ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN DUST BY GC/MS-SIM

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1.0 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) outlines the preparation and analysis of polynuclear aromatic hydrocarbons (PAHs) in dust matrices using gas chromatography/mass spectrometry (GC/MS) in the select ion monitoring (SIM) mode to achieve lower method detection limits (MDLs). The compounds of interest analyzed and the corresponding reporting limits (RLs) are included in Table 1, Appendix A.

2.0 METHOD SUMMARY

The dust sample is passed through a 100-mesh sieve prior to analysis. Approximately 0.5 gram (g) of the sieved sample is extracted with 140 milliliters (mL) of methylene chloride/acetone (80:20) in a Soxtherm extractor. The extracted solution is subsequently concentrated to 0.5 mL.

The final extract is spiked with an internal standard mix and analyzed using GC/MS in the SIM mode. Target analytes are identified by comparing the measured mass spectra and retention times with those obtained from calibration standards acquired under the same operating conditions used for the samples. Quantitation of each identified target compound is calculated based on the internal standard method. Table 2, Appendix A lists the characteristic ions of each target analyte and Table 3, Appendix A lists the internal standards with the corresponding target analytes assigned for quantitation.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

3.1 Sample Storage

Samples may be collected in plastic ziplock bags or in wide mouth glass containers with a Teflon-lined cap. From the time of collection until after analysis, extracts and unused samples must be protected from light. They must be refrigerated at 4±2 degrees Centigrade (^{o}C) for the periods specified by Task Leader and/or Work Assignment Manager (WAM) of the project.

Samples, sample extracts, and standards must be stored separately in an atmosphere free of all potential contaminants.

3.2 Holding Times

Extraction of samples shall be completed within 14 days from date of collection, and analysis completed within 40 days after sample extraction.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks on a routine basis. 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.

5.0 EQUIPMENT/ APPARATUS

The following equipment/apparatus is required:

- Soxtherm extractor, including extraction flask, sample holding vessel, chiller, manufactured by Gerhardt or equivalent
- Cellulose thimbles, commercially available
- Analytical balance, capable of accurately weighing " 0.001 g
- Class "S" weights for calibrating balance
- Spatula, stainless steel or Teflon
- Clear sampling jar, 4 and 8 ounce (oz)
- Pyrex glass wool, baked at 400EC for at least 4 hours
- Test tube rack
- Teflon boiling chips, approximately 10/40 mesh. Heat to 400EC for 30 minutes or Soxhlet extract with methylene chloride
- Volumetric flasks, Class A, 50 mL, 25 mL, 10 mL
- Desiccator with indicating desiccant
- Disposable glass Pasteur pipettes
- TurboVap concentrator, with six positions for concentrating extracts.
- TurboVap concentrator cells, 200 mL
- TurboVap concentrator cell rack
- Clean Bath solution, for use in TurboVap concentrator
- GC autosampler glass vials with crimp caps, 2 mL
- Agilent Technologies 6890 gas chromatograph (GC) and 5972/5973 mass selective detector (MSD) or equivalent, equipped with an autosampler and controlled by Enviroquant (or equivalent) software
- Restek Rtx-5 fused silica capillary column, 30 meter (m) x 0.25 millimeter (mm) inner diameter (ID), 0.5 micron (µm) film thickness (or equivalent)
- Syringes, 500 microliters (µL)
- 100-Mesh Sieve, 150 µm, brass or stainless steel, meeting American Society for Testing and Materials (ASTM) specifications E11

6.0 REAGENTS

- Sodium Sulfate, anhydrous powder, reagent grade, heated at 400°C for four hours, cooled in a desiccator and stored in a glass bottle

- Methylene Chloride, pesticide residue analysis grade or equivalent

- Acetone - pesticide residue analysis grade or equivalent

- PAH Stock Calibration Standard, custom mix, consisting of each of the target analytes in 50:50 benzene/methylene chloride at 1000 micrograms per milliliter (µg/mL) (Table 1, Appendix A)

- PAH Intermediate Calibration Standard, 10 µg/mL - Add 100 uL of the 1000 µg/mL to methylene chloride in a 10 mL Class A volumetric flask. Dilute to the mark with methylene chloride.

- PAH Working Calibration Standards - Using a serial dilution technique, prepare the other four standards from the 10 µg/mL intermediate standard at concentrations of 0.1, 0.5, 1.0 and 5.0 µg/mL in methylene chloride.

  Alternatively, calibration standards at the five concentration levels may be purchased from an outside vendor, if available.

- Surrogate Stock Solution, 1000 µg/mL, containing nitrobenzene-d_5, 2-fluorobiphenyl and terphenyl-d_{14} in methylene chloride, commercially available (Supelco #4-8925 or equivalent)

- Surrogate Working Solution, 2 µg/mL - Add 50 µL of the 1000 µg/mL surrogate stock solution to a 25-mL Class A volumetric flask containing methylene chloride. Dilute to the mark with methylene chloride.

- Matrix Spike (MS) Stock Solution, containing acenaphthene and pyrene each at 1000 µg/mL in methylene chloride , commercially available (Supelco #4-8869 or equivalent). This solution must be a different source from that used for calibration.

- MS Working Solution, 2 µg/mL - Add 50 µL of the 1000 :g/mL stock MS solution to methylene chloride in a 25-mL Class A volumetric flask. Dilute to the mark with methylene chloride. Alternatively, a MS stock solution containing acenaphthene and pyrene at 100 µg/mL may be purchased (AccuStandard or Ultra Scientific) and diluted accordingly.

- Internal Standard Stock Mix, 2000 µg/mL, consisting of six internal standards in methylene chloride (1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}), commercially available (Supelco #4-8902 or equivalent).

- Internal Standard Working Solution, 1000 µg/mL - Make a 1:1 mixture of the internal stock standard mix in methylene chloride. Add one µL of this solution to each 0.5-mL sample extract. The amount of each internal standard in each 1 µL injection will be 2 nanograms (ng).

- Decafluorotriphenylphosphine (DFTPP), 50 µg/mL, commercially available in methylene chloride (Supelco #4-7387 or equivalent). The amount of DFTPP in a 1-µL injection is 50 ng.

NOTE: All calibration standard, internal standard, surrogate and spiking solution preparation will

be documented in accordance with Scientific, Engineering, Response and Analytical Services (SERAS) SOP #1012, *Preparation of Standard Solutions and Reagents.*

NOTE: Store the working solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced every 6 months or sooner, if comparison with quality control (QC)check samples indicates a problem. Premixed pre-certified stock standards will be stored according to the manufacturer's documented storage requirements. These standards may be kept in storage up to the manufacturer's stated expiration date. Once the stock surrogate solutions are opened, the standards will be stored for a period not to exceed six months from the date opened or the original expiration date, whichever is less.

7.0 PROCEDURES

7.1 Sample Preparation

7.1.1 Sample Sieving Procedure

If the sample has not been sieved, use the following procedure. If the sample is already sieved, proceed to step 7.1.2.

- Clean the sieve using the procedure in Appendix B.
- Select a clean working area in a facility equipped with a fume hood (a 4-foot by 4-foot area is sufficient). Weigh the receiver pan on an analytical balance and record the weight.
- Empty the entire contents of the sample into the 100-mesh sieve with the receiver pan attached.
- Place the cover on the sieve and manually or mechanically shake the sieve for a minimum of 5 minutes and a maximum of 10 minutes until all the fine dust particles are collected in the bottom receiver pan. If manual shaking is performed, follow the instructions given in ASTM D-422: "Conduct the sieving operation by means of a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. Continue sieving until not more than 1 mass percent of the residue on a sieve passes that sieve during 1 minute of sieving".

  If mechanical shaking is performed, set up the recommended sieve shaker on an even and stable surface. Proceed with the sieving operation following directions in the manufacturer's manual.
- Re-weigh the receiver pan using an analytical balance. The difference in weight is the weight of the sieved sample. If total weight of material is desired, the coarse material remaining on top of the sieve must be collected on a pre-weighed sheet of aluminum foil, re-weighed and the weight added to the weight of the sieved sample.
- Transfer the sieved sample from the receiver pan to an 8-oz wide-mouth glass jar. Use a camel hair brush to ensure complete transfer of the sample. Cap the glass jar

securely.

- Before processing the next sample, thoroughly wipe clean the cover, sieve and receiver pan using a Kimwipe and deionized/distilled water. Let dry prior to sieving additional samples.

7.1.2. Soxtherm Extraction

- Calibrate the balance with class "S" weights prior to weighing samples or blanks. The balance should be calibrated with a weight that is similar to the weight used to extract the sample (i.e., 0.5 gram).

- Weigh approximately 0.5 g of each sieved sample to the nearest 0.001 g into a 4-oz sampling jar. The sample is then thoroughly mixed with 20 g of anhydrous granular sodium sulfate. The sample should have a sandy texture at this point.

- A method blank is prepared using 20 g of baked sodium sulfate at the frequency of one for every 20 samples using the same preparation technique as for the samples.

- Prepare a Laboratory Control Sample (LCS) by adding 0.25 mL of the MS working solution to 20 g of anhydrous sodium sulfate at the frequency of one for every 20 samples using the same preparation technique as for the samples.

- Select a sample to be used for the matrix spike/matrix spike duplicate (MS/MSD). Weigh two additional 0.5 g portions of this sample to the nearest 0.001 g. The MS/MSD is done with the frequency of one per 10 samples or ten percent of each batch.

  NOTE: The sample to be used for the MS/MSD may be specified on the Chain of Custody record.

- Place the blended sample and sodium sulfate in each prewashed cellulose thimble and insert the thimble into a Soxtherm extraction flask containing one or two clean boiling chips

- Add 0.25 mL of the surrogate working solution to method blanks, MS/MSD, and all samples.

- Add 0.25 mL of the MS working solution to each of the MS/MSD samples.

- In a fume hood, place 140 mL of 80:20 methylene chloride/acetone into the sample holding vessel.

- Connect the cooling hose from the Soxtherm to the chiller. Care must be taken to ensure that cooling is sufficient (e.g., the temperature of the chiller should not be higher than 6 EC).

- Attach each extraction flask to the Soxtherm extractor and extract the sample(s) for approximately 2 hours. The extraction conditions are listed in Table 5, Appendix A.

- Allow the extract to cool after the extraction is completed.
- Transfer the extract from Soxtherm to TurboVap tube.

7.1.3. TurboVap Concentration

- Fill the TurboVap water bath with approximately one gallon of deionized water mixed with 10-15 drops of Clean Bath solution. Set the water bath temperature at 45°C.
- Transfer the extract to a 200-mL TurboVap tube in a fume hood outside the concentrator. Rinse the Soxtherm extraction flask several times with methylene chloride and add solvent rinses to the Turbovap tube. Start concentrating the extract by blowing a gentle stream of nitrogen into the tube(s). Carefully adjust the nitrogen stream so that solvent does not splash out of the tube. Periodically, rinse the inner wall of the tube with methylene chloride.
- Concentrate the extract until the solvent level drops to the stem of the tube. This is visible by looking straight down into the tube and the solvent remains in the inner circle of the tube. At this point, the extract volume is approaching 0.5 mL and should be monitored carefully until it reaches 0.5 mL so the extract does not evaporate to dryness. When removing a tube from the water bath, ensure that water droplets do not fall into other extract tubes.
- Transfer the extract into a 2-mL GC autosampler vial. The extract is now ready for analysis. If the analysis is not performed immediately, the extract should be protected from light and refrigerated at 4°C (±2°C).

7.2 Total Solids (Optional)

The total solids of the sample is prepared in conjunction with the sample extraction. The total solids for the MS/MSD samples is based on the corresponding sample. The total solids of the blank is treated as 100 percent (%).

Weigh and record an empty aluminum dish to the nearest 0.01 g. Weigh at least 10 g of a dust sample into the aluminum dish. The sample dish is heated in an oven set at 103 to 105°C inside a fume hood overnight. Remove the sample dish from the oven the following day and place in a desiccator to cool before re-weighing. Weight the residue and calculate the percent total solids based on the following equation:

$$\%\,Total\ Solids = \frac{Weight\ of\ Dried\ Sample\ with\ Dish\ (g) - Dish\ Weight\ (g)}{Weight\ of\ Wet\ Sample\ with\ Dish\ (g) - Dish\ Weight\ (g)}\ x\ 100$$

7.3 GC/MS Operating Conditions

The typical operating conditions used for analysis of standards, samples and blanks on the GC/MSD are listed below. Other conditions may be used as long as quality assurance (QA)/QC

and peak identification criteria are met. Any deviations from this SOP must be documented in the case narrative.

Column ID	Restek Rtx-5, 30 m x 0.25 mm ID, 0.5 µm film thickness fused silica capillary (or equivalent)
Injector Temperature	280°C
Transfer Temperature	280 °C
Source Temperature	230 °C
Temperature Program	50 °C for 0.5 minutes 20 °C /min to 295 °C hold for 5.25 minutes 35 °C/min to 310°C hold for 6.57 minutes*
Injection Mode	Pulse splitless, pulse pressure= 16 psi for 0.5 min
Injection Volume	1 µL

* May be extended to reduce carryover from samples that contain a high concentration of target or non-target compounds.

MSD SIM conditions are as follows:

Group Number**	Monitoring ions	Dwell time
1 (4.5)	54, 82, 102, 108, 115, 128, 136 and 152	20 msec
2 (7.5)	76, 152, 153, 154, 162, 164, 165, 166, 171 and 172	20 msec
3 (10.0)	101, 122, 176, 178, 188, 189, 202, and 244	20 msec
4 (13.5)	120, 114, 228, and 240	20 msec
5 (16.0)	126, 132, 138, 139, 252, 264, 276, and 278	20 msec

** Numbers in parentheses represent approximate start time msec = milliseconds

7.4 DFTPP Tune

The instrument must be tuned by injecting 50 ng of DFTPP to meet the ion abundance criteria listed in Table 4, Appendix A. The tune is acquired using either the apex or ± one scan. The DFTPP tune criteria must be met every 12 hours during sample analysis.

7.5 Initial Calibration

1. Add 1 µL of the internal standard working solution to each 0.5 mL aliquot of the five calibration standards.

2. After DFTPP passed the criteria, set up the run using the five-level calibration standards.

3. Use the following equation to calculate and tabulate relative response factor (RRF) of all target compounds and surrogates in all five calibration standards. The primary ions of the internal standard must be used for calculation.

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

where:

A_X = Area of the characteristic ion of each target analyte
A_{IS} = Area of the characteristic ion of each internal standard assigned to target analytes
C_{IS} = Concentration of each internal standard, nanograms per microliter (ng/:L)
C_X = Concentration of each target analyte (ng/:L)

4. Use the following equations to calculate and tabulate average RRF and percent relative standard deviation (% RSD) for all target analytes:

$$RRF_{avg} = \frac{RF_1 + \ldots + RF_5}{5}$$

$$SD = \sqrt{\frac{\sum_{n=1}^{} RF_i - RF_{average}}{4}} \qquad \%RSD = \frac{SD}{RRF_{average}} x\ 100$$

5. The average RRF for each analyte must not be less than 0.050. The % RSD should be less than or equal to 15% for each target analyte with the exception of the calibration check compounds (CCCs). The %RSD for the CCCs must be equal to or less than 30% for the following analytes:

Acenaphthene
Fluoranthene
Benzo(a)pyrene

7.6 Continuing Calibration

A check of the initial calibration curve must be performed every 12 hours during sample analysis.

1. Inject 1 µL of the 1 µg/mL calibration standard that contains target analytes, surrogates, and internal standards.

2. Calculate and tabulate the daily RRF for all analytes.

3. Use the following equation to calculate percent difference (% D) between each daily RRF and average RRF from the initial calibration curve.

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

4. The initial calibration curve must be rerun if the minimum RRF of any target analyte in the continuing calibration is < 0.050.

5. Rerun the initial calibration curve if the %D of any quantitated target compound or any MS compound (acenaphthene and/or pyrene) exceed 20%.

7.7 Sample Analysis

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

1. Add 1 µL of the internal standard working solution into each method blank, MS/MSD, and all sample extracts.

2. Inject 1 µL of each sample, method blank or MS/MSD extract into the GC/MS.

3. If the response of any analyte exceeds that of the highest calibration standard (i.e., 10 µg/mL), the sample extract must be diluted so that the analyte response falls within the linear range established in the initial calibration. Ideally, the concentration of the analyte should fall between midrange and the upper portion of the curve after dilution.

4. If a dilution is prepared, the internal standard mix is added to the diluted sample to maintain the required concentration of 2 ng/µL of each internal standard in the diluted extract.

7.8 Identification of Target Analytes

The target analytes are identified by comparison of the SIM sample mass spectra with the SIM mass spectra of a calibration standard. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component at the GC relative retention time (RRT) as the standard component

- Correspondence of the sample component and standard component mass spectra

1. For establishing correspondence of the 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 on the same 12-hour clock as the sample. If co-elution 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 components, reference mass spectra must be obtained from the 1 :g/mL calibration standard. The standard mass spectra may be obtained from the run used to obtain the reference RRTs. In the case of co-elution of standard components, the analyst can use professional judgment to establish the presence of target analytes. If professional judgment is used, it will be documented in the case narrative.

3. The requirements for qualitative verification of mass spectra are as follows:

   a. All secondary ions present in the standard mass spectra (most abundant ion equals 100%)

must be present in the sample mass spectra

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

4. If a analyte cannot be verified by all of the criteria in Step 3 but is identified by the technical judgment of the mass spectral interpretation specialist, the analyst will report that identification and proceed with the calculation described in Section 8.0. The analyst must report in the case narrative that the technical judgment was utilized.

8.0 CALCULATIONS

8.1 Target Compounds

Identified target compounds must be quantitated by the internal standard method. The internal standard used must be the one nearest the retention time to that of the given analyte listed in Table 3, Appendix A. The area of the characteristic ion of each target analyte listed in Table 2, Appendix A is used for quantitation.

Use the following equation to calculate the concentration of the identified analytes using the daily RRF obtained from the continuing calibration curve in Section 7.6. If samples are analyzed after the initial calibration, the average RRF must be used.

$$C_c\,(\mu/kg) = \frac{(A_c)(I_{is})(V_T)(DF)}{(A_{is})(RRF)(W_S)(S)(V_i)}$$

where:

A_c = Area of the characteristic ion of each target analyte
I_{IS} = Amount of each internal standard injected (ng)
V_T = Volume of the concentrated extract (mL)
DF = Dilution factor
A_{IS} = Area of the characteristic ion of each internal standard
RRF = Relative response factor
W_S = Weight of dust extracted, kilograms (kg)
S = Decimal percent solid
V_i = Injection volume (usually 1 µL)

When the concentration of any identified target analyte is below the reporting limit but the mass spectrum meets the identification criteria, report the concentration by flagging the results with "J". All target analyte concentrations are reported to three significant figures.

8.2 Surrogate Spike Recoveries

Calculate surrogate standard recovery on all samples, blanks, and spikes by the following equation:

$$Percent\ Recovery\ (\%R) = \frac{Q_D}{Q_A}\ x\ 100$$

where:

Q_D = Quantity determined by analysis
Q_A = Quantity added to sample

8.3 Matrix Spike Recoveries

Matrix spike recoveries and the relative percent difference (RPD) between the recoveries of the two analytes in MS/MSD will be calculated by the following equations:

$$Matrix\ Spike Recovery (\%R) = \frac{SSR - SR}{SA}\ x\ 100$$

where:

SSR = Spike sample result
SR = Sample result
SA = Spike added

and

$$RPD = \frac{|MSR - MSDR|}{(MSR + MSDR)/2}\ x\ 100$$

where:

RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

Note: RPD is always expressed as a positive value.

8.4 Laboratory Control Sample

$$Laboratory\ Control\ Sample\ Recovery\ (\%R) = \left(\frac{SSR - SR}{SA}\right)\ x\ 100$$

where:

SSR = Spike sample result
SR = Sample result
SA = Spike added

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

9.1 DFTPP Tune

The GC/MS must meet the ion abundance tune criteria specified in Table 4, Appendix A, before initiating acquisition activities involving samples, blanks, or standards. The tune ensures correct mass calibration, mass resolution, and mass transmission. It must be performed every 12 hours during analysis.

9.2 Initial Calibration for Target Compounds and Surrogates

Once the tune criteria has been met, the GC/MS system must be initially calibrated using a minimum of five concentrations (0.1, 0.5, 1.0, 5.0, and 10µg/mL) to determine the linear response of target compounds and surrogates.

The initial calibration of the GC/MS is evaluated according to the magnitude and stability of the relative response factors of (RRF) of each target analyte and surrogate. The minimum RRF of each compound at all five levels must be equal to or greater than 0.050. The %RSD should be less than or equal to 15% for each target compound with the exception of the CCCs. The %RSD for the CCCs must be equal to or less than 30% for the following compounds:

- Acenaphthene
- Fluoranthene
- Benzo(a)pyrene

If the RSDs exceed criteria, then linearity through the origin cannot be assumed. A linear regression analysis, plot not forced through "zero", may be used to calculate concentrations using area counts on the "y" axis as the dependent variable versus concentrations on the "x" axis as the independent variable. The correlation coefficient (r) must be $0.99.

NOTE: All initial calibration standards must be analyzed prior to the analysis of any method blanks, QC samples or environmental samples.

9.3 Continuing Calibration for Target Compounds and Surrogates

After 12 hours of sample acquisition have passed, the GC/MS must be re-tuned using DFTPP and the initial calibration curve verified by the mid-level calibration standard.

1. The DFTPP tune must pass the criteria in Table 4, Appendix A.

2. The 1 µg/mL calibration standard must be used for the continuing calibration.

3. The continuing calibration of the GC/MS is evaluated based on the magnitude of RRF and %D 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 target analytes in the continuing calibration must be equal to or greater than 0.050. The %D for each CCC must not exceed 20%. For any target compounds present in the sample at a concentration greater than RL, those compounds must meet the minimum RRF of 0.050 and the %D criteria of #20%.

4. The quant ion area for each internal standard in the continuing calibration must be between 50% and 200% of the respective internal standard quant ion area in the mid-

point standard of the current initial calibration. If this criterion is not met, reanalysis is required.

5. A maximum of two continuing calibrations may be run to meet the requirements in item 3 above. A new calibration curve must be reanalyzed if both continuing calibrations are unacceptable.

   NOTE: It is not acceptable to use the first continuing calibration if the second continuing calibration is out.

6. If any of the requirements listed in Step 3 are not met, notify the Organic Group Leader and/or Analytical Section Leader.

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 target analytes 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 2 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. The area of each internal standard at 1 :g/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 40-day analysis holding time. If reanalysis confirms matrix effects, submit both sets of data but report the initial run.

9.5 Method Blank Analysis

A method blank is a known weight of sodium sulfate that is carried through the entire analytical procedure. The weight of the sodium sulfate is approximately equal to that added to the dust samples. The purpose of a method blank is to determine the level of contaminations associated with preparation and analysis of samples.

1. One method blank must be prepared for each batch of 20 samples.

2. A method blank must not contain target compounds at concentrations < the RL of the target analytes listed in Table 1, Appendix A.

3. If a method blank exceeds the contamination limit described above, the analytical system is considered unacceptable. The source of contamination must be investigated so that appropriate corrective actions can be taken and documented, before proceeding with any further sample analyses. All samples processed with a contaminated method blank must be re-extracted and reanalyzed and must be reported to the Organic Group Leader and/or Analytical Section Leader so that appropriate corrective actions may be taken.

9.6 Solvent Blank

A solvent blank (i.e., methylene chloride) may be run after any sample or dilutions that contain a level of any target analyte exceeding the initial calibration range to ensure that there is no carryover from a previous sample.

9.7 Surrogate Recoveries

The purpose of using surrogates is to evaluate the accuracy and precision associated with the preparation and analysis of samples. The recoveries of the three surrogates are calculated for all samples, method blanks, and MS/MSDs.

1. The surrogates are added to all samples, blanks, and MS/MSD prior to extraction.

2. The surrogate recoveries are calculated using the equation in Section 8.3.

3. The quality control limits of the recoveries are listed below:

Compound	% Recovery
Nitrobenzene-d_5	23 - 120
2-Fluorobiphenyl	30 - 115
Terphenyl-d_{14}	18 - 137

4. If any one surrogate is outside QC limits OR if one surrogate is below 10%, the following actions must be taken:

   a. Ensure that there are no errors in calculations, surrogate solutions, and internal standards. Check that the integration of the quantitation ions of the internal standards and surrogates have been performed properly.

   b. Reanalyze the sample at the discretion of the Organic Group Leader if there are no obvious errors. If a blank does not meet the specification, it may be reanalyzed alone.

   c. Do not reanalyze diluted samples with a dilution factor greater than 10.

   d. If the sample associated with the MS/MSD does not meet QC limits, it should be reanalyzed only if the MS/MSD recoveries are within the limits. If the sample and the associated MS/MSD show the same pattern (i.e., outside the limits), the sample does not require reanalysis. Document in the case narrative.

NOTE: Do not reanalyze the MS/MSD, even if their surrogate recoveries fall outside the QC limits.

5. If upon reanalysis of the sample, the surrogate recoveries fall within the QC limits, then the problem was within the laboratory's control. Submit only the data from the analysis with the surrogate recoveries within the QC limits. This will be considered the initial analysis and reported in the data package. If the reanalysis is outside the analysis holding time, both sets of data will be submitted in the data package.

6. If upon reanalysis of the sample, the surrogate recoveries still fall outside the QC limits, the sample must be re-extracted and reanalyzed as instructed by the Organic Group Leader. If the re-extraction and reanalysis of the sample solves the problem, submit only the data from the analysis with surrogate recoveries within the QC limits. This shall be considered the initial analysis and shall be reported in the data package. If the re-extraction is outside the holding time, provide the data from both analyses.

   a. If surrogate recoveries in a blank do not meet QC limits after reanalysis, all samples associated with that blank must be re-extracted along with the blank. The blank is intended to detect contamination in samples processed at the same time.

   b. If upon reanalysis of the sample associated with MS/MSD, the surrogate recoveries still fall outside the QC limits, the sample must be re-extracted.

7. If upon re-extraction and reanalysis of the sample, the surrogate recoveries fall within the QC limits, submit data only from this analysis if the holding time criteria has been met. This will be considered the initial analysis and will be reported in the data package. If the re-extraction is outside the holding time, submit data from both analyses.

8. If upon re-extraction and reanalysis of the sample, the surrogate recoveries fall outside the QC limits, submit both sets of data. Distinguish between the initial analysis and the reanalysis in the data package.

9. Notify the Organic Group Leader before re-extracting and re-analyzing the sample.

9.8 Matrix Spike and Matrix Spike Duplicate Analysis

The purpose of the MS/MSD is to evaluate the accuracy and precision of the extraction and analysis, including possible sample matrix effects. The MS solution must be a different source from the calibration standards.

1. One MS/MSD must be prepared every 10 samples or per project. The MS/MSD must be associated with a method blank that meets the criteria in Section 9.7and must be extracted and analyzed within holding time.

2. The MS solutions specified in Section 6.0 must be used.

3. Spike recoveries and the RPD of each MS compound in the MS/MSD are calculated according to the equations specified in Section 8.3.

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

   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.

Compound	% Recovery	RPD
Acenaphthene	31 - 137	19
Pyrene	35 - 142	36

9.9 Laboratory Control Sample Analysis

The LCS is a sodium sulfate sample spiked with the same spike compounds at the same concentration as those of MS/MSD.

1. One LCS must be prepared every 20 samples or per project. The LCS must be associated with a method blank that meets the criteria in Section 9.7and must be extracted and analyzed within holding time.

2. The MS solutions specified in Section 6.0 must be used.

3. Spike recoveries of each compound in the LCS are calculated according to the equation specified in Section 8.4.

4. The QC limits for recovery are as follows:

Compound	% Recovery
Acenaphthene	70 - 130
Pyrene	70 - 130

If LCS fails to meet the recovery QC limits on a routine basis, the Organic Group Leader must investigate the cause and take corrective action.

An additional LCS sample, which includes all target analytes in the second source, should be analyzed at least once every two years.

9.10 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 7.7.

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. If the screening procedure determines that the extract cannot be analyzed undiluted, submit the data from the first dilution and a subsequent dilution in which analytes fall within the calibration range. NOTE: Except in extreme cases, all extracts should be run undiluted to achieve the lowest RL.

9.11 Manual Integrations

Manual integration of all target analytes, surrogates, and internal standards will be submitted for review. The manual integration results will be flagged with a "M" and will be initialed and dated by the analyst and group leader indicating that the integration was performed properly. 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.*

9.12 Initial Demonstration of Capability

Initial proficiency in PAH analysis must be demonstrated by each analyst initially and each time significant changes are made in the procedure or for instrumentation. Each analyst will generate precision and accuracy data using a reference standard other than the source used for calibration. Four replicates of a well-mixed reference standard is analyzed using the procedures outlined in this SOP. Calculate the average mean in µg/L and the standard deviation (s) in µg/L. Once the data is received, the Quality Assurance Officer (QAO) will tabulate the results from all the analysts and calculate acceptance limits.

9.13 Method Detection Limit Studies

Method detection limit studies will be run on an annual basis for PAHs to verify the minimum concentration that can be measured and reported with 99% confidence. A minimum of seven replicates must be used for the study (EPA 1984). A typical MDL study using the Soxtherm can be found in Table 6, Appendix A.

10.0 DATA VALIDATION

Data will be assessed in accordance with the guidelines set forth in the draft version of SERAS SOP #1016, *Data Validation Procedures for Routine Semi-volatile Organic Analysis*. However, data are 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.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, refer to 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

Gerhardt. 2004. *Soxtherm/Multistat Instruction Manual*.

National Environmental Laboratory Accreditation Committee (NELAC). 2002. *Quality Systems*.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste*. SW-846. 3rd ed. Method 8270C.

U.S. EPA Contract Laboratory Program (CLP). 1999. *Statement of Work for Organic Analysis*, OLM04.2.

U.S. EPA. 1984. Federal Register, 40 CFR Part 136, Appendix B, *Definition and Procedures for the Determination of the Method Detection Limit,* Revision 1.11.

13.0 APPENDICES

A - Tables
B - Sieve Cleaning Procedure

APPENDIX A
Tables
SOP #1810
March 2005

TABLE 1. Target Compound List and Reporting Limits [1]

Compound	RL[2] (µg/kg)
Naphthalene	100[3]
Acenaphthylene	100
Acenaphthene	100
Fluorene	100
Phenanthrene	100
Anthracene	100
Fluoranthene	100
Pyrene	100
Benzo(a)anthracene	100
Chrysene	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Benzo(e)pyrene	100
Benzo(a)pyrene	100
Indeno(1,2,3-cd)pyrene	100
Dibenzo(a,h)anthracene	100
Benzo(g,h,i)perylene	100

[1] On a wet-weight basis
[2] RL denotes Reporting Limits
[3] Using 0.5 g of sieved dust samples and a final extract volume of 0.5 mL

TABLE 2. Characteristic Ions for Target Compounds and Surrogates

Compound	Primary Ion	Secondary Ion
1,4-Dichlorobenzene-d_4 (ISTD)[1]	152	115
Naphthalene-d_8 (ISTD)	136	108
Naphthalene	128	102
Acenaphthene-d_{10} (ISTD)	164	162
Acenaphthylene	152	76
Acenaphthene (CCC)[2]	153	154
Fluorene	166	165
Phenanthrene-d_{10} (ISTD)	188	189
Phenanthrene	178	176
Anthracene	178	176
Fluoranthene (CCC)	202	101
Pyrene	202	101
Chrysene-d_{12} (ISTD)	240	120
Benzo(a)anthracene	228	114
Chrysene	228	114
Perylene-d_{12} (ISTD)	264	132
Benzo(b)fluoranthene	252	126
Benzo(k)fluoranthene	252	126
Benzo(e)pyrene	252	126
Benzo(a)pyrene (CCC)	252	126
Indeno(1,2,3-cd)pyrene	276	138
Dibenzo(a,h)anthracene	278	139
Benzo(g,h,i)perylene	276	138

[1] ISTD denotes Internal Standard
[2] CCC denotes Calibration Check Compounds

PARAMETER	Primary Ion	Secondary Ion
SURROGATES		
Nitrobenzene-d_5	82	154
2-Fluorobipheny	172	171
Terphenyl-d	244	122

TABLE 3. Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenapthene-d_{10}
No Compounds	Naphthalene	Acenaphthylene
	Nitrobenzene-d_5 (surr)	Acenaphthene
		Fluorene
		2-Fluorobiphenyl (surr)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
Phenanthrene	Benzo(a)anthracene	Benzo(b)fluoranthene
Anthracene	Chrysene	Benzo(k)fluoranthene
Fluoranthene		Benzo(e)pyrene
Pyrene		Benzo(a)pyrene
Terphenyl-d_{14} (surr)		Indeno(1,2,3-cd) pyrene
		Dibenzo(a,h)anthracene
		Benzo(g,h,i)perylene

surr = surrogate compound

TABLE 4. 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	Present
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
275	10.0 - 30.0 percent of mass 198
365	Greater than 0.75 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110.0 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 5. Soxtherm Extraction Operating Conditions

Extraction temperature	140 °C	Solvent volume	140 mL	Solvent type	DCM:Acetone, 80:20	Volume expected	Total Time elapsed
Hot Ext. time	55 min					140 mL	55 min
Evaporation A interval	5x	Reduction time	5 min	Pulse	4s	65 mL	80 min
Rinsing time	30 min	Each macro interval for evaporation reduces ~15 mL				50 mL	110 min
Evaporation B interval		Reduction time	0			50 mL	110 min
Evaporation C time	15 min				Total	50 mL	125 min

Table 6. Typical Method Detection Limits (MDL) Using the Soxtherm [1]

Compound	MDL[2] µg/kg)
Naphthalene	34
Acenaphthylene	40
Acenaphthene	39
Fluorene	37
Phenanthrene	33
Anthracene	33
Fluoranthene	32
Pyrene	34
Benzo(a)anthracene	37
Chrysene	5
Benzo(b)fluoranthene	31
Benzo(k)fluoranthene	36
Benzo(e)pyrene	39
Benzo(a)pyrene	38
Indeno(1,2,3-cd)pyrene	30
Dibenzo(a,h)anthracene	43
Benzo(g,h,i)perylene	26

[1] On a wet-weight basis
[2] Based on 1 gram of sample and a final extract volume of 1.0 mL

APPENDIX B
Sieve Cleaning Procedure
SOP #1810
March 2005

SIEVE CLEANING

SCOPE AND APPLICATION

Sieves must be cleaned before each dust sample is separated into fractions. Most of the "near-mesh size" particles can usually be removed from the apertures by inverting the sieve and gently tapping the frame of the sieve. For sieves with apertures less than 1 millimeter (mm) (e.g., 100-mesh, 150 micron [:m] sieve), the most effective method for cleaning the apertures is the use of an ultrasonic bath.

EQUIPMENT/APPARATUS

- Ultrasonic bath, capable of holding a standard sieve
- Magnifying glass
- Source of air, standard hair dryer or compressed air
- Spray bottle

REAGENTS

- Ultrasonic cleaner or laboratory-grade detergent that leaves no interfering residues
- Deionized (DI) water, Type II water or equivalent
- Methanol, American Chemical Society (ACS) grade or equivalent

PROCEDURE

The following cleaning procedure will be used to clean sieves prior to use and after each sample.

1. Place the sieve into an ultrasonic bath containing detergent and DI water and sonicate for approximately 10 minutes.

2. Remove the sieve from the ultrasonic bath and rinse well with DI water.

3. Spray the sieve with methanol.

4. Dry the sieve using a standard hair dryer or a compressed air source.

5. Visually inspect the sieve to ensure that there are no remaining particles present in the apertures. A magnifying glass may be used to aid in this process.

6. Repeat steps 1 through 5 prior to sieving subsequent samples.