ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN AIR BY GC/MS

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ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN AIR BY GC/MS

1.0 SCOPE AND APPLICATION

The objective of this Standard Operating Procedure (SOP) is to provide guidance on the requirements for the analysis of Polynuclear Aromatic Hydrocarbons (PAH) compounds in air samples using gas chromatography/mass spectrometry (GC/MS). The method is based on modified National Institute for Occupational Safety and Health (NIOSH) Method 5515 for the analysis of PAHs in air samples. A list of compounds routinely analyzed by the Scientific, Engineering, Response and Analytical Services (SERAS) laboratory is provided in Table 1, Appendix A.

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

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

2.0 METHOD SUMMARY

The air samples are collected on two-stage XAD-2 resin tubes with or without a Teflon pre-filter, extracted with methylene chloride, and the extracts analyzed by GC/MS. Prior to GC/MS analysis, a 1 mL aliquot of the extract is spiked with internal standards. Identification and quantitation is made by comparing the retention times and mass spectral data of sample target compounds using the characteristic ions listed in Table 2 with those of known target compounds in the calibration standards.

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

This SOP contains procedures for PAH analysis by both linear scan and Selective Ion Monitoring (SIM) methods. In a linear scan analysis, all mass ions are scanned to detect target and non-target analytes. However, in SIM analysis, only specific mass ions are measured to achieve maximum sensitivity and lower detection limits.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

The XAD-2 resin used for sampling is housed in a glass tube that has been flame sealed. These tubes most often contain 150 or 600 milligrams (mg) of XAD resin. The larger tube (600 mg) can provide greater sensitivity (lower detection limit) by allowing a larger volume of air (up to 100 liters) with less chance of breakthrough and is therefore preferred.

To preserve and store air samples collected using XAD-2 tubes:

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

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

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

2. Solvent vapors in the laboratory and background impurities inherent in the XAD tubes from the manufacturer account for the majority of contamination problems. Each lot of methylene chloride is screened by GC/MS prior to use.

3. Samples can be contaminated by diffusion of PAHs into the sample during storage and handling. A field blank carried through the holding period and the analysis protocol serves as a check on such contamination. One field blank should be submitted and analyzed per sampling event.

5.0 EQUIPMENT/APPARATUS

- Micro syringes, Hamilton gas tight syringes: 10, 25, 50, 100, 500, and 1000 µL, 0.006 inch ID needle

- XAD-2 resin tubes, 150 mg and 600 mg two-stage (SKC, Inc. Catalog No. 226-30-06 or equivalent)

- Teflon filter cassettes, 2 microns (µm), 37 millimeter (mm) outer diameter (OD), optional

- Vials, 2-mL for GC autosampler

- Desorption vials, 4- mL, screw cap with Teflon® cap liner (Supelco Cat #2-3178 or equivalent)

- Hewlett Packard (HP) 6890 GC and 5972 mass selective detector (MSD) equipped with a HP 6890 autosampler and controlled by HP Enviroquant (or equivalent) software

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

6.0 REAGENTS

1. Methylene chloride, glass distilled, suitable for trace level GC analysis

2. Decafluorotriphenyl phosphine (DFTPP), 50 microgram/milliliter (µg/mL), commercially available (Supelco 4-7387, or equivalent. Protect DFTPP from light and refrigerate at 4°C (±2°C).

   Alternatively, this may be prepared diluting 50 microliters (µL) of a commercially available 25,000 µg/mL standard (Supelco 4-8724, or equivalent) in 25 mL of methylene chloride. The prepared solution must be replaced every 6 months or sooner if comparison with quality control check samples indicates a problem.

3. Internal standard mix, 2000 µg/mL, commercially available (Supelco 4-8902, or equivalent) containing the following compounds:

   Acenaphthene - d_{10}
   Naphthalene - d_8
   Phenanthrene - d_{10}
   Chrysene - d_{12}
   Perylene - d_{12}

   For a linear scan analysis, this solution is used without dilution. For a SIM analysis, this solution is diluted to 200 µg/mL prior to spiking. Protect the mixture from light and refrigerate at 4°C (±2°C). Prepared solutions must be replaced every 6 months or sooner if comparison with quality control check samples indicates a problem.

4. Spiking Solution, custom-made mix of the following compounds at 1000 µg/mL for a linear scan analysis. For a SIM scan analysis, this solution is diluted to 100 µg/mL prior to spiking.

   Acenaphthene
   Anthracene
   Acenaphthylene
   Benzo(a)anthracene
   Benzo(a)pyrene
   Benzo(b)fluoranthene
   Benzo(g,h,i)perylene
   Benzo(k)fluoranthene
   Chrysene
   Dibenzo(a,h)anthrarene
   Fluorene
   Fluoranthene
   Indeno(1,2,3-cd)pyrene
   Naphthalene
   Phenanthrene
   Pyrene
   1-Methylnaphthalene
   2-Methylnaphthalene
   2,6-Dimethylnaphthalene
   Benzo(e)pyrene

Biphenyl
Carbazole
Dibenzofuran

Store the spiking solution at 4°C (±2°C) in Teflon-sealed containers, protected from light. The solution should be checked frequently for stability. Prepared solutions must be replaced every 6 months or sooner if comparison with quality control check samples indicates a problem.

5. Stock Calibration Standard, 1000 µg/mL, custom mix, commercially available. For SIM analysis, a 100 µg/mL standard is prepared from this stock calibration standard prior to use.

7.0 PROCEDURES

7.1 Preparation and Extraction

7.1.1 Samples

This method is designed for preparing either 150-mg or 600-mg two-stage XAD resin tubes.

- Allow the XAD tubes and filters to warm up to ambient temperature prior to extraction.
- Remove the glass wool plug from the back portion of the tube and discard.
- The filters, front and back sections of the XAD-2 resin are routinely analyzed separately. Remove the XAD-2 resin packing from the back of the tube and place it in a 4-mL screw-top vial. Label this vial "back" along with the sample identifier. Remove the glass wool that supports the XAD resin in the front portion of the tube and discard. Place the front XAD packing in a second sample vial. Label this vial "front" along with the sample identifier. Remove the filter from the sampling cassette and transfer the Teflon pre-filter to a third vial and label as “filter”.
- Add 2 mL of methylene chloride to each vial and screw the caps on tightly.
- Shake the vials for 2 minutes.
- Let the vials settle 30 minutes. Transfer 1.0 mL of the extract from the vial containing the XAD resin or filter to a 1-mL autosampler vial.
- If the front and back sections are to be analyzed together, place both sections of the XAD resin into a 4-mL vial and add 4 mL of methylene chloride and extract.

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

Break the glass in the front portion of two separate tubes from the same lot used for

sample collection. Transfer the resin from the front section into two separate vials and add the spiking standard directly onto the resin in the vial. For a linear scan, spike the front portion of both tubes with 50 µL of the 1000 µg/mL spiking solution, taking care that the solution is discharged into the middle of the XAD resin. For a SIM analysis, dilute the spiking solution to 100 µg/mL and add 50 µL of 100 µg/mL solution to two separate tubes.

NOTE: If the back section of the lot blank contains target analytes, both portions of the BS/BSD will be extracted and analyzed.

NOTE: If filters are used, a BS/BSD will be prepared using the same lot of filters as that used for sample collection.

7.1.3 Lot Blank

An unopened tube from each lot of tubes used for sample collection and filter is included with every twenty samples or per project. The filter and front and back portions of the lot blank are extracted as in Section 7.1.1.

7.1.4 Field Blank

A blank tube and filter from the same lot may be submitted to the laboratory as a field blank. To qualify as a field blank, the ends of the tube are broken open but no air is drawn through. The field blank accompanies the samples to the laboratory and is extracted as described in Section 7.1.1.

7.2 GC/MS Operating Conditions

The operating conditions used for standard and sample analysis on the HP 6890/5972 GC/MS are listed below. Other conditions may be used as long as the QA/QC and peak identification criteria are met. Any deviation from this SOP must be documented in the case narrative.

The following GC/MS operating conditions are recommended for a linear scan analysis:

Column	Restek Rtx-5MS (crossbonded SE-54) or equivalent 30 meter x 0.25 mm ID, 0.50 µm film thickness
Injection Temperature	280°C
Transfer Temperature	280°C
Source Temperature	Controlled by thermal transfer of heat from transfer line
Temperature Program	70°C for 0.5 min 30°C/min to 295°C; hold for 8 minutes 30°C/min to 315oC; hold for 7 minutes
Pulsed Split Injection (if used)	Pressure pulse = 16 psi for 0.5 minutes, then normal 8:1 Split Ratio
Injection Volume	1 µL

The following GC/MS operating conditions are recommended for a SIM analysis:

Column	Restek Rtx-5MS or equivalent 30 meter x 0.25 mm ID, 0.50 µm film thickness
Injection Temperature	280°C
Transfer Temperature	280°C
Source Temperature	Controlled by thermal transfer of heat from transfer line
Temperature Program	70°C for 0.5 min 20°C/min to 295°C; hold for 10 minutes 30°C/min to 315°C; hold for 5 minutes
Split Injection	Split time = 0.75 min
Injection Volume	1 µL

7.3 DFTPP (Tune)

Tune the GC/MS system to meet the ion abundance criteria listed in Table 3, Appendix A by injecting 50 ng (1 µL) of DFTPP. This criteria must be demonstrated every 24 hours during analysis.

7.4 Initial Calibration

1. Prepare calibration standards at a minimum of six concentration levels (10, 25, 50, 75, 100, 150 µg/mL) for each target compound in methylene chloride from the 1000 µg/mL stock calibration standard for the linear scan. Prepare calibration standards at 0.1, 0.5, 1.0, 5.0, 10 and 25 µg/mL for the SIM analysis. Store all standard solutions at -10 to -20□C in crimp top vials with Teflon® liners protected from the light for a period up to 6 months.

2. For a linear scan analysis, add 20 µL of 2000 µg/ml internal standard solution to each 1 mL aliquot of the six calibration standards resulting in a final concentration of 40 µg/mL. For a SIM scan analysis, add 20 µg/ml of 200 µg/mL internal standard solution to each 1 mL aliquot of the six calibration standards.

3. Inject 1 µL of each of the calibration standards after an acceptable DFTPP analysis.

4. Calculate and tabulate the relative response factor (RRF) of all target analytes in the six calibration standards by using the equation listed in Section 8.0. The primary ions from the specific internal standard and target analyte must be used for quantitation.

5. Calculate and tabulate the average RRF and the percent relative standard deviation (%RSD) for all compounds using the equations in Section 8.0. The average RRF must not be less than 0.05 and the % RSD must be less than or equal to 30% for each compound.

7.5 Continuing Calibration

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

1. Inject 1 µL of a 50 µg/mL standard containing internal standards for a linear scan analysis. For SIM analyses, inject 1 µL of a 5.0 µg/mL standard containing internal standards.

2. Calculate and tabulate the daily RRF for each compound using the equations in Section 8.0. If the minimum RRF of any quantitated analyte (target) is <0.05, the initial calibration curve must be rerun.

3. Calculate the percent difference (% D) of each daily RRF compared to the average RRF from the initial calibration curve. The % D for all compounds can be calculated using the equation listed in Section 8.0. If the %D of any quantitated analyte (target) is >25%, the initial calibration curve must be rerun.

4. All samples are quantitated using the response factors from the daily calibration check unless analyzed on the same day as the initial calibration.

7.6 Sample Analysis

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

1. Add 20µL of the appropriate internal standard solution, depending on whether it is a linear scan or SIM analysis, to the lot blank, field blank, BS/BSD, and all sample extracts.

2. Inject 1 µL of the extract for each BS/BSD, lot blank, field blank, and sample extracts.

3. If the analyst has reason to believe that diluting the final extracts will be necessary, an undiluted run may not be required.

4. If analytes are detected at a level greater than the highest calibration standard, sample extracts must be diluted so that the analyte response is within the linear range established during calibration. Ideally, the concentration of the analyte should fall midrange of the curve after dilution.

5. If dilutions of sample extracts are made, additional internal standards must be added to maintain the required concentration (40 ng/µL for linear scan analysis and 4 ng/µL for SIM scan analysis) of each internal standard in the extract.

7.7 Identification of Target Compounds

Target compound identification will be conducted by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to

verify the identifications:

- *Elution of the sample component at the same GC relative retention time (RRT) as the standard component*
- *Correspondence of the sample component and standard component mass spectra (Not* applicable for SIM analysis)

1 For establishing correspondence of the GC RRT, the sample component RRT must compare within 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 24-hour clock as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

2 For comparison of standard and sample component mass spectra, reference mass spectra must be obtained from the 50 □g/mL standard for linear scan analysis and 5 □g/mL for SIM scan analysis. These standard spectra may be obtained from the run used to obtain reference RRTs.

3 The requirements for qualitative verification by comparison of mass spectra for a linear scan analysis are as follows:

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

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

c. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the quantitation limit, report the actual value followed by "J", e.g., "3J". This requirement is not applicable for SIM analyses.

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

7.8 Identification of Non-Target Compounds

A library search shall be executed for non-target compounds present in blanks and samples for the purpose of tentative identification. Non-target identifications are not made for SIM analyses. For

this purpose, the 1992 release of the National Institute of Standards and Technology (NIST) (or more recent release) shall be used. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

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

2. Guidelines for making tentative identification

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

   - The relative intensities of the major ions should agree within ± 20% between the standard and sample spectra. For example, if an ion has an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30-70%.

   - Molecular ions present in reference spectrum should be present in sample spectrum.

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

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

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

7.9 Desorption Efficiencies

The desorption efficiency (DE) or relative recoveries for a linear scan (Table 4, Appendix A) are determined for each compound at 20, 50, and 200 µg levels (for 600 mg tubes). For SIM analysis (Table 5, Appendix A), the DEs are determined using the 1.0, 10, and 50 µg levels. Three replicate XAD tubes are spiked with a standard solution mixture at each level, extracted with methylene chloride and analyzed by GC/MS. The desorption efficiencies are listed in Tables 3

and 4, Appendix A for the 600 mg XAD tubes. The desorption efficiencies will be determined for each lot of tubes, or once per year whichever is more frequent. Supporting documentation will be kept in a file in the laboratory. The DEs are calculated using the equation in Section 8.4.

7.10 Theoretical Detection Limits and Reportable Method Detection Limits

Theoretical Detection Limits (TDL) for 600 mg tubes listed in Table 6, Appendix A are determined by analyzing seven XAD-2 resin tubes spiked with analytes at 10 µg/mL. For SIM analysis, the TDLs were determined using a concentration of 0.5 µg/mL (Table 7, Appendix A). The 10 µg/mL standard solution represents the lowest concentration on the linear range of the five-point calibration curve. The spiked tubes are subsequently extracted with methylene chloride as in Section 7.1 and analyzed by GC/MS. The TDLs are not used for reporting but only to check extraction efficiency and instrument precision. Each time a desorption efficiency is run, a new set of TDLs will be calculated.

$$TDL = S \times t_{(n-1,1-alpha=0.99)}$$

where:

$t_{(n-1,1-alpha=0.99)}$	=	Student's t value for the 99% confidence level with n-1 degrees of freedom
n	=	number of replicates
S	=	the standard deviation of the replicate analyses
	=	$[\ \Sigma(X_j - \langle X \rangle)^2/(n-1)\ ]^{1/2}$

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

$$MDL = 3.143\ x\ S$$

The reportable Method Detection Limits (MDLs) are based on one half of the lowest calibration point of the calibration range according to the following equation:

$$\text{Reportable MDL} = 1/2\ \text{Low Standard}\ (\mu g/mL) \times \text{Fianl Volume (mL)} \times \text{DE}$$

where:
DE = Desorption Efficiency (from section 8.4)

Compounds detected at less than this concentration will be reported as "J" values.

8.0 CALCULATIONS

8.1 Response Factors and Relative Standard Deviation

The response factor (RRF) is calculated from the calibration standard solution mixture using:

$$RRF = \frac{(A_u)(C_s)}{(A_{is})(C_x)}$$

where:

A_U = Area of characteristic ion of analyte in the standard mixture
A_S = Area of characteristic ion of internal standard in the standard mixture
C_S = Concentration of internal standard in the standard mixture
C_U = Concentration of analyte in the standard mixture

The average RRF and %RSD are calculated using the following equations (for n standards):

$$RRF_{avg} = \frac{RRF_1 + \ldots + RRF_n}{n}$$

$$SD = \sqrt{\frac{\sum_{n=}^{n} (RRF_i - RRFaverage)^2}{n-}}$$

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

8.2 Target Compounds

The amount of analyte in □g is calculated as follows:

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

where:

A_S = Area of characteristic ion for the analyte to be measured
A_{IS} = Area of characteristic ion for the internal standard
C_{IS} = Concentration of internal standard
RRF = Relative response factor of analyte
V = Extraction Volume (mL)
DE = Desorption efficiency (used for tubes only) - lot specific

The concentration of analyte in µg/m^3 is calculated as follows

$$\text{Concentration}\left(\mu g/m^3\right) = \frac{(A+B+C)-(D+E)}{\text{Liters sampled}} \times \frac{1000}{1\ m^3}$$

where
A = µg in front (sample)
B = µg in back (sample)
C = µg on filter
D = µg in front (blank)
E = µg in back (blank)

The concentration of analyte in parts per billion by volume (ppbv) at conditions of 25°C and one atmosphere pressure is calculated as follows:

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

where:
MW = Molecular Weight of the analyte

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

8.3 Percent Difference

The %D is calculated as follows:

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

where:
%D = Percent Difference
RRF_{Daily} = Relative response factor from daily calibration
$RRF_{Average}$ = Average relative response factor from initial calibration

8.4 Desorption Efficiencies

The DEs are calculated as follows:

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

The amount recovered is calculated by:

$$\text{Amount Recovered}\left(\mu g/mL\right) = \frac{(A_s)(C_{is})}{(A_{is})(RRF)}$$

where:

A_S = Area of the characteristic ion for the compound to be measured
A_{IS} = Area of the characteristic ion for the specific internal standard (IS)
C_{IS} = Amount of internal standard added in nanograms
RRF = Average relative response factor from initial or continuing calibration

8.5 Blank Spike/Blank Spike Duplicate Recoveries

For a linear scan analysis, the BS/BSD is determined by spiking blank XAD tubes and/or filters with 50 µg of each analyte. For a SIM analysis, the BS/BSD spike is 5 µg of each analyte. No air is drawn through the XAD tubes. The amount recovered (µg/sample) is calculated using the equation in Section 8.0.

The percent recovery for the BS/BSD and relative percent difference (RPD) can be calculated using the equations below:

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

where:

SBR = spike blank result
BR = blank result

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

where:

RPD = relative percent difference
BSR = blank spike recovery
$BSDR$ = blank spike duplicate recovery

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 DFTPP Tune

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

9.2 Initial Calibration for Target Compounds

Once the tune performance criteria have been met, the GC/MS system must be initially calibrated at a minimum of six concentrations to determine the linear response of the target analytes and surrogate standards.

1. The levels of the initial calibration standards for PAH target compounds are 10, 25, 50, 75, 100, and 150 µg/mL. For SIM analysis, the levels of the initial calibration standards are 0.1, 0.5, 1.0, 5.0, 10, and 25 µg/mL.

2. The calibration of the GC/MS is evaluated on the basis of the magnitude and stability of the RRFs of each target compound. The minimum RRF of each compound at each concentration level must be equal to or greater than 0.05 and the %RSD must not exceed 30%. Once this criteria has been met, blanks and samples may be analyzed.

9.3 Continuing Calibration for Target Compounds

Once the GC/MS system has been calibrated, the initial calibration must be verified by the mid-level calibration standard each 24-hour time period for each GC/MS system during the analysis.

1. The concentration of the continuing calibration standard for target compounds is 50 µg/mL for linear scan analysis and 5.0 µg/mL for SIM.

2. This standard is to be analyzed every 24 hours after an acceptable DFTPP analysis.

3. The continuing calibration of the GC/MS system is evaluated on the basis of the magnitude of the relative response factors and the percent difference between the average RRF of each compound from the initial calibration and the RRF of that compound in the continuing calibration standard. The minimum RRF of each compound in the continuing calibration should be greater than or equal to 0.05 and the %D should not exceed 25%. For any target compounds present in the sample at a concentration greater than the detection limit, those compounds must meet the minimum RRF and %D criteria.

4. If any of the requirements listed in step 3 are not met, another initial calibration will be analyzed.

9.4 Internal Standard Responses and Retention Times

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

1. The amount of each internal standard in a 1 µL injection of sample extract must be 40 ng.

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

3. If samples are quantitated by the initial calibration, the area of each internal standard at 50

µg/mL calibration standard must be used for evaluation.

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

9.5 Lot Blank Analysis

A lot blank is an unopened XAD-2 resin tube and filter from the same lot as the sample tubes. The purpose of the lot blank is to determine the levels of contamination associated with the manufacture, extraction, and analysis of the samples.

1. One lot blank must be extracted and analyzed for every XAD tube and filter lot represented in the sampling event for each project.

2. The lot blank must contain less than or equal to the reportable MDL of any single target compound.

3. If a lot blank exceeds the limits for contamination above, the analyst must investigate the source of contamination and take appropriate corrective before further sample analysis proceeds.

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

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

1. One BS/BSD must be prepared every 20 samples or per project. The BS/BSD must be associated with a method blank that meets the criteria in Section 9.5and must be extracted and analyzed within holding time.

2. The spike solutions specified in Step 4 of Section 6.0 must be used.

3. Spike recoveries and relative percent difference (RPD) of each spike compound in the BS/BSD are calculated according to the equations specified in Section 8.5.

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

Recovery	75 - 125%
RPD	20%

Note: If the laboratory fails to meet the recovery QC limits and the RPD limits on a

routine basis, the Organic Group Leader must investigate the cause and take corrective action.

9.7 Dilution Analysis

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

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

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

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

4. Do not dilute BS/BSD pairs to bring the non-spike compounds into the linear calibration range. When BS/BSD pairs have compounds which are outside the linear calibration range, check with the Organics Group Leader for further instruction.

9.8 Manual Integrations

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

9.9 Tentatively Identified Compounds (TICs)

An estimated concentration for TICs must be calculated by the internal standard method for linear scan only. For quantitation, the nearest preceding internal standard free of interferences shall be used. The formula for calculating concentrations is the same as in Section 8.2 except that the area count or peak height of the TICs and their assigned internal standard from the total ion chromatogram is used for quantitation. An RRF of 1.0 is assumed. All non-target concentrations are reported to two significant figures

10.0 DATA VALIDATION

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

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

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

11.0 HEALTH AND SAFETY

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

12.0 REFERENCES

National Institute for Occupational Safety and Health. 1994. NIOSH Manual of Analytical Methods. Method 5515.

United States Environmental Protection Agency, Contract Laboratory Program. 1999. *Statement of Work for Organic Analysis*. OLM04.2.

13.0 APPENDICES

A - Tables
B - Data Validation Criteria

ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN AIR BY GC/MS

APPENDIX A
Tables
SOP #1817
March 2002

ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN AIR BY GC/MS

TABLE 1. Target Compound List

Naphthalene	Fluoranthene
2-Methylnaphthalene	Pyrene
1-Methylnaphthalene	Benzo(a)anthracene
Biphenyl	Chrysene
2,6-Dimethylnaphthalene	Benzo (b) fluoranthene
Acenaphthylene	Benzo (k) fluoranthene
Acenaphthene	Benzo (e) pyrene
Dibenzofuran	Benzo (a) pyrene
Fluorene	Indeno (1,2,3-cd) pyrene
Phenanthrene	Dibenzo (a,h) anthracene
Anthracene	Benzo (g,h,i) perylene
Carbazole	

ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN AIR BY GC/MS

TABLE 2. Characteristic Ions for Target Compounds and Surrogates

COMPOUND	PRIMARY ION	SECONDARY ION
d8-Naphthalene (IS)	136	108
Naphthalene	128	129, 127
2-Methylnaphthalene	142	141, 115
1-Methylnaphthalene	142	141, 115
Biphenyl	154	153, 152
2,6-Dimethylnaphthalene	156	141, 128
d10-Acenaphthene (IS)	164	162
Acenaphthylene	152	151, 153
Acenaphthene	153	152, 151
Dibenzofuran	168	139
Fluorene	166	165, 167
d10-Phenanthrene (IS)	188	189
Phenanthrene	178	176, 179
Anthracene	178	176, 179
Carbazole	167	166, 168
Fluoranthene	202	101, 200
Pyrene	202	200, 101
d12-Chrysene (IS)	240	236
Benzo (a) anthracene	228	226, 229
Chrysene	228	226, 229
d12-Perylene (IS)	264	260
Benzo (b) fluoranthene	252	126, 250
Benzo (k) fluoranthene	252	126, 250
Benzo (e)pyrene	252	250, 126
Benzo (a) pyrene	252	250, 126
Indeno (1,2,3-cd) pyrene	276	138, 277
Dibenzo (a,h)anthracene	278	279, 138
Benzo (g,h,i) perylene	276	277, 138

IS denotes Internal Standard.

TABLE 3. Ion Abundance Criteria for Tune (DFTPP)

Mass	Ion Abundance Criteria
51	30.0 - 80.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	0 - 100 percent of mass 198
70	Less than 2.0 percent of mass 69
127	25.0 - 75.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0 - 9.0 percent of mass 198
75	10.0 - 30.0 percent of mass 198
65	Greater than 0.75 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110 percent of mass 198
443	15.0 - 24.0 percent of mass 442

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

TABLE 4. Typical Desorption Efficiencies (Linear Scan)

	20 µg	50 µg	200 µg
Naphthalene	1.0534	1.0469	1.1406
2-Methylnaphthalene	1.1103	1.0759	1.1472
1-Methylnaphthalene	1.0823	1.0672	1.1590
Biphenyl	1.1249	1.0754	1.1503
2,6-Dimethlynaphthalene	1.1194	1.0719	1.1369
Acenaphthylene	1.1619	1.0843	1.1458
Acenaphthene	1.0760	1.0359	1.1511
Dibenzofuran	1.1385	1.0785	1.1591
Fluorene	1.1494	1.0710	1.1412
Phenanthrene	1.0718	1.0326	1.1263
Anthracene	1.0225	0.9782	1.0542
Carbazole	1.1696	1.0830	1.1159
Fluoranthene	1.1862	1.1108	1.1576
Pyrene	1.1788	1.0997	1.1594
Benzo(a)anthracene	1.4375	1.3889	1.3327
Benzo(b)fluoranthene	1.0703	1.1794	1.1632
Benzo(k)fluoranthene	1.1468	1.1743	1.1740
Benzo(e)pyrene	1.1909	1.2126	1.2254
Benzo(a)pyrene	1.2341	1.2546	1.2215
Indeno(1,2,3-cd)pyrene	1.2579	1.2364	1.2126
Dibenzo(a,h)anthracene	1.2195	1.2039	1.1860
Benzo(g,h,i)perylene	1.2443	1.2452	1.2289

TABLE 5. Typical SIM Desorption Efficiencies

	1.0 µg	10 µg	50 µg
Naphthalene	1.0949	1.0142	1.0412
2-Methylnaphthalene	1.2821	0.9980	0.9832
1-Methylnaphthalene	1.2397	0.9753	0.9943
Biphenyl	1.2712	0.9940	0.9850
2,6-Dimethlynaphthalene	1.2712	0.9843	0.9663
Acenaphythylene	1.2931	0.9778	0.9624
Acenaphthene	1.2097	1.0128	1.0541
Dibenzofuran	1.2712	1.0087	1.0138
Fluorene	1.2605	0.9927	0.9893
Phenanthrene	1.2397	1.0737	1.0619
Anthracene	1.2295	0.9452	0.9361
Carbazole	1.3393	0.9954	0.9387
Fluoranthene	1.1905	0.9524	0.9596
Pyrene	1.1905	0.9759	0.9738
Benzo(a)anthracene	1.2397	0.9677	0.9611
Chrysene	1.2000	1.0359	1.0675
Benzo(b)fluoranthene	.7895	0.9530	0.9495
Benzo(k)fluoranthene	1.1628	0.9628	1.0098
Benzo(e)pyrene	1.2821	1.0246	1.0294
Benzo(a)pyrene	1.3761	0.9191	0.8637
Indeno(1,2,3-cd)pyrene	1.5957	0.9921	0.9263
Dibenzo(a,h)anthracene	1.5000	1.0020	0.9524
Benzo(g,h,i)perylene	1.4423	1.0653	1.0349

TABLE 6. Typical TDL Results for PAH Compounds in 600 mg XAD-2 Tubes
Results (µg/ml in extract)

Compound	TDL
Naphthalene	1.1
2-Methylnaphthalene	1.2
1-Methylnaphthalene	1.1
Biphenyl	1.3
2,6-Dimethlynaphthalene	1.3
Acenaphthylene	1.4
Acenaphthene	1.2
Dibenzofuran	1.3
Fluorene	1.3
Phenanthrene	0.9
Anthracene	1.4
Carbazole	1.1
Fluoranthene	1.5
Pyrene	1.3
Benzo(a)anthracene	2.9
Chrysene	4.0
Benzo(b)fluoranthene	3.1
Benzo(k)fluoranthene	4.6
Benzo(e)pyrene	3.3
Benzo(a)pyrene	3.6
Indeno(1,2,3-cd)pyrene	3.3
Dibenzo(a,h)anthracene	3.3
Benzo(g,h,i)perylene	3.3

Results based on □g/mL in extract. Actual spike = 10 □g/tube.

TABLE 7. Typical TDL SIM Results for PAH Compounds in 600 mg XAD-2 Tubes
Results (µg/ml in extract)

Compound	TDL
Naphthalene	0.09
2-Methylnaphthalene	0.10
1-Methylnaphthalene	0.10
Biphenyl	0.10
2,6-Dimethlynaphthalene	0.21
Acenaphythylene	0.12
Acenaphthene	0.12
Dibenzofuran	0.10
Fluorene	0.11
Phenanthrene	0.09
Anthracene	0.13
Carbazole	0.11
Fluoranthene	0.10
Pyrene	0.12
Benzo (a) anthracene	0.10
Chrysene	0.08
Benzo (b) fluoranthene	0.39
Benzo (k)fluoranthene	0.10
Benzo (e)pyrene	0.10
Benzo (a) pyrene	0.10
Indeno (1,2,3-cd) pyrene	0.13
Dibenzo (a,h) anthracene	0.16
Benzo (g,h,i) perylene	0.12

Results based on µg/mL in extract. Actual spike = 0.5 µg/tube.

ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN AIR BY GC/MS

APPENDIX B
Data Validation Criteria
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ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN AIR BY GC/MS

Data Validation Criteria

Parameter	**Method SERAS #1817**
Extract Hold Times	14 days from sampling; < 21d□J; >21d □ J detects, □R non-detects
Lot Blank Contamination	Background subtraction of lot blank from front and back separately.
Mass Spectrometer Tuning	DFTPP - CLP criteria every 24 hrs.; if not met □R
R. F. Minimum	0.05; if <0.05 □J detects, □R non-detects
ICAL Conc. Range	10,25, 50, 75, 100, and 150 ppm for linear scan 0.1, 0.5, 1.0, 5.0, 10, 25 ppm for SIM
ICAL Number of Stds.	6 standards
ICAL %RSD	≤30; >30% □ J detects; 50-90 % □- >J non-detects;>90% □R non-detects,
CCAL Standard. Concentration	50 ppm for linear scan/5.0 ppm for SIM (mid-point)
CCAL %D	25%;>25% □J detects; 50-90% □J non-detects; >90% □R non-detects
Internal Standards	RT 0.5 min., 50 - 200 % corr. Cal. Area., > 25% □J detects and non-detects; < 25 % □ non-detects R
Compound Identification	RT ± 0.06 RRT; all ions >10% present, within 20% of reference
BS/BSD	50 □g total - 0 % recovery detects□J, non-detects □R
Field Blank	All associated sample results <5X blank □ non-detect
Desorption Efficiencies	New set every year or for every new media lot.