.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within ± 20% of true value. If pentachlorophenol is a target analyte, a %D from true value of ± 50% is allowed.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.

Table B-22. Organic Semi-Volatile Analysis by GC/MS in SIM Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Continuing Calibration Verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	Concentration the same as the mid-point calibration standard (or lower). All reported analytes within ± 20% of true value. If pentachlorophenol is a target analyte, a %D from true value of ± 50% is allowed. All reported analytes within ± 50% for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) until a passing CCV is attained, and then reanalyze all associated samples since last acceptable CCV. Alternatively, perform an ICAL (including appropriate instrument QC) if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without valid CCVs. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g., average RFs), these additional requirements must also be met.

Table B-22. Organic Semi-Volatile Analysis by GC/MS in SIM Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Internal Standards (IS)	Every field sample, Standards, blanks, and QC sample.	Retention time within ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the initial CCV is used.	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the Case Narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging is not appropriate for failed standards.	Internal Standard is spiked no greater than 0.40 ng/µL concentration. According to the EPA Contract Laboratory Program Statement of Work (CLP SOW), this is the concentration of internal standard specified for SIM analysis. The SOW indicates calibration standards range from 0.10 to 1.0 ng/µL, so 0.40 ng/µL is mid- range. 1, 4-dichlorobenzene-d4 is ignored for SIM.

Table B-22. Organic Semi-Volatile Analysis by GC/MS in SIM Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method Blank (MB)	One per preparation batch, prior to analysis of any field samples.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Conduct investigation to determine the source of the contamination and take appropriate corrective actions. Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated analytical batch.	Laboratories may use the same extract for full scan and SIM analysis provided the applicable DMCs and IS are spiked at the appropriate concentrations. Results may not be reported without a valid Method Blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Laboratory Control Sample (LCS)	One per preparation batch.	A laboratory must use the QSM Appendix C Limits (8270 SIM) for batch control if project specific limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, and then reanalyze the LCS and all samples in the associated analytical batch for failed analytes if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to specific analyte(s) in all samples in the associated analytical batch.	Must contain all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table B-22. Organic Semi-Volatile Analysis by GC/MS in SIM Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Matrix Spike (MS)	One per preparation batch.	A laboratory must use the QSM Appendix C Limits (8270 SIM) for batch control if project specific limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply the J-flag if acceptance criteria are not met and explain in the Case Narrative.	Must contain all analytes to be reported spiked at concentrations appropriate for SIM analysis. For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparation batch.	A laboratory must use the QSM Appendix C Limits (8270 SIM) for batch control if project specific limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 40% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply the J-flag if acceptance criteria are not met and explain in the Case Narrative.	The MSD must contain all analytes to be reported spiked at concentrations appropriate for SIM analysis. All data must be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.

Table B-22. Organic Semi-Volatile Analysis by GC/MS in SIM Mode

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Characteristic ions for MS confirmation	Minimum 3 ions.	The relative intensities of the characteristic ions of target analytes agree within 30% of the relative intensities in the reference spectrum and the relative intensities must be > 0. Confirmation requires S/N ratio of ≥ 3 for each quant and confirmation ion.	No data can be reported without MS confirmation.	NA.	Need 3 structurally significant ions that are logical fragments – not isotopic clusters. Internal standard and DMC can use fewer than 3 ions.

24.12 Table 10 -DoD/DOE QSM 5.3 method 8270 LCS Acceptance Criteria Appendix C Table 27 for all SIM mode analysis.

Table C-27. Method 8270 SIM Solid Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
90-12-0	1-Methylnaphthalene	2267	76.6	11.3	43	111
95-95-4	2,4,5-Trichlorophenol	169	79.9	14.9	35	125
91-58-7	2-Chloronaphthalene	615	76.7	10.5	45	108
321-60-8	2-Fluorobiphenyl	1961	80.6	11.6	46	115
91-57-6	2-Methylnaphthalene	2535	76.8	12.5	39	114
83-32-9	Acenaphthene	2813	77|7	11.2	44	111
208-96-8	Acenaphthylene	2761	77.1	12.8	39	116
120-12-7	Anthracene	2812	82.1	10.7	50	114
56-55-3	Benz(a)anthracene	2827	88	11.4	54	122
50-32-8	Benzo(a)pyrene	2789	87.3	12.5	50	125
205-99-2	Benzo(b)fluoranthene	2790	90.3	12.6	53	128
191-24-2	Benzo(g,h,i)perylene	2739	87.8	13	49	127
207-08-9	Benzo(k)fluoranthene	2761	89.3	11.2	56	123
111-44-4	Bis(2-chloroethyl) ether	192	65.4	15.8	18	113
117-81-7	Bis(2-ethylhexyl) phthalate	181	108.9	13.9	67	150
85-68-7	Butyl benzyl phthalate	144	103.5	10.6	72	135
86-74-8	Carbazole	183	79.3	14.6	36	123

Table C-27. Method 8270 SIM Solid Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
218-01-9	Chrysene	2812	87.5	10.2	57	118
84-74-2	Di-n-butyl phthalate	150	106.5	12.9	68	145
117-84-0	Di-n-octyl phthalate	144	105.5	16.8	55	156
53-70-3	Dibenzo(a,h)anthracene	2778	89.2	13.2	50	129
132-64-9	Dibenzofuran	282	71.9	12.2	35	108
84-66-2	Diethyl phthalate	147	99.3	10.9	67	132
131-11-3	Dimethyl phthalate	149	99.3	9.3	71	127
206-44-0	Fluoranthene	2782	87.3	10.7	55	119
86-73-7	Fluorene	2795	80.6	11.2	47	114
118-74-1	Hexachlorobenzene	201	81.9	14.2	39	125
193-39-5	Indeno(1,2,3-cd)pyrene	2812	89.6	13.5	49	130
62-75-9	n-Nitrosodimethylamine	117	90.7	10.9	58	124
91-20-3	Naphthalene	2823	74.7	12.2	38	111
87-86-5	Pentachlorophenol	259	82.4	15.5	36	129
85-01-8	Phenanthrene	2792	80.8	10.6	49	113
129-00-0	Pyrene	2792	85.8	10.2	55	117

24.13 Table 11 -DoD/DOE QSM 5.3 method 8270 LCS Acceptance Criteria Appendix C Table 28 for all SIM mode analysis.

Table C-28. Method 8270 SIM Water Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
92-52-4	1,1-Biphenyl	106	77.3	7.3	56	99
90-12-0	1-Methylnaphthalene	2566	77.9	12.5	41	115
95-95-4	2,4,5-Trichlorophenol	488	84.1	13.4	44	124
118-79-6	2,4,6-Tribromophenol	164	83.7	12.7	46	122
606-20-2	2,6-Dinitrotoluene	118	67.2	15.8	20	115
91-58-7	2-Chloronaphthalene	717	72.4	12.7	34	111
321-60-8	2-Fluorobiphenyl	747	79.2	8.8	53	106
91-57-6	2-Methylnaphthalene	2984	76.5	12.6	39	114
83-32-9	Acenaphthene	3241	80.9	11.1	48	114
208-96-8	Acenaphthylene	3234	77.8	14.4	35	121
120-12-7	Anthracene	3224	85.8	11	53	119

Table C-28. Method 8270 SIM Water Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
56-55-3	Benz(a)anthracene	3277	89.3	10.1	59	120
50-32-8	Benzo(a)pyrene	3284	86.4	11.2	53	120
205-99-2	Benzo(b)fluoranthene	3248	89.7	12.3	53	126
191-24-2	Benzo(g,h,i)perylene	3178	86	14.1	44	128
207-08-9	Benzo(k)fluoranthene	3167	89.3	11.9	54	125
111-44-4	Bis(2-chloroethyl) ether	775	77.8	12.6	40	116
117-81-7	Bis(2-ethylhexyl) phthalate	275	114.1	19.6	55	173
85-68-7	Butyl benzyl phthalate	159	90.7	17.3	39	143
86-74-8	Carbazole	631	84	13.1	45	123
218-01-9	Chrysene	3215	88.3	10.4	57	120
84-74-2	Di-n-butyl phthalate	153	102.5	14.2	60	145
117-84-0	Di-n-octyl phthalate	157	103.3	19	46	160
53-70-3	Dibenzo(a,h)anthracene	3233	87.2	14.5	44	131
132-64-9	Dibenzofuran	864	77.5	14.1	35	120
84-66-2	Diethyl phthalate	142	94.5	13.5	54	135
206-44-0	Fluoranthene	3242	89.1	10.4	58	120
86-73-7	Fluorene	3232	84.1	11.3	50	118
118-74-1	Hexachlorobenzene	947	84.8	13	46	124
87-68-3	Hexachlorobutadiene	187	84.5	14.7	40	129
193-39-5	Indeno(1,2,3-cd)pyrene	3244	88.7	13.7	48	130
62-75-9	N-Nitrosodimethylamine	162	62.5	10	33	92
91-20-3	Naphthalene	3277	78.8	11.9	43	114
4165-60-0	Nitrobenzene-d5	444	83.1	9.2	55	111
87-86-5	Pentachlorophenol	808	88.4	17.6	36	141
85-01-8	Phenanthrene	3240	83.6	10.3	53	115
129-00-0	Pyrene	3252	87.1	11.3	53	121
1718-51-0	Terphenyl-d14	642	95.1	12.4	58	132

24.14 Table 12 – 1,4-Dioxane water LCS Acceptance Criteria

LCS Acceptance Range for Water for Method SIM 8270

Analyte	Acceptable % Recovery
1,4-Dioxane	59-139