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Standard Operation Procedure For:

Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS) EPA Method TO-13A

Department of Environmental Protection
Chemistry Section
Tallahassee Florida

Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS) EPA Method TO-13A

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1 Scope and Application

1.1 This EPA method TO-13A describes a sampling and analysis procedure for common Polycyclic Aromatic Hydrocarbons (PAHs) involving the use of a combination of quartz filter and polyurethane foam (PUF) cartridge with subsequent analysis by gas chromatography with mass spectrometry detection (GC/MS) and is based on EPA Method 8270D. Using this method, the analytes listed in Table 1 are determined in an ambient air and reported in the LIMS for the test A-PAH.

2 Summary of The Method

2.1 Filter cartridges containing PUF are cleaned in solvents and vacuum dried. The certified filter cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler. Before sending them to the field for sampling, field surrogates are added to the PUF trap cartidges and stored at 4 °C temperature or on ice until sampling. After sampling, the filter cartridges are extracted by Soxhlet extraction with methylene chloride. The PUF extarcts are then analyzed by GC/MS in full scan mode.

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2.2 Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of two or three characteristic masses (m/z). Quantitative analysis is performed using an internal standard technique.

2.3 Interference:

2.3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

2.3.2 Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. To reduce carryover, rinse the syringe several times with solvent between samples. In extreme cases, it may be necessary to analyze a solvent blank between samples.

2.3.3 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that result in discrete artifacts and/or elevated baselines in the detector profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

2.3.4 Glassware must be scrupulously cleaned. The glassware should then be drained dry and heated in a muffle furnace at 550 °C for 8 hours.

2.3.5 The use of high purity water, reagents, and solvents are required to minimize interference problems. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Matrix interferences may be caused by contaminants that are co-extracted from the sample. Additional clean-up by silica gel column chromatography may be required.

3 Apparatus and Equipment

3.1 Glassware

3.1.1 Soxhlet apparatus extractor 8 position, capable of extracting filter and PUF cartridges (6-cm x 7.5-cm length), 500 mL flask, and condenser

3.1.2 S-Evap® sample concentration system: Kuderna-Danish (K&D) concentrator tubes -- 15 mL, Ground glass stoppers to fit concentrator tubes, K&D 500 mL evaporative flasks; attach to concentrator tubes with clips, Snyder columns -- three ball macro or equivalent and clips -- used to attach concentrator tube to K&D flask, and Teflon boiling chips.

3.1.3 Centrifuge tubes, graduated (10-15 mL), with screw caps with Teflon-lined septa (Calibrate tubes to the volume used before use and record in the Extraction Log Book)

3.1.4 Gas-tight micro-syringes or volumetric pipets, 250 µL, 500 µL and 1000 µL (Required from the manufacturer, the certificate stating that the volume is

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accurate to < 1%, otherwise calibrate and keep the record of these gas-tight micro-syringes or volumetric pipets every quarterly)

3.1.5 Vacuum desiccator for drying PUFs.

3.2 S-Evap® - 500 mL: Consists of heated water bath and water-cooled condensers; capable of concentrating eight sample extracts simultaneously.

3.3 N-Evap®: Consists of heated water bath and apparatus to further concentrate the extract, and Nitrogen gas.

3.4 Shimadzu HPLC Auto Prep system for GPC cleanup. Phenomenex high performance GPC column. ISCO Foxy 200XT Fraction collector. Mobile phase is methylene chloride.

3.5 Autosampler vials--1.5 mL and 0.35 mL, with crimp tops with Teflon-lined septa, to fit the Agilent 7683 and 7693 autosamplers.

3.6 GC/MS system:

3.6.1 Gas chromatograph, Agilent 7890A and Agilent 6890 series II or equivalent. Must be temperature programmable with an injector port designed for splitless injection.

3.6.2 Autosampler, Agilent 7693 and 7683 or equivalent, capable of 1 to 2 µL injections and equipped with solvent vials for flushing syringe between injections.

3.6.3 Mass spectrometer, Agilent 5975C and 5973 or equivalent; Must be capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of decafluorotriphenyl phosphine (DFTPP) is injected through the GC inlet.

3.6.4 Data system: A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z and plotting such m/z abundance versus time or scan number (an Extracted Ion Current Profile, or EICP). Software must also allow integrating the abundance in any EICP between specified time or scan number limits. See the Enviroquant soft ware manual for details.

GC/MS Operating Conditions: (this serves as a guideline only for regular PAH analysis, different instrument may have different settings)

Parameter	Setting
Mass Range:	35-450 amu
Scan Time:	4.5 to 34 min. 1 scan/sec minimum
GC Oven Temperature Program:	50 °C for 0.5 min., to 330 °C at 18 °C/min., hold at 330 °C for 4 min.

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Inlet:	Temp: 275 °C; Mode: Splitless; Pressure: Constant Flow ON, 6.0 psi at 50 °C (1.2 mL/min); Purge Time 0.75 min. Purge Flow: 30 mL/min. Total Flow 23.8 mL/min. Gas Saver: ON; Saver Flow 20 mL/min. Saver Time: 3.0 min.
MS interface temperature:	280 °C
Injection Volume:	1µL
Total Run Time:	20 min.

3.7 Helium, UPC grade, is the carrier gas in the gas chromatographs. The helium must be passed through an oxygen filter before entering the gas chromatographs.

3.8 J&W Scientific DB-5MS capillary column (or equivalent), 30m x 0.25 mm x 0.5 µm (or 0.25 µm).
Zebron Capillary GC Column, Phenomenex (ZB-5ms), 30m x 0.25 mm x 0.5 µm (or 0.25 µm).

4 Reagents and Chemicals

NOTE: Record Lot Numbers of all the reagents and solvents used in the Note Book.

4.1 Standards (see SOP SV-009 for all the required standards preparation instructions)

4.1.1 Prepare Calibration Standards for PAHs at the following concentration levels: 0.05,0.1, 0.25, 0.5, 1.25 and 2.50 µg/mL (with 0.5 µg/mL internal standards presents in each of the six levels) and 0.5 µg/mL second source CCV.

4.1.2 Prepare internal standard solution at 100 µg/mL, 10 µg/mL and 0.5 µg/mL, and use 0.5 µg/mL solution when sample dilution is needed.

1,4-Dichlorobenzene-d_4	Phenanthrene-d_{10}
Naphthalene-d_8	Chrysene-d_{12}
Acenaphthene-d_{10}	Perylene-d_{12}

4.1.3 DFTPP (Decafluorotriphenylphosphine) Tuning Standard Mixture, 50 µg/mL each.

4.1.4 Laboratory Surrogate Mix (10 µg/mL)

Nitrobenzene-d_5	Fluorene-d_{10}
2-Fluorobiphenyl	Pyrene-d_{10}
p-Terphenyl-d_{14}	

4.1.5 Field Surrogate Mix (50 µg/mL)

Acenaphthylene-d_8	Benzo(a)pyrene-d_{12}
Fluoranthene-d_{10}	

4.1.6 PAH Matrix Spike Mix (5 µg/mL)

4.1.7 GPC Calibration Solution.

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Prepare a solution in methylene chloride that contains the following analytes in the concentration listed below:

Analyte	mg/mL
Corn oil	12.5
Bis-2-ethylhexyl phthalate	0.5
Methoxychlor	0.1
Perylene	0.01
Sulfur	0.04

4.2 Solvents: Methylene chloride, Acetone and Methanol, HPLC grade (or equivalent).

4.3 Materials for Sample Collection

4.3.1 Quartz fiber filter, 102 millimeter binder less quartz microfiber filter, Whatman Inc., 6 Just Road, Fairfield, NJ 07004, Filter Type QMA-4. Bake the Whatman QMA-4 quartz filters at 400 °C for 5 hours before use. Set aside the filters in a clean container for shipment to the field.

4.3.2 Polyurethane foam (PUF) plugs, pre-cleaned 60 mm x 75 mm, 10 each (SKY Inc.com, catalog number P226131C). Certify a batch of 8 PUFs each time before sending them to field. Carefully place the PUF in Soxhlet apparatus and extract with methylene chloride for 5 hours at approximately 4 cycles per hour. Collect the methylene chloride for contamination check and continue Soxhlet extraction fresh methylene chloride overnight. Concentrate these separately and check for contamination. Carefully remove the PUFs from Soxhlet and vacuum dry in desiccator until no more solvent left 2 to 4 hours. Give sample number in Lims to track the certification. Certified PUFs are good for 4 months. Prior to sampling, the cartridges are spiked with field surrogate compounds. Use the following guidelines in determining whether a cartridge is clean for field use:

- Naphthalene <500 ng/cartridge
- Other PAHs <200 ng total/cartridge

Cartridges are considered clean for up to 30 days from date of certification when sealed in their containers.

4.3.3 Glass sample cartridge for sample collection, Teflon® end caps, for sample cartridge and sample cartridge aluminum shipping containers for sample cartridge shipping.

4.4 Aluminum foil, heat 400 °C for 8 hours, to wrap the glass sample cartridge to protect from light.

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4.5 Sodium sulfate, granular and powder: Bake in a muffle furnace at 700 ºC for 12 hours. Allow to cool before using. Store in a large mouth bottle with backed aluminum foil cover in 200 °C oven.

4.6 Silica cartridges 1g (6 mL) - Sep-Pak Cartridge, J&W brand or equivalent.

5 Sample Preparation Procedure

5.1 Deployment of Cartridges for Field Sampling: The following field surrogate compounds should be added to each PUF cartridge prior to field deployment to monitor matrix effects, breakthrough, etc. Add field surrogate compounds to the center of the PUF cartridge, using a micro syringe. Spike 20 µL of a 50 µg/mL solution of the surrogates onto the center bed of the PUF trap to yield a final concentration of 1 µg.

Field Surrogate Compound	**Total Spiked Amount (µg)**
Fluoranthene-d_{10}	1
Benzo (a) pyrene-d_{12}	1
Acenaphthylene-d_8	1

5.2 Fill out a "chain-of-custody" indicating cartridge number, surrogate concentration, date of cartridge certification, etc. The chain-of-custody must accompany the cartridge to the field and return to the laboratory.

5.3 Use the recoveries of the surrogate compounds to monitor for unusual matrix effects and gross sample processing errors. Evaluate surrogate recovery for acceptance by determining whether the measured concentration falls within the acceptance limits of 60-120 percent.

5.4 Cartridges are placed in their shipping containers and shipped to the field.

5.5 After collection, the chilled (<4 °C) samples are returned in the aluminum shipping container (containing the filter and puf) to the laboratory for analysis. The "chain-of-custody" should be completed. The samples are logged in the laboratory logbook according to sample location, filter and sorbent cartridge number identification, and total air volume sampled (uncorrected). If the time span between sample collection and laboratory analysis is to exceed 24 hours, refrigerate sample at 4 °C. Return at least one field blank filter/PUF cartridge to the laboratory with each group of samples. Treat a field blank exactly as the sample except that air is not drawn through the filter/sorbent cartridge assembly. All samples should be extracted within 7 days and the extracts should be analyzed within 40 days of extraction.

5.6 Assemble the Soxhlet apparatus. Immediately before use, charge the Soxhlet apparatus with methylene chloride and reflux for 2 hours. Let the apparatus cool, disassemble it, transfer the solvent to a clean glass container, and retain it as a blank for later analysis, if required. Place the filter and puf together in the Soxhlet apparatus. Prior to extraction, add laboratory surrogate standards mix (Nitrobenzene-d_5, 2-Fluorobiphenyl, Fluorene-d_{10}, Pyrene-d_{10} and p-Terphenyl-d_{14}) to each sample, blank, and laboratory-fortified blank. The recovery of the laboratory surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measure concentration falls within the acceptance

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limits. Spike 20 µL of a 50 µg/mL solution of the surrogates onto the PUF cartridge, to yield a final concentration of 1 µg. Add 400 mL of methylene chloride to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour. Allow to cool, and then disassemble the apparatus. Dry the extract from the Soxhlet extraction by passing it though a drying column containing about 10 grams of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator assembly. Wash the extractor flask and sodium sulfate column with methylene chloride to complete the quantitative transfer.

5.7 Concentrate sample extracts using the S-Evap® System Kuderna-Danish (K&D) Concentration at 70 °C and record the temperature in the notebook. It is best to K&D samples to a volume of 3-5 mL and do not let them go dry. Remove the concentrator tube from the K&D flask. There may be water on the outside of the flask -- do not allow it to drip into the sample (The water can be removed with a Kim wipe.). Rinse the joint of the K&D flask with methylene chloride.

5.8 Nitrogen blow down to 1 mL using N-Evap® Concentration. Nitrogen blow down under gentle stream of nitrogen at 40 °C water bath temperature. If the extract is cloudy, impurities may be removed from the extract by solid phase extraction using activated silica gel. Clean-up procedures may not be needed for relatively clean matrix samples. Perform one gram silica gel cleanup on the entire extract.

5.9 Condition a 1 g silica gel solid-phase extraction cartridge with 5 mL of methylene chloride and discard the solvent. Transfer the extract to the silica gel cartridge, and collect in a centrifuge tube. Rinse the concentrator tube, which held the extract with 2 mL methylene chloride, adding the rinsate to the cartridge, and collecting it along with the sample extract. Repeat the rinse at least twice more. Continue collecting until you have collected a total of 12 mL. Nitrogen blow down to 0.8 mL under a gentle stream of nitrogen as previously described and add 100 µL of 5 µg/mL internal standard. Make up to 1 mL with methylene chloride and proceed with PAH analysis by GC/MS analysis.

6 GC/MS Tuning/Calibration

6.1 Tuning

6.1.1 At the beginning of a run (and after any subsequent “retuning”) ensure that the spectrometer’s mass calibration is accurate: Using Perfluorotributylamine (PFTBA) and the manual tune section of Chemstation, adjust the tuning lenses so that the PFTBA alignment ions (69, 219, 502) are centered (± 0.10 amu) on their respective amu calibration points and that their widths are 0.45 to 0.55 amu at half height. Print out a tune report from the manual tune section of Chemstation. This is a good time to check for air leaks with ions 18 and 28. These need to be less than 5% of ion 69. This mass calibration report is then stored in the run’s QA/QC folder.

6.1.2 Tune the GC/MS system prior to the beginning of an analysis run and every 12 hours thereafter. The tune analysis must meet the criteria in Table 2 for a 50-ng injection of DFTPP within two scans on either side of the DFTPP apex. Check the scan at the apex first. If the tune does not pass, then use the auto find DFTPP feature in the Enviroquant software, which averages 3 scans around the apex. If the tune fails again, then adjust DFTPP target tune parameters and perform a

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DFTPP tune by re-injecting the DFTPP standard. If the tune pass, then check the DDT breakdown and Tailing Factor (TF) for Benzidine and Pentachlorophenol criteria (Table 2). Once the instrument has failed to successfully tune after making several attempts, then it is time to clean the ion source and perform other preventative maintenance. Other instrumental problems, which can prevent the mass spectrometer from tuning properly, include a contaminated column, a poorly responding EM, or air leaks. Sample analyses MUST not begin until all the tuning criteria are met.

6.1.3 Background subtraction, if needed, should be straightforward and designed only to eliminate column bleed or instrument background ions.

6.1.4 Include a DFTPP standard injection at twelve hour intervals during an analysis sequence and check the tune criteria. If the tune check happens to fail any of the criteria, then re-analyze all samples that were analyzed after the failed tune check standard.

6.1.5 The instrument tune must be maintained not only for environmental samples, but also for instrument calibration standards.

6.2 Initial Calibration

6.2.1 Analyze the PAH calibration standards at the following levels: 2.5, 1.25, 0.50, 0.25, 0.1 and 0.05 µg/mL. At each level, the internal standards should be present at 0.5 µg/mL.

6.2.2 For each compound determine the retention time, the primary quantitation ion and two or three secondary ions to use for qualitative identification. The primary and secondary ions are already given in the EPA methods 625, 8270D and TO-13A. The major ions (>10% of the most abundant ion) should be present and the relative intensities of the major ions should agree within ±20% of the reference mass spectrum.

6.2.3 Enviroquant software tabulates the area of the primary ions against concentration for each compound and internal standard in the calibration standard mixes, and calculates response factors for each compound using the equation below.

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

where :

RF_i is the average response factor from the initial calibration
A_s is the area of the quantitation ion for the compound measured
C_{is} is the concentration for the internal standard
A_{is} is the area of the quantitation ion for the internal standard
C_s is the concentration of the compound measured

6.2.4 The initial calibration curve must meet the following criteria:

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6.2.4.1 The %RSD of the response factors for each of the target compounds must be ≤20% for linear fit (or correlation coefficient must be equal or greater than 0.99 for quad. fit), or the instrument system is considered to be out of calibration. It is also recommonded that a minimum response factor for the most common target analytes, as noted in Table 4, be demonstrated for each individual calibration level as a means to ensure these componds are behaving as expected. In addition , meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. However, the %RSD must be <30 % for each of the calibration check compounds. If the %RSD for the compounds are out of these ranges, then the instrument system must be corrected. Some possible problems include standard mixture degradation, injection port inlet contamination, and analytical column contamination and active sites in the column or chromatographic system.

6.2.5 A method blank should be analyzed prior to sample analyses in order to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

6.2.6 The relative retention time (RRT) of each target analyte in each calibration standard, CCV and samples should agree within 0.06 RRT units.

6.3 Daily GC/MS Performance and Calibration Check

The initial calibration curve and instrument performance must be verified on each day by the measurement of one or more check standards from a second source.

6.3.1 Analyze continuing calibration check standard. These calibration check standard must be analyzed at the start of each run and at 12 hour intervals thereafter.

6.3.2 Calibration verification standard criteria: Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 4. This criteria is particularly important when the common target analytes are also critical project-required compounds. This is the same check that is applied during the initial calibration.

6.3.4 If the minimum response factors are not met, the system should be evaluated, and corrective action should 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.

6.3.5 Calibration Check Compounds (CCC): After the system performance check is met, CCCs listed in Table 1 are used to check the validity of the initial calibration. Enviroquant software calculates the relative percent difference (RPD) for linear fit using:

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$$RPD = \frac{(RF_I avg - Rf_C) \times 100\%}{RF_I avg}$$

where:

$RF_I avg$ is the average response factor from the initial calibration
RF_C is the response factor from current verification check standard

or calculates percent difference for quad. fit.

** The RPD for all compounds should be less than 30 %. The RPD for any CCC must be less than 30%. If the percent difference for each CCC is less than 30%, then the initial calibration is assumed to be valid. If the percent difference is greater than 30% for any one CCC, corrective action must be taken. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins.

7 GC/MS Sample Analysis

7.1 Each sample extract MUST contain 0.5 µg/mL of internal standard. Any extract that is dark in color, suspected of containing petroleum hydrocarbons or high concentrations of any analytes should be screened on the GC/FID before analyzing on the mass spec. The extracts should be diluted as deemed necessary. The concentration of internal standard must remain at 0.5 µg/mL when diluting samples by using 0.5 µg/mL of internal standard solution as diluting agent.

7.2 Analyze the extracts by GC/MS by loading the auto sampler tray and setting up a run sequence in the GC/MS software. A vial of DFTPP and the appropriate calibration check standards (dependent on the customer requested analysis) must be inserted every 22-25 samples to check the tuning and calibration response every 12 hours. If the DFTPP or calibration check standard fail their criteria, any samples run after them must be reanalyzed after the criteria have been passed.

7.3 Print out a hard copy of the run sequence, and place it in the final data folder.

7.4 Examine the quantitation reports soon after the samples have been analyzed.

7.4.1 Check all of the calibration check standards and DFTPP tune standards analyzed during the run sequence and insure that they met the criteria given above.

7.4.2 If the response for any of the compounds exceeds the calibration curve, the extract must be diluted so that the response will be within the limits of the curve, and then reanalyzed. Make sure when performing dilutions to use methylene chloride spiked with the appropriate levels of internal standard so that their response will be the same in the dilution as it was in the original extract.

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7.4.3 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after data acquisition. If the retention time for any internal standard changes by more than 0.06 RRT from the last check calibration, then the chromatographic system must be inspected for malfunctions and corrections must be made. The m/z abundance for all of the internal standards must be within a factor of two (50% to 200%) from the abundance in the daily calibration standard check. Corrective action is indicated if the m/z abundance is outside of these limits. If the holding time for a sample has expired and the internal standard areas are out of the acceptance range, then the final report must be commented and any positives detected must be qualified with a "J" to indicate that the result is an estimate.

7.4.4 Surrogate Recoveries: The recoveries must be within the following acceptance limits. Table 1 lists the surrogate association for all the BNA analytes. If any of these surrogates fall out side control limits (lower side), re-extract the effected sample with proper QC even after expiration and follow DEP SOP LB-027 for reporting.

Compound	% Rec Water & Sediment
Base/Neutral Surrogates	
Nitrobenzene-d_5	30-150
2-Fluorobiphenyl	30-150
Terphenyl-d_{14}	30-150
Fluorene-d_{10} for Air PAHs	60-120
Pyrene-d_{10} for Air PAHs	60-120
Field Surrogates for Air PAHs	
Acenaphthylene-d_8	60-120
Fluoranthene-d_{10}	60-120
Benzo(a)pyrene-d_{12}	60-120

7.4.5 Check the Matrix Spike and Lab Fortified Blank recoveries. They must be within the current acceptance range for each analyte, see Table 1. The acceptance limits are evaluated once a year or problem with the method performance. A comment must be added to the qualified data in the final report explaining any deviation from the routine limits whenever the spikes or surrogates are out of range (DEP SOP LB-027).

7.4.6 Check the method blank for any interfering contaminants. The MDL's may have to be elevated if the blank(s) indicate contamination.

7.5 Data Interpretation and Quantitation

7.5.1 Two criteria must be satisfied to verify identification of a compound: 1) Elution of the sample component at the same GC relative retention time as the standard component: and 2) Correspondence of the sample component and the standard component mass spectrum. The computer system will check these criteria automatically (as long as the retention times and mass spectra have been updated recently with the calibration standard's retention times/spectra) but ALWAYS manually assess each chromatogram/mass spectrum.

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7.5.2 Concentrations (Cs) of each compound and surrogate identified should be calculated as follows (the computer program will automatically calculate the concentrations for water samples, including any dilution factors entered; the calculations for sediments must be adjusted for the weight of the sample and conversion of units to µg/kg):

$$Cs = \frac{(A_S)(I_{IS})(V_t)(DF)}{(A_{IS})(RF)(Vair)}$$ ai**r samples**

where:

A_S is the corrected area of the compound peak
I_{IS} is the concentration of the appropriate internal standard (in µg/mL)
V_t is the total volume of the extract (usually 1 mL)
DF is the appropriate dilution factor (i.e., 1:10 dilution = a DF of 10)
A_{IS} is the corrected area of the internal standard
RF is the response factor for the compound being measured
Vair is the volume of air sampled

8 Library Search Protocol For BNA GC/MS

8.1 If there are any unidentifiable peaks in the chromatogram that are at least 10 % of the nearest internal standards response (discounting any in-house contaminants in the extraction blank), conduct a library search. Exceptions to this rule:

8.1.1 If the unknown peaks appear to be part of a petroleum hydrocarbon pattern (like diesel or kerosene, etc.), it is unnecessary to search individual peaks, since they are mostly elements of the petroleum product.

8.1.2 If the peak pattern is a petroleum hydrocarbon, identify the petroleum hydrocarbon using pattern-std. comparison. If the pattern is unrecognizable, report as "unidentifiable petroleum hydrocarbon pattern ". Estimate the amount of pet. hydrocarbon present using total ion area calculation of the envelope. Assume the RF is 1. Quantitate as in step 7.5.2., using Ax as the total petroleum hydrocarbon area. Report result in the comment section of LIMS (using only ONE significant figure) as follows:

Example 1:

Chromatographic pattern similar to diesel, estimated concentration = 3.0E5 µg/L.

Example 2:

Unidentifiable petroleum hydrocarbon pattern, estimated concentration = 5.0E6 µg/kg.

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8.2 Use the library search program to estimate the concentrations for the unknown peaks. When reviewing the results from the library search, look at the probability value assigned to the listed compounds in addition to the mass spectra. Usually, if the search program assigns a probability of about 60% or greater, it is a pretty good match and the compound may be reported tentatively.

8.3 If the search program resulted in multiple hits with probabilities of 60% or greater and they all look like possible matches, then you must attempt to classify the compound. For example, if you get a 80% match for undecane and a 83% match for dodecane and a 88 % match for tricosane, and all of the spectra look like plausible matches, report result as "alkane" and give estimated concentration. If there are a lot of hits for a variety of alkanes, report as "total alkanes" with the estimated total concentration. This will simplify reporting if your sample has a lot of unknown alkanes. The same goes for other class of organic compounds.

8.4 If the match is below about 60%, or the search program resulted in no matches (i.e., " No data base entries were retrieved") the spectra will usually suggest a poor match. In this case, the peak is an "unknown extractable organics". You only need to report the <u>total</u> estimated amount for all unknown extractable organics, not each individual estimated concentration.

WARNING: Do not trust any library search program over your own scientific judgment. Just because the program returns a probability of 35% does not mean that it is not a match. Look at the spectra; you may have additional information about the sample that will lead you to a different conclusion than what the search program concluded. However, it is not necessary to turn each unknown identification practice into a research project. Exercise caution when utilizing the search results and do not neglect to examine the returned spectra against the sample spectra.

8.5 The library search program returns estimated concentration results in µg/mL. You must apply the correct sample volume or weight extracted to correct the result and calculated the final estimated result.

8.6 Report final result in the comment section of the final report.

9 Reporting and Documentation

9.1 When analysis is complete, the QC Manager is used to download the final sample results into the Laboratory Information Management System (LIMS). If a sample has been diluted then make sure that the information was entered properly into the QC Manager.

9.2 Add the appropriate qualifiers and comments to the sample data in the QC Manager after performing a complete review of the sample data and QC data. Follow DEP SOP SV-011, BNA Group Data Review/Authorization Checklist for details of data review and reporting, and Section 11 (QUALITY CONTROL). See DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

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9.3 Definitions of the available qualifying codes are listed in DEP SOP LB-027

9.4 All quantitation reports for samples and QC should be placed in a results folder labeled with the job number, the sample numbers, and the type of analysis.

9.5 Enter the results for each sample in the analysis results form. Print out QC results from the QC Manager. Include a copy of dilutions page if any. Also include a print out of sample positives from the data review and file it in the data folder.

9.6 Submit the result folder to the BNA section supervisor. The supervisor will review results and then authorize the sample. The supervisor will then file the folders in the BNA GC/MS lab.

10 Data Archival

10.1 For the Enviroquant GC-MS system:

10.1.1 Move the valid data files (tune, ICALS, CCC, QC and sample data files) soon after collection from the hard disk of the instrument computers to the network drive \\TLHLAB3\BNA\BULK_ARCHIVE. Raw data files on the hard disk of each instrument may be deleted after 3 to 4 months or they are no longer in need.

10.1.2 Copy the processed data files (quantitation reports) into \\TLHLAB3\BNA\BNA1 or BNA2 or BNA3 or BNA5 or BNA6 to convert in QC Manager for reporting in LIMS. These files may be deleted after all results are authorized.

10.1.3 The archived data may be retrieved by making a request to the data group or the BNA supervisor. Make sure when setting up an injection sequence to write down the name of the data files with the associated sample information in the injection log. Include mass spectrometer number in the data file name. (Example: 07502100.d indicates - year 2007; month 1 to 9 and o, n, d; day 01 to 31; instrument number 1 to 3; and file number 00 to 99) This is the only way that data files may be cross referenced to their sample ID.

11 Quality Control

11.1 See BNA DEP SOP SV-010, Quality Assurance/Quality Control in the Semi-Volatile Organics Laboratory (BNA-GC/MS) for detailed information on quality control, definitions and interferences. See DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

12 Method Detection Limit (MDL) and Practical Quantitation Limit (PQL) Determination Procedures

12.1 Determination of Method Detection Limits and Demonstration of Capability

Refer to the DEP SOP LB-007 Procedure and Policy for Method and Instrument Validation and refer to DEP SOP LB-031. Limit of Detection Verification for specific procedural details

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The Limit of Detection (LOD) and Demonstration of Capability (DOCs) shall be determined for each main quality system matrix group identified by NELAP (air, drinking water, non-potable water, biological materials and solids/chemical materials). These groups represent the minimum matrix distinctions for LOD determinations and DOCs where there is evidence that the method performance will not be affected by sub-matrix distinctions within these group, Otherwise LODs and DOCs shall be determined separately for the quality system matrix sub-groups listed below. Where a suitable matrix cannot be found for preparing samples for LOD determinations or DOCs, another similar matrix type may need to be used or samples may need to be prepared in the absence of a matrix (e.g. method blanks). Reasons for matrix substitution may include (but are not limited to): inappropriate background analyte levels in the matrix for the intended study, no analyte-free matrix is available for method blanks, no reference materials are available for a matrix, etc,

12.1.1 Quality System Matrices:

- Aqueous – all aqueous samples excluding drinking water (see below) and salt or estuarine waters;
- Drinking Water – water from a designated potable source;
- Saline/Estuarine – an aqueous sample from an ocean or estuarine. The effects of this matrix type may from analysis to analysis and with salt content. Therefore, the decision to what extent if any this matrix has on the LOD and what salt levels may affect the LOD is left to the discretion of experienced supervisory staff;

12.1.2 Method Detection Limit (MDL) and Practical Quantitation Limit (PQL) Determination Procedures

12.1.2.1 The MDLs were established using procedures given in EPA Chapter 40 Part 136, Appendix B of the Federal Register. Also refer to Reference 14.1 and 14.2.

12.1.2.2 Seven replicate samples are analyzed near the MDL. The MDL is the concentration of analyte at which there is analyte present with 99% confidence.

12.1.2.3 The results of the seven replicate data sets are tabulated and the statistical calculations are performed electronically on at least an annual basis to establish or update the MDLs and PQLs for each analyte and matrix. A list of MDLs is given in the Laboratory Comprehensive Quality Control Plan, see Reference 14.9.

13 Safety/Hazardous Waste Management

13.1 See DEP SOP OG-001, Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories) for specific details on safety and hazardous waste management.

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14 References

14.1 EPA Method TO-13A. Compendium of methods for Toxic Organic Air Pollutants, January 1999.

14.2 Test Methods for Evaluating Solid Wastes, Third Edition, SW-846, Method 8270D, Semi-volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS).

14.3 DEP SOP SV-009. BNA Standard Preparation.

14.4 DEP SOP LB-027. Standard Operating Procedure for Reporting Qualified Data.

14.5 DEP SOP SV-011. BNA Group Data Review/Authorization Checklist.

14.6 DEP SOP SV-010. Quality Assurance/Quality Control in the Semi-Volatile Organics Laboratory (BNA-GC/MS).

14.7 Florida Department of Environmental Protection, Standard Operating Procedure LB-007 Procedure and Policy for Method and Instrument Validation.

14.8 Florida Department of Environmental Protection, Standard Operating Procedure LB-031 Limit of Detection Verification.

14.9 Comprehensive Quality Assurance Plan, Chemistry Section, Bureau of Labs, DEP, 2010.

14.10 DEP SOP OG-001. Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories).

TABLE 1: Target Analytes, Surrogate association, MDLs/PQLs, Spike Recovery Acceptance Range and Precision for Low Level PAHs in PUF Filters

Analyte	**MDL ng/m^3**	**PQL ng/m^3**	**Accuracy Range (%)**	**Prcsn (% RPD)**
Nitrobenzene-d_5 Surrogate/Fluorene-d_{10}				
Naphthalene	100	500	60 - 120	<40
2-Fluorobiphenyl Surrogate/Fluorene-d_{10}				
Acenaphthene	100	500	60 - 120	<40
Acenaphthylene	100	500	60 - 120	<40
Biphenyl	100	500	60 - 120	<40
2,6-Dimethylnaphthalene	100	500	60 - 120	<40
Fluorene	100	500	60 - 120	<40
1-Methylnaphthalene	100	500	60 - 120	<40
2-Methylnaphthalene	100	500	60 - 120	<40
2,3,5-Trimethynaphthalene	100	500	60 - 120	<40
Terphenyl-d_{14} Surrogate/Pyrene-d_{10}				
Anthracene	100	500	60 - 120	<40
Benzo[a]anthracene	100	500	60 - 120	<40

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Benzo[b]fluoranthene	100	500	60 - 120	<40
Benzo[k]fluoranthene	100	500	60 - 120	<40
Benzo[a]pyrene	100	500	60 - 120	<40
Benzo[e]pyrene	100	500	60 - 120	<40
Benzo[g,h,i]perylene	100	500	60 - 120	<40
Chrysene	100	500	60 - 120	<40
Dibenzo[a,h]anthracene	100	500	60 - 120	<40
Dibenzothiophene	100	500	60 - 120	<40
Fluoranthene	100	500	60 - 120	<40
Indeno[1,2,3-cd]pyrene	100	500	60 - 120	<40
1-Methylphenanthrene	100	500	60 - 120	<40
Phenanthrene	100	500	60 - 120	<40
Pyrene	100	500	60 - 120	<40

TABLE 2: DFTPP Tuning Criteria

m/z	Ion Abundance Criteria
51	10-80% of Base Peak
68	less than 2% of mass 69
70	less than 2% of mass 69
127	10-80% of base peak 198
197	less than 2% of mass 198
198	Base peak, or >50% of Mass 442
199	5-9% of mass 198
275	10-60% of Base Peak
365	greater than 1% of mass 198
441	Present but <24% of mass 442
442	Base Peak, or greater than 50% of mass 198
443	15-24% of mass 442
DDT	DDT breakdown should be less than 20%
TF	Tailing Factor (TF) for Benzidine and Pentachlorophenol (<2)

TABLE 3: Characteristic Ions For Internal Standards and Surrogates

Analyte	**Primary ion**	**Secondary Ions**
1,4-Dichlorobenzene-d_4**(IS)**	152	150, 115
Naphthalene-d_8 **(IS)**	136	68, 137
Acenaphthene-d_{10} **(IS)**	164	165, 162
Phenanthrene-d_{10} **(IS)**	188	94, 189
Chrysene-d_{12} **(IS)**	240	120, 241
Perylene-d_{12} **(IS)**	264	260, 265, 132
Nitrobenzene-d_5 **(S)**	82	128, 54
2-Fluorobiphenyl **(S)**	172	171
Terphenyl-d_{14} **(S)**	244	122, 212
Fluorene-d_{10} (S)	176	88, 177

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Pyrene-d_{10} (S)	212	106, 213
Fluoranthene-d_{10} (FS)	212	106, 213
Benzo(a)pyrene-d_{12} (FS)	264	132, 265
Acenaphthylene-d_8 (FS)	160	80, 161

TABLE 4: Characteristic Ions and Minimum Response Factors

Analyte	Primary ion	Secondary Ions	Minimum Response Factor
Naphthalene	128	129,127	0.700
Acenaphthene	154	153, 152	0.800
Acenaphthylene	152	151, 153	1.300
Fluorene*	166	165, 167	0.900
1-Methylnaphthalene	142	141, 115	-
2-Methylnaphthalene	142	141	0.40
Anthracene	178	176, 179	0.700
Benzo[a]anthracene	228	229, 226	0.800
Benzo[b]fluoranthene	252	253, 126	0.700
Benzo[k]fluoranthene	252	253, 126	0.700
Benzo[a]pyrene	252	253, 126	0.700
Benzo[e]pyrene	252	253, 126	0.700
Benzo[g,h,i]perylene	276	138, 277	0.500
Chrysene	228	226, 229	0.700
Dibenzo[a,h]anthracene	278	139, 279	0.400
Fluoranthene	202	101, 203	0.600
Indeno[1,2,3-cd]pyrene	276	138. 277	0.500
Phenanthrene	178	179, 176	0.700
Pyrene	202	101, 203	0.600
Biphenyl	154	153, 152	
2,6-Dimethylnaphthalene	156	155, 141, 115	
2,3,5-Trimethylnaphthalene	155	169, 170	
Dibenzothiophene	184	185, 139	
1-Methylphenanthrene	192	191, 189, 165	

Appendix of Changes

01/26/2011 Complete SOP re-edited to include TO-13A, Air PAH analysis

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