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EPA METHOD TO-13A: PAHs in Ambient Air using GC/MS

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1 Scope and Application

1.1 Method TO-13A is used to determine the concentrations of various polycyclic aromatic compounds in ambient air samples collected on PUFs. The PUFs are Soxhlet extracted with 10% v/v Diethyl ether in Hexane. The extract is solvent exchanged to Hexane. The extract is injected in a gas chromatograph equipped with a mass spectrometer. The laboratory currently analyzes the following compounds:

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

Laboratory Surrogate Standards:
Fluorene-d10
Pyrene-d10

Field Surrogate Standards:
Fluoranthene-d10
Benzo[a]pyrene-d12

Internal Standards
Naphthalene-d8
Acenaphthene-d10
Phenanthrene-d10
Chrysene-d12
Pherylene-d12

1.2 Each sample consisting of a 104mm quartz filter and sorbent cartridge, containing 3 inches of PUF plugs and 15 gms of XAD resin (defined as a PUF cartridge). PUF is extracted by Soxhlet extraction with 10% Diethyl ether / 90% Hexane solvent v/v. The extracts are filtered through a drying column then concentrated using a TurboVap® and RapidVap® evaporator to a 1ml volume under controlled conditions. The resulting extracts are then analyzed.

1.2.1 EPA Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, October 2016 requires the PUF contain 15gm of XAD resin and PUF plugs totaling 3" in height. Vendor Resins and PUF foams will affect flow rates for sample collection. New vendor product must be field tested for flow before use.

1.3 This method describes chromatography conditions that will allow for the GC separation of the compounds in the extract and for their qualitative and quantitative analysis by mass spectrometry.

1.4 Tier 1 NATTS compounds Benzo(a)pyrene and Naphthalene must meet MQO which are incorporated into this SOP from the EPA Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, October 2016 or later.

2 Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions (See SOP reference 13.4).

3 Interferences

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. Take corrective action to eliminate the problem. Contamination by carryover can occur whenever high concentration and low concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent (both Methylene chloride and Hexane). Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of pure solvent to clean any cross contamination in the system.

3.2 Interferences by phthalate esters can pose a major problem in TO13A analysis. Common flexible plastics are a primary source of phthalate contamination. Care must be taken during the extraction process to minimize this source of contamination.

4 Safety

4.1 For general safety information, refer to Laboratory Chemical Hygiene Plan, online revision.

4.2 Preparation of standards must take place in a fume hood. A lab coat, gloves, and safety glasses are required due to the hazardous nature of the compounds involved.

4.3 Due to the flammable and explosive nature of the solvents used for PUF extractions, additional safety precautions and procedures are required.

4.3.1 The safety of the analysts in the room takes priority over completing a sample.

4.3.2 **Full face shields** (regular and safety glasses do not offer sufficient protection) **should be worn** by the primary or helping analyst when performing any of the following actions:

- Setup and takedown of PUF Soxhlet extractions
- Raising the hood sash to inspect an actively heating PUF Soxhlet extraction
- Preparing the hexane/ether solvent mixture (**must be performed in the fume hood with heating mantels cool and unplugged**)

4.2.3 The spike witness for the extraction must wear safety glasses unless performing any of the above actions, in which case a full face shield should be worn.

4.2.4 Inspect active extractions for conditions listed below whenever entering or leaving the area.

4.2.5 All heating mantles must be turned off and allowed to cool to room temperature before any extraction glassware is removed.

4.2.6 Soxhlet setup must have a "raising" coil inserted before the PUF cartridge is inserted into the glassware to prevent a cartridge/glassware seal.

4.2.7 A sample will be considered "Failed" results flagged as a laboratory accident should if any of the following occur:

- Soxhlet device does not cycle when heated
- If the collection flask goes dry during Soxhlet extraction
- Mantle fails to heat correctly (catastrophic failure) after cycling has begun (although small adjustments to mantle heat settings to control drip/cycling rates may be required occasionally during normal operation).

4.2.8 If any of the conditions of 4.2.7 occur **do not attempt to rescue the sample**. Do not bump the glassware in an attempt to restart cycling. Do not add solvent to a to a dry collection flask. Simply fail the sample and flag data.

4.2.9 If any of the conditions of 4.2.7 occur turn the mantle(s) off immediately and allow cooling to room temperature before taking further actions.

4.2.10 Soxhlet glassware that does not cycle (when properly heated) or that is found to be damaged is to be destroyed. **Do not have this glassware repaired.**

4.3 The Ethyl Ether solvent bottle must have the Peroxides measured with peroxide test strips before extraction, the test strip value is entered on the extraction sheet and has a flag of <20 PPM. A value of >20 PPM Peroxides indicates the solvent bottle must be disposed of in the hazardous waste mixed solvent drum.

5 Apparatus and Equipment

5.1 TO-13A cartridge assembly or Rocket

5.1.1 Flat metal plate for closing the intake end of the assembly

5.1.2 Filter retaining ring with bolt slots

5.1.3 Two white Teflon rings

5.1.4 Filter holder with filter support screen and 3 swiveling bolts

5.1.5 Two red silicone gaskets

5.1.6 Glass cartridge with PUF/XAD-2 retained by a screen within the glass cartridge

5.1.7 Cartridge holder

5.1.8 Whatman QMA 10.16 mm quartz Microfibre filter (Catalog #1851-101) or equivalent

5.1.9 Scrub brush with stiff nylon bristles

5.1.10 See Image 5.1.10.1 for Cartridge Assembly

Image 5.1.10.1 Cartridge Assembly

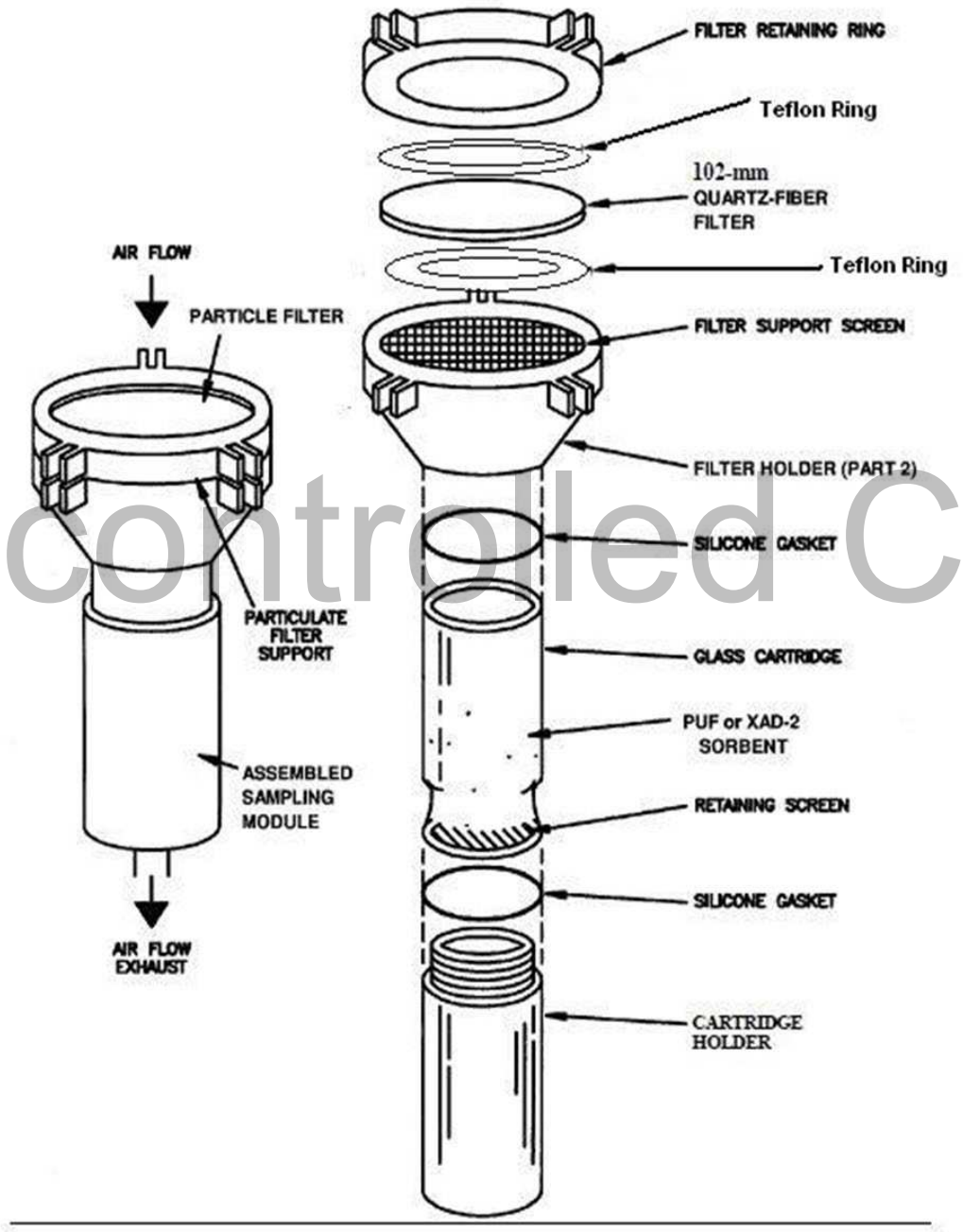


Figure 3. Typical absorbent cartridge assembly for sampling PAHs.

5.2 Soxhlet heating mantle platform
5.3 Glass sample cartridge: For sample collection
5.4 Polyurethane foam (PUF) plugs: Supelco, Restek, Tisch or equivalent.
5.5 The PUF cylinders 1 and 2 inch thick (plugs) should be slightly larger in diameter than the internal diameter of the cartridge.
5.6 Quartz fiber filter: 102 mm quartz microfiber filter (QMA), Whatman Inc.
5.6.1 Quartz fiber filters must be prepared for use by heating to 400˚ C in a muffle furnace for 5 hours prior to usage.
5.7 XAD-2® resin: SKC
5.7.1 Resin must be prepared for use by heating to 400˚ C in a muffle furnace for 5 hours prior to usage.
5.8 Screw cap amber jars: Clean, for storing glass sample cartridge.
5.9 Boiling chips: Solid Borosilicate glass beads (4mm size)
5.9.1 Boiling chips must be prepared for use by heating to 400˚ C in a muffle furnace for 2 hours prior to usage.
5.10 De-activated/pre-cleaned glass wool: Thermo
5.11 White cotton or nitrile gloves: For handling cartridges and filters and solvent
5.12 Teflon-coated TipsTweezers
5.13 Filter and Sorbent Cartridges: washed, oven dried and Hexane rinsed
5.14 Soxhlet apparatus glassware with Allihn Condenser at the top
5.15 RapidVap Vacuum Evaporator System with 450ml volume size glassware
5.16 TurboVap II Evaporator System with 50ml volume size glassware
5.17 GC/MS autosampler 2 ml borosilicate amber glass with screw caps lined with Teflon-faced silicone disks
5.18 Recirculating water chiller systems for Soxhlet extractors/condensers
5.19 Peroxide Test Strips
5.20 GC/MS systems are used with cold on column (COC) injection.
5.20.1 Gas Chromatographic column is a 15 m DB-5MS column with a diameter of 0.25 mm and a film thickness of 0.25 µm (or equivalent) with a 0.32 I.D. guard column of approximately 2 meters attached via an inert press tight column connector to the analytical column.
5.20.2 An Agilent autosampler to auto-inject the sample into a COC injector. The effluent of the column is plumbed directly into the ion source of the mass spectrometer.
5.20.3 A computer with Agilent Enviroquant software, network capability, and sufficient speed to analyze raw data and present it in a chromatographic report.
5.21 Syringes in several volumes ranging from 5 µl to 1000 µl are needed for sample dilutions and internal spiking of all extracts.
5.22 Sample extracts are stored in amber glass autosampler vials with graduations in 0.5 ml increments, screw caps, Teflon sealed septa for sample removal without opening the vial to the atmosphere. Extra caps should be available to reseal sample extracts after the septa have been punctured for analysis.
5.22.1 Each vial lot must be tested and marked for 1ml volume
5.23 5 ml and 10 ml volumetric flasks with ground glass stoppers

6 Reagents

6.1 All reagents are logged into the GCMS reagent logbook, including filter paper, glass wool, and Sodium Sulfate.

6.1.1 Solvents are Diethyl Ether, Methylene Chloride, Hexane, all trace analysis grade.

6.1.2 10% v/v Diethyl Ether in Hexane for PUF extraction.

6.1.3 High purity grade Helium

6.1.4 All TO13A standards that are received must have a receiving date written on the original box. All standards must have an expiration date on either the box or ampule.

6.1.5 Mark each vial with the proper concentration and store at 4ºC ± 2ºC until ready to use. Warm to room temperature before use. Note: Opened primary stock standard vials are valid for up to 6 months. All diluted stock standard solutions expire within 6 months of preparation.

6.2 LCS Spiking Standard 250µl of a 2000 µg/ml standard vial (or equivalent concentration as purchased from another vendor) of the target compounds is added to a 10 ml volumetric flask containing a few ml of Hexane and diluted to volume with Hexane. Final concentration is 50.0 µg/ml for each component.

Table 6.2.1 – TO-13A Spiking Stock Standard in Hexane for LCS/LCSD

Standard Vile Mix	Compound	Initial Concentration	Aliquot	Final Concentration
Mix #1	Benzo(a)pyrene	2000 µg/ml	250 µl	50.0 µg/ml
Mix #2	Perylene	2000 µg/ml	250 µl	50.0 µg/ml
Mix #3	Naphthalene	2000 µg/ml	250 µl	50.0 µg/ml
	Acenaphthylene	2000 µg/ml		50.0 µg/ml
	Acenaphthene	2000 µg/ml		50.0 µg/ml
	Fluorene	2000 µg/ml		50.0 µg/ml
	Phenanthrene	2000 µg/ml		50.0 µg/ml
	Anthracene	2000 µg/ml		50.0 µg/ml
	Fluoranthene	2000 µg/ml		50.0 µg/ml
	Pyrene	2000 µg/ml		50.0 µg/ml
	Benz(a)anthracene	2000 µg/ml		50.0 µg/ml
	Chrysene	2000 µg/ml		50.0 µg/ml
	Benzo(b)fluoranthene	2000 µg/ml		50.0 µg/ml
	Benzo(k)fluoranthene	2000 µg/ml		50.0 µg/ml
	Benzo(e)pyrene	2000 µg/ml		50.0 µg/ml
	Indeno(1,2,3-cd)pyrene	2000 µg/ml		50.0 µg/ml
	Dibenz(a,h)anthracene	2000 µg/ml		50.0 µg/ml
	Benzo(g,h,i)perylene	2000 µg/ml		50.0 µg/ml

Final Volume of LCS Spiking Stock Standard in Hexane	10.0 ml
Total Volume of Standard Aliquots	0.75 ml
Total Volume of Hexane added	9.25 ml

Table 6.2.2 – TO13A LCS/LCSD Stock Spiking into PUF for extraction**			
**Final Sample Extract Volume will be 1.0 ml			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Benzo(a)pyrene	50 µg/ml	20 µl	1.0 µg/ml/PUF
Perylene	50 µg/ml		1.0 µg/ml/PUF
Naphthalene	50 µg/ml		1.0 µg/ml/PUF
Acenaphthylene	50 µg/ml		1.0 µg/ml/PUF
Acenaphthene	50 µg/ml		1.0 µg/ml/PUF
Fluorene	50 µg/ml		1.0 µg/ml/PUF
Phenanthrene	50 µg/ml		1.0 µg/ml/PUF
Anthracene	50 µg/ml		1.0 µg/ml/PUF
Fluoranthene	50 µg/ml		1.0 µg/ml/PUF
Pyrene	50 µg/ml		1.0 µg/ml/PUF
Benz(a)anthracene	50 µg/ml		1.0 µg/ml/PUF
Chrysene	50 µg/ml		1.0 µg/ml/PUF
Benzo(b)fluoranthene	50 µg/ml		1.0 µg/ml/PUF
Benzo(k)fluoranthene	50 µg/ml		1.0 µg/ml/PUF
Benzo(e)pyrene	50 µg/ml		1.0 µg/ml/PUF
Indeno(1,2,3-cd)pyrene	50 µg/ml		1.0 µg/ml/PUF
Dibenz(a,h)anthracene	50 µg/ml		1.0 µg/ml/PUF
Benzo(g,h,i)perylene	50 µg/ml		1.0 µg/ml/PUF

6.3 Internal Standards: Vendor stock solution at a concentration of 4000 µg/ml or equivalent for each component.

Table 6.3.1 – TO13A Internal Standard Stock Standard			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Naphthalene-d8	4000 µg/ml	125 µl	50.0 µg/ml
Acenaphthene-d10	4000 µg/ml		50.0 µg/ml
Phenanthrene-d10	4000 µg/ml		50.0 µg/ml
Chrysene-d12	4000 µg/ml		50.0 µg/ml
Perylene-d12	4000 µg/ml		50.0 µg/ml

Final Volume of Internal Standard Stock Standard in Hexane	10.0 ml
Total Volume of Standard Aliquots	0.125 ml
Total Volume of Hexane added	0.9875 ml

Table 6.3.2 – TO13A Internal Standard Spiking Standard For Samples**			
**Final Sample Extract Volume is 1.0 ml			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Naphthalene-d8	50.0 µg/ml	10 µl	0.5 µg/ml
Acenaphthene-d10	50.0 µg/ml		0.5 µg/ml
Phenanthrene-d10	50.0 µg/ml		0.5 µg/ml
Chrysene-d12	50.0 µg/ml		0.5 µg/ml
Perylene-d12	50.0 µg/ml		0.5 µg/ml

6.4 Field Spiking Solution is 250 µl of vendor stock of mix of surrogates at a concentration of 2000 µg/ml per component are added to a 10 ml volumetric flask containing a few ml of Hexane and diluted to volume with Hexane. Final concentration for each component is 50.0 µg/ml.

Table 6.4.1 – TO-13A Field Surrogate Stock Spiking Standard				
Standard Vile Mix	**Compound**	**Initial Concentration**	**Aliquot**	**Final Concentration**
Mix #1	Fluoranthene-d10	2000 µg/ml	250 µl	50.0 µg/ml
	Benzo(a)pyrene-d12	2000 µg/ml		50.0 µg/ml

Final Volume of Field Surrogate Spiking Stock Standard in Hexane	10.0 ml
Total Volume of Standard Aliquots	0.75 ml
Total Volume of Hexane added	9.25 ml

Table 6.4.2 – TO-13A Field Surrogate Spiking Standard**			
**Final Sample Extracted Volume will be 1.0 ml			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Fluoranthene-d10	50 µg/ml	20 µl	1.0 µg/ml/PUF
Benzo(a)pyrene-d12	50 µg/ml		1.0 µg/ml/PUF

6.5 Laboratory Surrogate Standard Spiking Solution is 250 µl of vendor stock of mix of surrogates at a concentration of 1000 µg/ml per component are added to a 10 ml volumetric flask containing a few ml of Hexane and diluted to volume with Hexane. Final concentration for each component is 50.0 µg/ml.

Table 6.5.1 – TO-13A Laboratory Surrogate Spiking Standard in Hexane				
Standard Vile Mix	**Compound**	**Initial Concentration**	**Aliquot**	**Final Concentration**
Mix #1	Fluoroene-d10	1000 µg/ml	500 µl	50.0 µg/ml
	pyrene-d10	1000 µg/ml		50.0 µg/ml

Final Volume of Laboratory Surrogate Spiking Stock Standard in Hexane	10.0 ml
Total Volume of Standard Aliquots	0.75 ml
Total Volume of Hexane added	9.25 ml

Table 6.5.2 – TO-13A Field Surrogate Spiking Standard**			
**Final Sample Extracted Volume will be 1.0 ml			
Compound	**Initial Concentration**	**Aliquot**	**Final Concentration**
Fluoranthene-d10	50 µg/ml	20 µl	1.0 µg/ml/PUF
Benzo(a)pyrene-d12	50 µg/ml		1.0 µg/ml/PUF

6.6. DFTPP Standard After opening the glass sealed vials for preparation of the DFTPP the remaining solution is stored in new, clean, glass amber autosampler vials, properly identified, and store at 4ºC ± 2ºC for up to 6 months.

Table 6.6.1 - TO-13A DFTPP Tuning Standard Solution			
Compound	**Initial Concentration**	**Aliquot**	**Final**
DFTPP	1,000 µg/ml	250 µl	50 µg/ml

Final Volume of DFTPP in Hexane	5.0 ml
Total Volume of Standard Aliquot	0.250 ml
Total Volume of Hexane added	4.750 ml

6.7 The stock solutions of the standards are used to prepare the 5 different concentration mixes for a curve.

Table 6.7.1 – TO13A Calibration Curve					
LCS Stock Solution 50 µg/ml	**Field Surrogate 50 µg/ml**	**Lab Surrogate 50 µg/ml**	**Internal Standard 50 µg/ml**	**Hexane Volume**	**Final Concentration 1 ml Final Volume**
Aliquot	**Aliquot**	**Aliquot**	**Aliquot**	**Aliquot**	
2 µl	2 µl	2 µl	10 µl	984 µl	0.10 µg/ml
5 µl	5 µl	5 µl	10 µl	975 µl	0.25 µg/ml
10 µl	10 µl	10 µl	10 µl	960 µl	0.50 µg/ml
25 µl	25 µl	25 µl	10 µl	915 µl	1.25 µg/ml
50 µl	50 µl	50 µl	10 µl	840 µl	2.50 µg/ml

6.7.1 While preparing the curve, also prepare several 0.50 µg/ml standard vials to use as a curve mid-point continuing calibration standard (daily CCV). CCV standards are used frequently and are subjected to evaporation, heating, cooling, and exposure to light. CCVs in use will degrade over time.

6.7.2 If a CCV mid-point vial is suspected of being degraded, analyze the 0.50 µg/ml level from the initial calibration curve standards and compare it to the daily CCV. If both show poor response for these or other compounds, the system is contaminated and the standard is good. If the initial calibration standard shows good response for all target compounds (< 30%D), then the daily calibration standard is degrading and should be discarded. A new previously prepared vial should be used.

6.8 The ICV Standard, a second source standard must also be prepared to verify the concentrations of the primary standard used to make the initial curve. This standard is prepared exactly as the calibration curve 0.5 µg/ml standard but the target PAH compounds must be from another supplier or use a different lot number from initial curve vendor.

6.8.1 ICV is analyzed after each curve to verify the curve. The second source contains all the PAH target compounds and is be prepared at a concentration of 0.5 µg/ml.

6.8.2 The percent deviation should be ± 30% of true value for all analyte target compounds.

7 Sample Collection

7.0 The EPD Laboratory provides cleaned and certified PUF cartridges for collection of PAH's in Air. PUF cartridges are cleaned as a batch and are certified clean for field use if the levels of all PAHs are each ≤ 10 ng/PUF.

7.1 PUF Rocket assembly, disassembled and left on a cart designated for dirty glassware must be cleaned before re-use.

7.1.2 Disassembled rockets are soaked in warm water for 2 or more hours. No detergent is used due to contamination.

7.1.3 Following the first soaking, rockets are brushed with a large round nylon bristle

brush if a white residue is present.

7.1.4 If white residue was present after first soaking, soak rockets in warm water a second time for 2 or more hours.

7.1.5 Drain the water from the rocket parts and set on counter to air dry.

7.1.6 After drying the parts are stored on the shelf and covered with white lab towels.

7.2 For Field use assemble the clean Rocket with a clean certified PUF.

7.2.1 The PUF cartridge are spiked with field surrogates by the GC/MS Lab. Each spiked PUF cartridge is stored in a 1 L amber glass jar with the sampling location for shipping on the jar lid.

7.2.2 Refer to figure 1.1.10.1 for an exploded view of a Rocket assembly including the glass PUF/XAD-2 cartridge.

7.2.3 Check the underside of the Rocket for a red silicone gasket. Replace if not present or if the gasket appears to be damaged.

7.2.4 Set the Rocket base on the lab counter with the metal frit (filter support screen) turned up.

7.2.5 Place one white Teflon ring on top of the base.

7.2.6 Using tweezers or gloves, place quartz filter on the Teflon ring.

7.2.7 Place a second Teflon ring over the filter.

7.2.8 Place a filter retaining ring on top followed by a closing plate .

7.2.9 Secure with the three bolts attached to the base. Flip the assembled base over so that the closing plate rests on the counter.

7.2.10 Place a red silicone gasket inside the cartridge holder.

7.2.11 Remove a glass PUF cartridge from the amber glass jar and insert into the cartridge holder with the open end of the glass cartridge up and the PUF/XAD-2/retaining screen towards the closed end of the cartridge holder. The glass cartridge should be resting on the red silicone gasket inserted in the cartridge holder.

7.2.12 Screw the cartridge holder onto the base.

7.2.13 Wrap the air flow exhaust tip end of the assembly with aluminum foil.

7.3 Each batch of prepared PUF assemblies must be certified prior to shipment to the field by analysis of one QC PUF cartridge per extraction batch of up to 12 PUF cartridge assemblies.

7.3.1 The acceptance criteria for a clean PUF cartridge for field use is analyzing a 5ml extracted cleaned PUF with all target compounds are each <0.01ug/PUF.

7.3.2 All Reagents and Standards are logged into Reagent Logbook and Standards Logbook.

7.3.3 Each new production autosampler vial lot number must be verified with 1gm of lab deionized water on a certified balance to be at a marked volume of 1ml prior to use. The logsheet of the verification is to be kept in the extract logbook.

7.3.4 Each certified clean PUF cartridge is pre-logged into the LIMS system (Labworks) and assigned a unique sample identification number. This number is used to track the PUF cartridge out to the field, back to the laboratory on the chain of custody form, and is used for identification for sample analysis and reporting.

7.4 Cleaning of new and unwashed PUF foam 1-inch plugs

7.4.1 Place four 2 inch new/unwashed PUF plugs in Soxhlet apparatus (height cannot exceed drain loop), charge the 1,000 ml round bottom flask with 500 ml acetone

with heater set at "5" and turn the chillers on. Extract for 16 hours to 18 hours at approximately 4 cycles per hour.

7.4.2 After 16 hours place PUF plugs in hood for 24 hours to dry, then place in vacuum jar and vacuum with Nitrogen flow at room temperature until no solvent odor is detected, about 2 days.

7.4.3 Use the cleaned PUF 1-inch foam plugs to assemble new PUF cartridges

7.5.1 Assembly of a PUF cartridge

7.5.1 Using Acetone rinsed 1-inch PUF foams, 3 foams are used with 15 gm pre-certified XAD-2 in between, 2 one-inch foams are placed against the wire, then the XAD-2, the one foam on top. 15 gm of pre-cleaned and certified XAD-2 resin is used in the cartridge. Press the sandwich slightly together to keep the resin in place.

7.6 The newly assembled PUF cartridges must be certified clean in a batch before use. Place spacing rings, then PUF cartridges, one PUF(the QC PUF) will also have a folded pre-baked Quartz filter into the Soxhlet apparatus. Up to 12 PUF can be certified clean in one batch.

7.6.1 Pour 500 ml of 10% v/v Diethyl ether in Hexane into the 1000 ml round bottom flask.

7.6.2 Turn heater mantle to a setting of approximately "5", turn chillers on, and reflux for 16 hours. Adjust the power to the mantle as necessary to achieve approximately 4 cycles per hour.

7.6.3 After 16 hours, allow to cool, and disassemble the apparatus.

7.6.4 Drain all solvent from the PUF cartridge and Soxhlet apparatus into the 1000 ml round bottom flask.

7.6.5 The QC PUF cartridge solvent (the cartridge containing the filter if cleaning multiple cartridges) extract must be concentrated and analyzed for contamination after the cleaning process.

7.6.6 Dry the extract from the Soxhlet extraction by passing it though drying column that has a plug of pre-cleaned glass wool and about 10 g of pre-baked anhydrous Sodium sulfate. Collect the dried extract in a 450 ml RapidVap cup. Wash the round flask and drying column with about 100 ml of 10% v/v Diethyl ether in Hexane. Use a squeeze ball to blow out remaining extract from dry column.

7.6.7 Place the RapidVap cups into RapidVap Vacuum Evaporation Systems with the following settings:
Vortex Speed:
30% for volumes between 300 – 450 ml, then increase to
50% for volumes between 0 – 300 ml
Nitrogen pressure:
4 psi for volumes between 300 – 450 ml, then increase to
10 psi for volumes between 0 – 300 ml
Block heat and block set point temperature:
32° C for volumes between 300 – 450 ml
38° C for volumes between 0 – 300 ml

7.6.8 The internal wall of the RapidVap cup must be rinsed down several times with hexane during concentration process.

7.6.9 Reduce the extract to between 30 – 40 ml and remove from the RapidVap

concentration unit.

7.6.10 Transfer the extract to a 50ml TurboVap vial and rinse the RapidVap cup several times during the transfer. Place TurboVap vial into a TurboVap concentration unit set up as follows:
Nitrogen pressure:
3 psi for volumes between 3 – 7 ml, then increase to
10 psi for volumes between 0 – 3 ml
Water bath temperature: 38˚C

7.6.11 In the TurboVap vial the final volume is now reduced to 5ml. Then a 1ml aliquot of this extract is transferred to a 2ml amber autosampler vial and spiked with 10µl of internal standard spiking solution and mixed. The extract is ready for GC/MS analysis

7.6.12 The PUFs are removed from the Soxhlets and placed in the fume hood to dry for at least 6hrs due to Ether residue in the PUFs. (Ether is very flammable and any cleaned/extracted PUF must remain in the hood until all Ether residue has evaporated). After 6 hrs the PUFs are placed into a vacuum jar with a low Nitrogen bleed to completely dry the PUF. After >48hrs in the vacuum jar the PUFs are removed and stored in amber screw top jars in a dark cabinet until use.

7.6.13 When the acceptance level is met then all cleaned PUF cartridges from that batch are certified and ready for field use. Cartridges are considered clean for up to 30 days from date of cleaning when sealed in their cleaned amber jars.

7.6.14 If the acceptance level is not met for the QC PUF cartridge, then all PUF cartridges from the cleaning batch must be cleaned again.

7.7 Shipping PUF/Rockets to the field

7.7.1 The GC/MS Lab provides the mailing/pickup schedule. The schedules are stored in a green binder in Lab Room “Labeled PUFs Shipping Log for TO13A by GC/MS”.

7.7.2 Each assembled Rocket is wrapped in bubble wrap then placed inside a white Thermosafe Storage/Transport chest or hard shell cooler containing either 9 blue Freeze PAKs, or 6 Rubbermaid Blue Ice Packs in the bottom of the chest.

7.7.3 PUFs are shipped by UPS using the PUF profile on the computer in the Organic Lab shipping room.

7.7.4 The appropriate mailing/pick-up schedule in the green binder is initialed and dated by the Lab personnel shipping the PUFs.

7.7.5 PUFs that are picked up by field collectors are signed for (green binder) when they are picked up from.

7.7.6 Prior to field sampling the PUF cartridges are spiked with field surrogate compounds. 20 µl of the Field Surrogate Spiking Standard (50 µg/ml) are spiked into each PUF resulting in a final concentration of 1 µg/PUF for each surrogate. The PUF is spiked just prior to being assembled into the “rockets” and shipped to the field.

7.7.7 The PUF must be extracted within 14 days from the sample collection day per the 2016 NATTS TAD. (NOTE: This is a change from EPA TO-13A Second Edition Jan 1999 which allows for only 7 days).

7.7.8 Upon receipt at the laboratory, the temperature is checked and recorded on the COC. The PUF sample cartridge from the field is stored in a screw cap amber jar

along with the 104mm filter. Nothing else is stored in the jar (i.e. no ID Label)

7.7.9 Received temperature must be ≤ 4°C, unless the PUF is received at the laboratory ≤ 4 hours after being removed from the field sampler. (the travel time from the field site to the laboratory must be ≤ 4 hours.)

7.7.10 The PUF cartridge and filter must be stored in a freezer at ≤ 4º C and protected from light (freezing is permitted). The final 1 ml extract is stored at 4º C ± 2º C, protected from light, and must be analyzed within 40 days from the extraction date.

8 Calibration

8.1 An Instrument Solvent Blank must be analyzed before any DFTPP solution tune verification analysis, prepared using 1ml of 100% Hexane in an autosampler vial

8.2 DFTPP Tune Before any sample or QC analysis, including a curve calibration, the mass spectrometer must be "tuned" to meet tuning and standard mass spectral abundance. The instrument software runs a special DFTPP tuning calibration program which optimizes the voltage settings of the mass spectrometer. Afterwards instrument tuning, a 50 ng injection of a DFTPP solution verifies the mass spectrometer is tuned based on mass abundances of the DFTPP.

8.2.1 50 ng of DFTPP is analyzed at the beginning of each 12 hour analysis period and prior to initial curve calibration to verify that the mass spectrometer is calibrated. The sequence must run a Solvent Blank then the DFTPP analysis. The DFTPP run method and is short because it is focused only on the analysis of DFTPP.

8.2.2 Table 8.2.2.1 lists the Method TO-13A requirements for a mass spectrometer to be considered "in tune" for each 12 hour analysis sequence:

Table 8.2.2.1 DFTPP Mass Ion Tune Criteria

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

8.2.3 After the tune check has been analyzed, Enviroquant will print out a chromatogram and table that will determine if the tune "passed". If all criteria pass then the tune is valid. If any ion abundance fails, analyze another tune check standard. If the

second tune fails criteria, then some type of system cleanup is probably in order and should be performed before any further analyses are performed. Another DFTPP injection must be performed after each 12 hour tune time lapse.

8.3 Following a successful tune criteria check (DFTPP), inject 1 µl each of the 5 concentrations of standards for the PAHs target compounds. After the raw data has been processed for correct peak identification and integration, upload the results into the appropriate calibration levels of the EnviroQuant Software.

8.3.1 The 5-point internal standard calibration curve is evaluated with Enviroquant. Select the "Initial Cal" menu item from the top menu bar, then select the "Response Factors to Printer" menu item. The software automatically calculates and prints the average response factor and the %RSD for all compounds.

8.3.2 All compounds in all levels must meet the minimum Relative Response Factors (RRF) listed in Table 8.3.2.1.

Table 8.3.2.1 – Minimum Relative Response Factors for Initial Calibrations, ICVs and CCVs

Compound	Minimum RRF
Naphthalene	0.700
Acenaphthylene	1.300
Acenaphthene	0.800
Fluorene	0.900
Phenanthrene	0.700
Anthracene	0.700
Fluoranthene	0.600
Pyrene	0.600
Benz(a)anthracene	0.800
Chrysene	0.700
Benzo[b]fluoranthene	0.700
Benzo[k]fluoranthene	0.700
Benzo[a]pyrene	0.700
Benzo[e]pyrene	No assigned minimum
Perylene	0.500
Indeno[1,2,3-cd]pyrene	0.500
Dibenzo[a,h]anthracene	0.400
Benzo[g,h,i]perylene	0.500

8.3.3 All compounds must have a maximum Percent Relative Standard Deviation (%RSD) of the Relative Response Factors ($\overline{RRF}$) of ≤ 30%, and each level must be re-quanted and be within 30% of nominal for that level.

8.3.4 If a Quadratic or Linear regression is used, r ≥ 0.995 and each level must be re-quanted and be within 30% of nominal for that level.

8.3.5 For the curve to be valid each internal standard in each level must have an absolute retention time of ± 20.0 seconds (0.333 minutes) of the average retention time (RT)

8.3.5.1 For the curve to be valid each target analyte and surrogate in each level must have a RRT index drift of no more than ± 0.06 units of the mean RRT of the initial calibration.

8.3.5.2 For each of the 5 calibration levels, run the retention time custom report ("RTReport.crt"). This custom report generates the RRT for a file and is saved to an Excel data file (.xls). Save the .xls file to "S:\GCMSLAB\TO-13 RRT Files".

8.3.5.3 At a laboratory computer that has the Microsoft program "Excel", open the RRT Excel form located at "S:\GCMSLAB\FORMS\TO-13". The name of the calculation form is "TO-13A RRT Study Initial Calibration Curve.xls"

8.3.5.4 For each calibration curve level, open the custom RRT file created and with the mouse cursor, highlight and copy the RT and RRT columns. Remember to include the top line containing the data file name. Copy and paste this data to the RRT Study Initial Calibration Curve spreadsheet. Put the appropriate curve level RRT into the appropriate place on the form. Make sure the data is lined up with the analyte names. Review to verify that the correct data file name is associated with the correct curve level.

8.3.5.5 Review the RRT Study spreadsheet to determine if any compounds fail RRT criteria.

8.3.5.6 The Calibration Curve "RRT Average" is copied and saved to a file folder on the "S" drive and will be used to verify that the retention time of targets and surrogates for analyzed samples are ±0.06 RRT of the initial calibration curve RRT average.

8.3.6 The calibration curve is saved with the file is named for the calibration date and the method. A curve saved on June 6, 2012 would be named 060612TO13A.m.

8.3.7 A second source standard (ICV) must also be analyzed to verify the concentrations of the primary standard used to make the initial curve. The ICV is analyzed after each curve to verify the curve. The second source contains all the PAH target compounds and is be prepared at 0.5 µg/ml.

8.3.7.1 The Percent Difference for the ICV must be ± 30% of the Mean Initial Calibration Relative Response Factors ($\overline{RRF}$), or ± 30% of nominal, for all analytes.

8.3.7.2 The minimum RRFs of the ICV must meet the criteria listed in Table 8.2.2.1.1.

8.3.7.3 If the ICV does not meet minimum RRF or %D criteria, troubleshoot the system and correct any problems found, then re-run the initial calibration.

9 Quality Control

9.1 The initial calibration for each compound of interest must be verified once for every 12 hours of sample analyses, before sample analysis can continue, using the same introduction technique and conditions used for the calibration curve. This is accomplished by analyzing a calibration standard verification sample (CCV) at a concentration of 0.5 µg/ml (midpoint of the calibrating range). The results from the calibration standard analysis should meet the verification acceptance criteria listed below:

9.1.1 The Percent Difference (%D) should be within □ 30% of the Mean Relative Response Factors ($\overline{(RRF)}$) of the initial calibration for all analytes. If Quadratic or Linear fit, the recovery must be □ 30% of nominal.

The minimum RRFs of the CCV must meet the criteria listed in Table 8.2.2.1.1. Internal Standard Responses of the CCV must be within 50% to 200% from the mid-point standard of the initial calibration curve.
The daily CCV with the updated target retention times is saved with a file name indicating the date of the CCV and the method. The name should also indicate that the file is for a CCV. An example, a CCV is analyzed on June 10, therefore the calibration saved for that day would be named 06102012TO13ACCV.m.

9.1.2 NOTE: This CCV file is only used for reporting Internal Standard Retention Time shifts between the retention times of the Internal Standards of a sample to that of the daily or most recent CCV Internal Standards. Quantitation must still be performed against the original calibration curve file. The retention time shift of the internal standards of samples must be within ±0.33 min of the daily or most recent CCV.

9.1.3 If the CCV fails to meet the criteria, run another CCV and examine the compounds according to the verification acceptance criteria. If it meets QC then analyze samples. If it does not meet QC perform maintenance and run another curve.

9.1.4 If the CCV "passes" the system has a valid calibration and analysis of samples can begin. Note that the 12 hour clock begins after the tune criteria check has been injected. If the 12 hours is exceeded another passing tune check and another CCV must be injected before samples can be analyzed. Any samples injected after the 12-hour DFTPP cut off time must be re-analyzed within a valid clock time.

9.1.5 Update the CCV internal standard retention time in Enviroquant by opening the Continuing Calibration window, then clicking on "Update continuing evaluation", also "Save continuing INSTD report". Note: Be sure the quantitation is set up for using initial calibration response factors and not the daily CCV response factors. Exit and save the method.

9.2 Record Keeping: Documentation of an instrument calibration is reviewed for adherence to quality criteria and archived after review and approval by a supervisor or manager.

9.3 Initial calibration is recommended at every six weeks, but if the instrument and calibration curve are stable can be used for up to 3 months.

9.4 A certificate of analysis data sheet is shipped with the standards and is filed in the TO-13A QC Certificate of Analysis standards logbook.

9.4.1 Standards that are opened for use are recorded into the standard logbook and assigned a log number. After opening for use the solution is transferred into a new clean glass amber autosampler vial, identified with the standard log number, and stored in the refrigerator at 4º C ± 2º C. This non-diluted standard can be stored for up to 6 months from date of opening.

9.4.2 Prepared standard mixtures are stored at 4º C ± 2º C for up to 6 months.

9.4.3 All prepared standards have individual numbers recorded in the standards logbook to provide proper identification and traceability. The expiration dates of all standards should be checked to make sure they are not expired prior to use. Any standards past the expiration date must be disposed of according to laboratory hazardous waste procedures (See SOP reference 13.3)

9.4.4 Prior to use all standards must be removed from cold storage and allowed to equilibrate to room temperature.

9.5 Refer to Appendix A Reporting Limits (RLs) and MDLs, Table 14.1 for Quality Assurance criteria and Table 14.2 for a summary of Quality Control procedures associated with this method.

9.6 A Method Detection Limit Study for all analytes must be performed initially, after major instrument repairs or changes to extraction procedures. MDL studies performed for these purposes can be done by the extraction and analysis of 7 samples and 7 blanks over 3 separate days. The preferred MDL study is performed on a continuous basis with each extraction batch having one MDL spiked PUF.

9.6.1 The 7 MDL samples study is performed by extracting 7 spiked PUFs, MDL_{Spike} , spiked below the lowest point of the curve and extracted along with 7 clean blank PUF assemblies, MDL_{Blank}. These sets of spiked and blank PUFs are extracted over 3 separate days and analyzed over a period of 3 separate days, there is a non-analysis day between each of the 3 days. A total of 14 PUFs are extracted, 7 spiked and 7 blank.

9.6.2 **On a continuous basis** MDLs are performed by extraction and analysis of one PUF spiked as an MDL_{Spike} , below the lowest point of the curve and extracted with every batch of samples along with the method blank PUF, MDL_{Blank} per each batch of samples. The results of the MDL_{Spike} and MDL_{Blank} will be entered into Labworks using the blank test code $B_TO13AGCMS, and the MDL test code, $MLTO13AGCMS, and the MDL Spiked Amount $MATO13AGCMS. The instrument used for the MDL and Blank analysis will selected using INSTR-TO13AGCMS. MDL reports will be pulled from Labworks on a minimum of once per year (See SOP reference 13.8).

9.6.3 Tier 1 NATTS compounds Benzo(a)pyrene and Naphthalene must meet 10^{-6} Cancer Risk MDL MQO, See Table 9.6.3.1.

Table 9.6.3.1 NATTS MDL MQO

Analyte	Cancer Risk 10^{-6} µg/m³	MDL MQO µg/m³	MDL µg/PUF (based on 300m³)
Naphthalene	0.029	0.029	8.7
Benzo(a)pyrene	0.00091	0.00091	0.273

9.6.4 The higher value of the 2 MDLs, MDL_{Blank} or MDL_{Spike} will be used as the reporting MDL.

9.6.5 If the MDL_{Spike} is used the following must be true for the MDL to be valid: MDL < Spike Amount < 10 x MDL

9.7 Sample Analysis QC Batch: Method TO13A requires additional QC samples that are extracted and/or analyzed. These include the Method Blank, LCS and LCSD, a Solvent Method Blank, and a Replicate Extract Analysis. These QC samples are extracted with the field PAHs PUF analysis, up to a maximum of 20 samples per batch. The group of 20 samples and the QC samples are extracted within a 5 day (Monday-Friday) work week and are defined as a batch.

9.8 Method Blank: The Method Blank is a certified cleaned PUF cartridge extracted with a batch and is used as a quality control measure for the extraction process. It is used to check the analysis results and prove no laboratory contamination of the samples in the batch has occurred. The Method Blank is extracted with 10% v/v Diethyl ether in 90% Hexane and with field and laboratory surrogates and internal standards added. It also uses a clean/baked

PUF sample quartz filter. Method Blank results must be ≤ 2xMDL for all analytes.

9.8.1 If a Method Blank is found to have detected compounds that exceed MDL criteria, these compounds in the Blank and associated sample(s) are assigned the <LB> qualifier in the Labworks qualifier field. No comment is required in the "Sample Comments" for these flags.

9.8.2 Every sequence of field samples on the instrument must include a Method Blank analysis in the sequence run.

9.9 Field Blank: A Field Blank is extracted/analyzed with each group of non-NATTS sites for a sampling event. The laboratory sends Field Blanks out in a round robin schedule.

9.9.1 One Field Blank is analyzed at least once per month for each NATTS site. A NATTS site Field Blank may serve as a non-NATTS round robin blank.

9.9.2 Field Blank acceptance criteria: all target PAH ≤ 5xMDL, and failed compounds will be assigned <FB> in the Qualifier Field.

9.10 Instrument Solvent Blank is an aliquot of solvent (without any Int Std or targets) analyzed to ensure the GC/MS instrument is free of interferences and compounds of interest (target PAHs, internal standards, and surrogates). It is analyzed prior to DFTPP tune analysis, or calibration, or any sample analysis on the instrument.

9.10.1 Instrument Solvent Blank acceptance criteria is no target compounds, IS, or surrogates are *qualitatively* detected.

9.11 *Solvent Method Blank* is a 1ml aliquot of the batch extraction solvent used for sample extraction, fortified with IS to ensure extraction solvent is free of interferences and target compounds.

9.11.1 Solvent Method Blank acceptance criteria is all target compounds <MDL.

9.12 *Extracted Reagent Blank* is similar to the Method Blank and includes the entire Soxhlet extraction procedure using 500ml of extraction fluid…however no PUF cartridge, or foam, or XAD resin is included in the assembly for extraction. Only extraction solvent is used, no surrogates are spiked into the solvent. One per 18hr extracted field samples.

9.12.1 Extracted Reagent Blank acceptance criteria is the same as certified clean PUFs, a 5ml sample is analyzed and all target compounds each <0.01ug/Blank.

9.13 Field Surrogates, 1 µg/PUF, are spiked into PUF just before shipment.

9.13.1 Percent recoveries these surrogate compounds must fall within acceptable limits of 60-120%.

9.14 Laboratory Surrogates, 1ug/PUF are spiked into PUF just before extraction.

9.14.1 Percent recoveries of these surrogate compounds must fall within acceptable limits of 60-120%.

9.15 Samples with failed surrogates need a corrective action initiated for the sample.

9.16 The Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) consist of a clean PUF spiked with 1 µg of PAH target standards, 1 µg of laboratory surrogates, and extracted with 10% v/v Diethyl ether in Hexane.

9.16.1 The percent recovery for the LCS and LCSD must be within 60% to 120% of the nominal spike. The Precision between the LCS and LCSD must be ≤20%RPD. All samples associated with an LCS compound that is out of control will require data

qualifiers to be attached to the analytical results for that compound.

9.17 Printouts of the DFTPP pass criteria, the daily standard quantitation report, and the continuing calibration report of the daily standard are stored with the calibration curve. The 5-point curve percent relative standard deviation report is saved along with the 5 quantitation raw data reports of the 5 concentration levels.

9.18 The results of the batch are uploaded to Labworks which performs calculations between the LCS and LCSD analysis. The required batch calculations for the method for all QC and samples are processed and stored by the LIMS system.

9.19 Null code qualifiers to be used for TO-13A samples, Null qualifier flags listed in the table below are applied to samples if warranted. During result entry, an appropriate null flag is entered in the "Result" field of the affected compound(s) as one of the two letter flags from the table below unless otherwise noted for a specific flag.

Table 9.19.1 – NATTS Null Qualifier Flags

Qualifier Flags	Description
AA	Sample pressure out of limits
AB	Technician unavailable
AC	Construction repairs in the area
AD	Shelter storm damage
AE	Shelter temperature out of specification
AF	Scheduled but not collected
AG	Sample time out of limits
AH	Sample flow rate out of limits
AI	Insufficient data to make calculation
AL	Voided by operator
AM	Miscellaneous void (comment required)
AN	Machine malfunction
AO	Bad weather
AP	Vandalism
AQ	Collection Error
AR	General lab error
AS	Poor quality assurance results
AT	Calibration
AU	Monitoring waived
AV	Power failure
AW	Wildfire damage
AX	Precision check performed
AY	QC Control points (Zero / Span)

Table 9.19.1 – NATTS Null Qualifier Flags	
Qualifier Flags	**Description**
AZ	QC audit
BA	Maintenance / routine repairs
BB	Unable to reach site
BC	Multipoint calibration
BD	Auto calibration
BE	Building site repair
BF	Precision, zero or span performed
BH	Interference / co-elution
BI	Lost or damaged in transit
BJ	Operator error
BK	Site computer/data logger down
MC	Module end cap missing
TS	Holding time or transport temperature is out of specs.

9.19.1 Quality Control and Detection Flags to be used for TO-13A results. If a Null qualifier from the Null Qualifier Flags table above is entered, no Quality Control or Detection Flags are to be entered. If no Null flags are entered, up to six Quality Control or Detection Flags may be entered for a single TO-13A result.

9.19.2 The Air data exporting routine automatically combines the "Result" and "Qualifier" fields for the purposes of uploading to the EPA reporting database.

Table 9.19.2.1 - Quality Control and Detection Flags, Laboratory Generated Flags, and Field Generated Flags	
Qualifier Flags	**Description**
SQ	Values between SQL and MDL
MD	Values less-than or equal to MDL
ND	No value detected*
FB	Field blank value above acceptable limit
LB	Lab blank value above acceptable limit
TB	Trip blank value above acceptable limit
LJ	Identification of analyte is acceptable; reported value is an estimate
LK	Analyte identified; reported value may be biased high
LL	Analyte identified; reported value may be biased low
EH	Estimated; exceeds upper range
2	Operational Deviation

Table 9.19.2.1 - Quality Control and Detection Flags, Laboratory Generated Flags, and Field Generated Flags	
Qualifier Flags	**Description**
3	Field issue
V	Validated value
W	Flow rate average out of spec.
HT	Sample pick-up hold time exceeded; data questionable

**Note: The ND qualifier is technically a Null qualifier. "ND" is entered into the Labworks result field (which automatically is expanded to "Not Detected" by the LIMS) and the ND qualifier is entered into the qualifier field. As it is a Null qualifier, no other data or qualifiers should be entered.*

9.20 For the South Dekalb site, NATTS requires precision calculation between the Primary/Collocated sample and between the Collocated sample/Collocated replicate sample 6 times per year. The EPD Laboratory performs one set per month to make sure the 6 required are met if any fail due to field sampling problems.

9.20.1 Precision between the Primary and Collocated sample should be ≤20%RPD for any detect ≥ 0.5ug/ml.

9.20.2 Precision between the Collocated sample and its Replicate sample must be <10% RPD for any detect ≥0.5ug/ml.

9.20.3 Any QC failure is re-run on the instrument to verify the failure; a failure is flagged with the appropriate qualifier flag.

9.20.4 Precision results for Primary/Collocated samples are printed and scanned as a PDF and placed on the export drive "Q" for review by the Air Branch.

9.21 In each field sample analysis sequence, a replicate of a field sample must be analyzed.

9.21.1 Precision between the sample and its replicate sample should be <10% RPD for any detect ≥0.5ug/ml.

9.22 Retention Time for each Target and Surrogate compound and Internal Standard

9.22.1 For all sample and QC the target compounds and surrogates must be within ±0.06 RRT units of mean initial calibration RRT.

9.22.2 Internal Standards for all samples and QC must have RT within ± 0.33 minutes of most recent CCV.

9.22.3 Print out the QA/QC report to verify internal standard area responses. Internal standard area responses for all samples must be 50% - 200% area against the mid-level Initial Calibration.

9.23 Before shipping, PUF cartridges that have been cleaned and certified clean are logged in and assigned a LIMS number. This number is used for tracking the sample to the field, recorded on the COC, and used for laboratory ID when returned to the lab for analysis after sample collection, and for reporting results.

9.24 For Compound Identification refer to Figure 9.24.4.1 for an example of the qualitative identification criteria listed for the discussion of figures below, followed by required A,B,C,D identification parameters of a target compound in a sample.

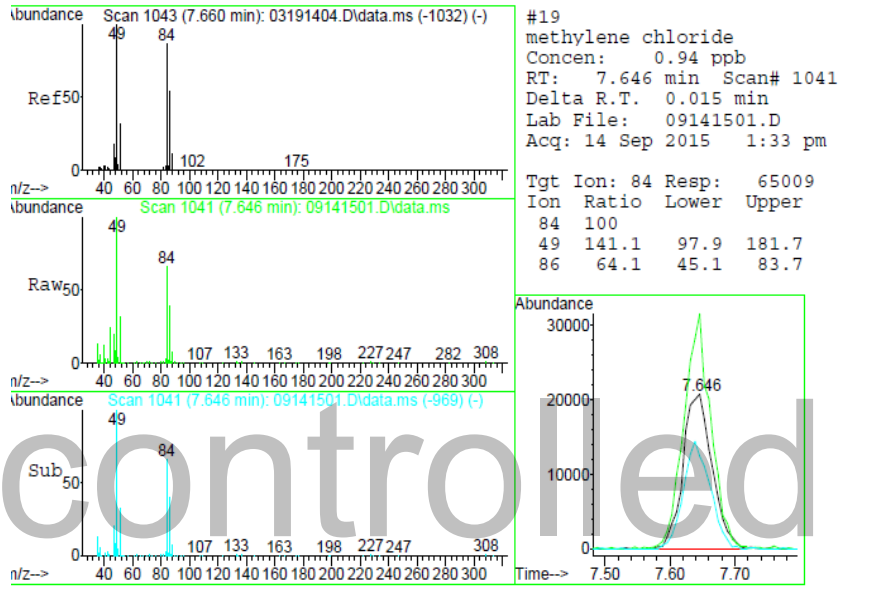
9.24.1 RT: Delta R.T. is within the retention time window defined by the method.

9.24.2 Ratios: the abundance ratios of the qualifier ions are within 30% of the ICAL average ratio: Fig. 9.18.2 “Ion” 49 and 86 have “Ratio” within “Lower” and “Upper” limits. These ratios must be set in the Chemstation software to be “Relative” (NOT Absolute).

9.24.3 Signal-to-noise ratio: the large abundance Gaussian peak is shown to be greater than 5:1 (largest peak signal is well above noise levels at baseline just before peak begins)

9.24.4 Target and qualifier ion abundance peaks are co-maximized (largest peak and smaller peaks within the large peak so that all are within 1 scan of each other).

Figure 9.24.4.1



9.24.5 A. Signal to noise ratio of the target and qualifier ions >3:1, preferable >5:1

9.24.6 B. Target and qualifier ions co-maximized (peak apexes within 1 scan of each other)

9.24.7 C. RT of compound must be within acceptable RT from ICAL average

9.24.8 D. Abundance ratio of qualifier ion response to target ion response for at least 1 qualifier ion must be within ±15% relative of the average ratio from the ICAL.

9.24.9 Using ion response ratios Chemstation will print a Q-Value on the quantitation report. If the target ion response ratios of the unknown peak matches with the saved known ion ratios, Chemstation will print a high value of up to 100, if the unknown peak does not match, a lower value will be printed, down to 10. If a value lower than 75 is printed, the peak must be investigated by the analyst using Q-Edit to determine if the peak is the target compound or is determined to not be the target compound.

9.24.10 If criteria A-D not met, compound is not positively identified. Compounds that do not meet criteria A will be compounds below the MDL concentration and will be flagged with “MD”.

9.24.11 An exception to A-D is allowed if an experienced analyst examines the mass

spectrum and it is their opinion that the unknown peak is positively identified as the target compound. The analyst must be note on the paperwork that the compound's peak was determined to be real, the analyst will also initial and date the approval of the peak as being positively identified.

9.25 Surrogate recovery, LCS and LCSDup Recovery, LCS/LCSDup Precision, Sample/Sample Duplicate Precision are charted annually for trend monitoring purposes. Limits are static, see Table 14.1.

9.26 Any failure in QC or SOP procedures of QC manual guidelines must be addressed with a Corrective Action, and copy of the Corrective Action is placed in the folder of the affected sample batch or QC folder.

10 Procedure

10.1 Extract field PUFs using Soxhlet extraction for 18 hours

10.1.1 Place spacing rings into the bottom of the Soxhlet, then field PUF cartridge, and the folded field Quartz filter into the Soxhlet apparatus.

10.1.2 One Blank PUF is spiked with field and lab surrogates, it will also have a folded pre-baked and clean Quartz filter in a Soxhlet apparatus.

10.1.3 One LCS PUF will be prepared and spiked with target compounds and field and lab surrogates, no filter.

10.1.4 One LCS Duplicate PUF will be prepared and spiked with target compounds and field and lab surrogates, no filter.

10.1.5 One solvent only Soxhlet will be prepared with solvent only, no PUF cartridge is used.

10.1.6 Pour 500 ml of 10% v/v Diethyl ether in Hexane into the 1000 ml round bottom flask of each Soxhlet, make sure to label each Soxhlet with lab tape.

10.1.7 Turn heater mantle to a setting of approximately "5", turn chillers on, and reflux for 16 to 18 hours. Adjust the power to the mantle as necessary to achieve approximately 4 cycles per hour.

10.1.8 After 16 hours to 18 hours, allow to cool, and disassemble the apparatus.

10.1.9 Drain all solvent from the PUF cartridge and Soxhlet apparatus into the 1000 ml round bottom flask.

10.1.10 The round bottom flask extract must be labeled and concentrated to be analyzed.

10.1.11 Dry the extract from the Soxhlet extraction by passing it though drying column that has a plug of pre-cleaned glass wool and about 10 g of pre-baked anhydrous Sodium Sulfate.

10.1.11.1 Collect the dried extract in a 450 ml RapidVap cup.

10.1.11.2 Wash the round flask and drying column with about 100 ml of 10% v/v Diethyl ether in Hexane. Use a squeeze ball to blow out remaining extract from dry column.

10.1.12 Place the RapidVap cups into RapidVap Vacuum Evaporation Systems with the following settings:

Vortex Speed:
30% for volumes between 300 – 450 ml, then increase to
50% for volumes between 0 – 300 ml

Nitrogen pressure:
4 psi for volumes between 300 – 450 ml, then increase to
10 psi for volumes between 0 – 300 ml
Block heat and block set point temperature:
32° C for volumes between 300 – 450 ml
38° C for volumes between 0 – 300 ml

10.1.13 The internal wall of the RapidVap cup must be rinsed down several times with hexane during concentration process.

10.1.14 Reduce the extract to between 30 – 40 ml and remove from the RapidVap concentration unit.

10.1.15 Transfer the extract to a 50ml TurboVap vial and rinse the RapidVap cup several times during the transfer. Place TurboVap vial into a TurboVap concentration unit set up as follows:
Nitrogen pressure:
3 psi for volumes between 3 – 7 ml, then increase to
10 psi for volumes between 0 – 3 ml
Water bath temperature: 38˚C

10.1.16 In the TurboVap vial the final volume is now reduced to 1ml. The 1ml aliquot of this extract is transferred to a 2ml amber autosampler vial and spiked with 10µl of internal standard spiking solution and mixed. The extract is ready for GC/MS analysis.

10.2 For GC/MS analysis the parameters for the GC are as follows in Table 10.2.1

Table 10.2.1 GC Parameters

GC Parameters	GCMS01 5975	GCMS02 5973
Inlet Mode	Cold On-Column	Cold On-Column
Volume injection	1µL	1µL
Transfer Line Temperature	250ºC	250ºC
Oven Equib Time	1.5 min	1.5 min
Oven Temp Max	325ºC	325ºC
Column Type Used	DB-5	DB-5
Column Length	30.00 meters	30.00 meters
Column Diameter	0.25 millimeters	0.25 millimeters
Column thickness	0.25µm	0.25µm
Carrier Gas	Helium	Helium
Vacuum Compensation	On	On
Solvent Delay	2.0 minutes	2.0 minutes

Table 10.2.1 GC Parameters		
GC Parameters	**GCMS01 5975**	**GCMS02 5973**
DFTPP Parameters	Flow: Constant 1.1ml/min Initial Temp: 50°C / Hold 1 min Ramp: 30°C to 280°C / Hold 2 min	Flow: Constant 1.1ml/min Initial Temp 50C/ Hold 1 min Ramp 30C to 280C/Hold 2 min
SIM Parameters	Flow: Constant 1.1 ml/min Initial Temp: 60°C / Hold 1 min Ramp-1: 30°C to 180°C / Hold 0 min Ramp-2: 15°C to 310°C / Hold 5 min	Flow: Constant 1.1 ml/min Initial Temp: 60°C / Hold 1 min Ramp-1: 30°C to 180°C / Hold 0 min Ramp-2: 15°C to 310°C / Hold 5 min

10.2.1 For GC/MS analysis the following are mass spectrometer parameters

Table 10.2.1.1 Mass Spec Parameters		
Mass Spec Parameters	**GCMS01 5795**	**GCMS02 5973**
Tune File	Dftpp.u	Dftpp.u
EM Voltage	Relative	Relative
Acquisition Mode: DFTPP	Scan	Scan
Scan: Low Mass	35	35
Scan: High mass	550	550
Scan: Threshold	150	150
Acquisition Mode: Samples	SIM	SIM
SIM Ions	Reference 13.1 Table 5 & 6	Reference 13.1 Table 5 & 6

10.2.2 For GC/MS analysis, prior to any sample analysis and before any DFTPP tune verification an instrument solvent blank must be analyzed to verify the instrument is clean. There can be no qualitative detects of any Internal Standards, Surrogates, or Target Compounds in any significant amount.

10.2.2.1 Prepare the instrument solvent blank by filling an autosampler vial with 1ml of Hexane and injecting it using the same methods as for the calibration curve and used for method analysis.

10.3 Remove all sample 1ml vials, standards and reagents from cold storage and allow equilibration to room temperature prior to sample preparation and/or analysis.

10.4 DFTPP Tune Check Procedure, 1 µl of the DFTPP standard (50 ng of DFTPP) is injected into the GC column inlet.

10.4.1 With the DFTPP vial in the auto-sampler tray, open the sequence menu and select the "edit sample log table" option. In the window, change the file name to match the current date, ending the file name with “T1” (example 09152012t1 for September 15, 2012). Change the path to match the current date (example: C:\HPCHEM\I\DATA\09152012). Select "OK".

10.4.2 Open the sequence menu and select "position and run".

10.4.3 Select OK for the next window, and then in the next window change the path to match the current date.

10.4.4 Upon completion of analysis, the software will print a tune report indicating if the tune passed the requirements. See table below for mass ion criteria

Table 10.4.4.1 DFTPP Mass Ion Tune Criteria	
Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40 - 60% of mass 198
197	< 2% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	40% of mass 198
443	17 - 23% of mass 442

10.4.5 A tune is valid for only 12 hours. For the next 12-hour shift, a new DFTPP tune must be run and passed.

10.4.6 If the DFTPP evaluation run fails, the first possible solution is to check the area count of the peak. If it is low, the injector liner may be dirty, cut the guard column, the syringe needle may be clogged, or maybe it was just a bad injection requiring a re-injection. If this all fails and will not pass then a re-tuning of the mass spec will be required. The new tune file is saved, and the DFTPP re-run. If all this is done and the tune still fails it indicates that the ion source in the mass spec is contaminated. The mass spec must be disassembled and the ion source cleaned. This cleaning will take about one entire day, and the instrument must pump out overnight to remove all water and air in the mass spec. With this new DFTPP tune the daily standard will also fail so a new curve will have to be rebuilt. If it passes, sample analysis can take place.

10.5 The daily CCV must be analyzed to verify calibration after DFTPP. The CCV must meet the requirements. Save the result file name to the current date.

10.5.1 If the CCV fails acceptance criteria review the chromatogram in QEdit for faulty integration of peaks. If there are no integration issues, analyze the CCV a second time. If the second analysis fails, the instrument probably requires maintenance ranging from routine (replacing the injector insert, clipping the column) to major (installing a new column, cleaning the source). Following maintenance, a new initial calibration may be required.

10.5.2 Update the daily retention time windows with the retention times of the CCV. Also, update the Continuing INSTD report.

10.5.3 The DFTPP and CCV report is saved with associated sample data folder.

10.6 Following a successful tune and CCV, samples may be analyzed for the 12 hour period which starts with the tune standard injection.

10.6.1 For sample analysis the 1ml extracts must be equilibrated to room temperature,

then 10 µl of room temperature Internal Standard Spiking Solution (0.5 µg per internal standard component) is added to each sample vial, also to the Method Blank vial, the Solvent Blank vial, the LCS and LCSD vials.

10.6.2 Analyze samples on the GC/MS using same conditions and methods as calibration curve and the CCV.

10.6.3 A closing CCV must be analyzed after the samples in the sequence have completed in order to "bracket" the analyzed samples on the instrument sequence. If the CCV fails acceptance criteria and there are no integration issues, analyze a second closing CCV. If the second analysis fails, the instrument probably requires maintenance. The samples run between the last good CCV and the failed CCV must be reanalyzed on a new sequence with acceptable QC.

10.6.4 To avoid the failure of a complete sequence of samples, a closing CCV should be analyzed between samples during a sequence. The samples that are bracketed between CCVs with acceptable QC will be valid and reportable. Those bracketed with unacceptable QC must be reanalyzed on a new sequence with acceptable QC.

10.7 All sample chromatograms must be reviewed in "QEdit" by an analyst before the data can be reported. Any sample data not reviewed of TIC chromatograms will be noted by the Enviroquant printed report at the top of the report page.

10.7.1 Chromatograms are reviewed using the Q-Edit module of Enviroquant. In this module, ion abundances, retention times, quality of baseline integration, etc. are reviewed and corrected as is appropriate and target compounds are determined to be detects or false positive detects or false negative detects..

10.7.2 NATTS requirements of reporting below the method reporting limit and also reporting below theoretical MDL levels, this requires that 2 quantitation ions from a peak detected within the retention time window will be reported with a qualifier.

10.7.3 Any detected ion peak within the retention time window above 3.18 times the method detection limit will <u>not</u> have a qualifier flag.

10.7.4 Flags for any detected ion peak in the retention window below the method detection limit the qualifier flag will be SQ (less than method minimum reporting limit but greater than the MDL for that compound) or MD (less than the MDL for that compound).

10.7.4.1 RAW test codes ($RW) were created in Labworks to automatically upload data from the instrument and based on reporting limits and the MDL assign SQ or MD or ND qualifier to a target compound.

10.7.5 For the NATTS Replicate/Collocated/Precision calculations once per month, the following test codes must be added manually to the NATTS sample: $XQTO13AGCMS, $RWCOLTO13AGCMS, $COLTO13AGCMS, $XPTO13AGCMS, $XXTO13AGCMS, $RWXXTO13AGCMS

10.8 All documentation relating to any sample or project, GC sequences, maintenance, sample preparation, standard preparation, etc. must be documented and stored per the GCMS Laboratory procedures or the Georgia EPD Laboratory Quality Assurance Manual. Storage is 10 years.

10.9 Laboratory Information Management System (LIMS) - After a sample batch has been analyzed it is uploaded to the Laboratory Information Management System (LIMS), Labworks.

10.10.1 $TO13AGCMS Test Codes in Labworks

- $LATO13AGCMS Spike amount of LCS/LCSD for TO13A analysis
- $TO13AGCMS Results for samples
- $RWTO13AGCMS Raw Instrument Result for Sample
- $B_TO13AGCMS Results for blanks
- $RWBKTO13AGCMS Raw Instrument Result for Method Blank
- $LDTO13AGCMS Results for Laboratory Control Spike Duplicate
- $LRTO13AGCMS Recovery for Laboratory Control Spike
- $L2TO13AGCMS Recovery for LCSD
- $LSTO13AGCMS Results for Laboratory Control Spike
- $LPTO13AGCMS Calculation of precision between LCS and LCSD
- #Q$TO13AGCMS QC batch group for TO13A analysis
- $MLTO13AGCMS MDL results
- INSTRTO13AGCMS Instrument used for MDL analysis
- $MATO13AGCMS MDL amount spiked into PUF
- $D_TO13AGCMS Sample replicate analysis during a sequence
- $P_TO13AGCMS Precision between sample and sample replicate

10.10.2 NATTS Required Test Codes in Labworks for the South Dekalb Site

- $XQTO13AGCMS Precision between Primary and Collocated Sample
- $COLLOCATEDQATO13AGCMS Collocated Sample
- $RWCOLTO13AGCMS Raw Instrument Result for Collocated Sample
- $XPTO13AGCMS Precision between Collocated and Replicate
- $XXTO13AGCMS Replicate Sample Result
- $RWXXTO13AGCMS Raw Instrument Result for Replicate Sample

11 Calculations

11.1 Relative Response Factor (RRF):

$$RRF = \frac{A_{X*} C_{IS}}{A_{IS*} C_X}$$

11.1.1 Where:
RRF = Relative Response Factor
A_{Xe} = Area of the primary quant ion for the analyte of interest
C_X = Concentration of the analyte of interest in µg/ml
A_{IS} = Area of the primary quant ion for the internal standard
C_{IS} = Concentration of the internal standard in µg/ml

11.2 Mean Relative Response Factor ($\overline{RRF}$):

$$\overline{\text{RRF}} = \sum \frac{\text{RRF}_i}{n}$$

11.2.1 Where:
$\overline{\text{RRF}}$ = Mean relative response factor
RRF_i = Relative response factor of compound at each level *i*
n = Number of values

11.3 Percent Relative Standard Deviation (%RSD):
11.3.1 Standard Deviation of Relative Response Factors (RRF_{SD}):

$$\text{RRF}_{SD} = \sqrt{\sum_{i=1}^{n} \frac{(RRF_i - \overline{\text{RRF}})^2}{n-1}}$$

11.3.2 %RSD:

$$\%\text{RSD} = \frac{\text{RRF}_{SD}}{\overline{\text{RRF}}} * 100$$

11.3.3 Where:
RRF_{SD} = Sample standard deviation (n-1) of relative response factors
$\overline{\text{RRF}}$ = Mean of relative response factors
$\text{RRF}_i = i_{th}$ relative response factor
n = Number of values
%RSD = Percent relative standard deviation of relative response factors

11.3.4 Linearity through the origin is not assumed in a least squares fit. The instrument responses versus the concentration of the standards for the calibration points are evaluated using the instrument data analysis software. The regression will produce the slope and intercept terms for a linear equation. The regression calculation will regenerate a correlation, r, a measure of goodness of fit of the regression line to the data. A value of 1.0 is a perfect fit. An acceptable correlation of coefficient should be $r \geq 0.995$ (or $r^2 \geq 0.990$). See calculations 11.3.4.1

11.3.4.1 First Order Linear Regression Response Equation

$$Y = ax + b$$

This rearranges to:
$$x = Y - b/a$$

Where:

Y = Instrument response
a = Slope of the line
b = Intercept
x = Concentration in the extract or standard

11.3.5Alternatively, second order quadratic fit may be used with an acceptable correlation of coefficient of $r \geq 0.995$ (or $r^2 \geq 0.990$). Note: quadratic fit will be calculated by chromatographic software. See calculation 11.3.5.1.

11.3.5.1 Second Order Quadratic Fit Equation

$$Y = ax^2 + bx + c$$

Where:
Y = Instrument response
a = Slope of the line
b = Intercept
c = constant
x = Concentration in the extract or standard

11.3.5.3 Subtract Y from c to get modified equation $0 = ax^2 + bx + c$
11.3.5.4 Solve for x using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

A positive and negative value will be generated. Use positive value.

11.4 Average Retention Time, $\overline{RT}$:

$$\overline{RT} = \sum \frac{RT}{n}$$

11.4.1 Where:
$\overline{RT}$ = Mean retention time for the target compound or internal standard
RT = Retention time for the target compound or internal standard
n = Number of values

11.5 Relative Retention Time (RRT):

$$RRT = \frac{RT_C}{RT_{IS}}$$

11.5.1 Where:
RT_c = Analyte retention time
RT_{IS} = Internal standard retention time

11.6 Mean Relative Retention Time ($\overline{RRT}$):

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

11.6.1 Where:
$\overline{RRT}$ = Mean relative retention time
RRT = Relative retention time
n = Number of values

11.7 Mean Area Response of Internal Standard ($\overline{Y}$):

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

11.7.1 Where:
$\overline{Y}$ = Mean area response
Y_i = i_{th} area value
n = number of values

11.8 Percent Difference (%D) between Relative Response Factors:

$$\%D = \frac{(RRF_C - \overline{RRF_I})}{\overline{RRF_I}} * 100$$

11.8.1 Where:
RRF_C = Relative response factor from a CCV or ICV
$\overline{RRF_I}$ = Average relative response factor from the most recent initial calibration

11.9 Sample Concentration Calculation ($\mu g/_{PUF}$):

$$\mu g/_{PUF} = \frac{C_s * V_t}{V_s}$$

11.9.1 Where:
C_s = Extract concentration in µg/ml
V_t = Extract volume in ml
V_s = Original sample size of one PUF

11.9.2 The units cancel out in the above equation so that the extract concentration value is equal to the true value of the PUF concentration as:

$$\mu g/_{PUF} = C_s$$

11.10 Quality Control Calculations:

$$\text{LCS/LCSD/ICV \% Recovery} = \frac{R_{spike}}{\text{Expected Result}} X\,100$$

$$\%\,\text{RPD(precision)} = \frac{\left|R_{sample} - R_{duplicate}\right|}{\left(\frac{R_{sample} + R_{duplicate}}{2}\right)} X\,100$$

11 Waste Management

11.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures (SOP reference 13.3).

12 References

13.1 EPA/625/R-96/010b – Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd Edition, Compendium Method TO-13A, Determination of Polycyclic Aromatic Hydrocarbons in Ambient Air using Gas Chromatorgraphy/Mass Spectroscopy (GC/MS), January, 1999

13.2 GA EPD Laboratory SOP's- Initial Demonstration of Capability SOP 6-001, online revision or Continuing Demonstration of Capability SOP 6-002, online revision.

13.3 GA EPD Laboratory SOP- EPD Laboratory Waste Management SOP, SOP 6-015, online revision.

13.4 GA EPD Laboratory Quality Assurance Plan, online revision.

13.5 GA EPD Laboratory SOP- Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.

13.6 EPA Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, October 2016

13.7 GA EPD Laboratory SOP – Standard Operating Procedure for Manual Integration SOP 6-020, online revision.

13.8 GA EPD Laboratory SOP – Data Integrity Verification and Validation SOP 6-016, online revision.

14 Precision and Accuracy Criteria, and Quality Control Approach

Table 14.1 Acceptance Criteria for EPA TO-13A

Method TO13A	Analyte	Accuracy (%R)	Precision (RPD)
SS*	Fluorene-d10	60-120	≤ 20%
	Pyrene-d10	60-120	≤ 20%
	Fluoranthene-d10	60-120	≤ 20%
	Benzo(e)pyrene-d10	60-120	≤ 20%
LCS/LCSD*	Naphthalene	60-120	≤ 20%
	Acenaphthylene	60-120	≤ 20%

Table 14.1 Acceptance Criteria for EPA TO-13A

Method TO13A	Analyte	Accuracy (%R)	Precision (RPD)
LCS/LCSD*	Acenaphthene	60-120	≤ 20%
	Fluorene	60-120	≤ 20%
	Phenanthrene	60-120	≤ 20%
	Anthracene	60-120	≤ 20%
	Fluoranthene	60-120	≤ 20%
	Pyrene	60-120	≤ 20%
	Benz(a)anthracene	60-120	≤ 20%
	Chrysene	60-120	≤ 20%
	Benzo[b]fluoranthene	60-120	≤ 20%
	Benzo[k]fluoranthene	60-120	≤ 20%
	Benzo[a]pyrene	60-120	≤ 20%
	Benzo[e]pyrene	60-120	≤ 20%
	Perylene	60-120	≤ 20%
	Indeno[1,2,3-cd]pyrene	60-120	≤ 20%
	Dibenzo[a,h]anthracene	60-120	≤ 20%
	Benzo[g,h,i]perylene	60-120	≤ 20%

*LCS/LCSD recovery and precision limits are static based on the default limits in the Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, Oct. 2016. Control Charts will be generated annually for this method. They will be used for trend monitoring of analytical systems.

Table 14.2 Summary of Calibration and QC Procedures for Method EPA TO13A

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA TO13A	**PAHs**	Minimum of 5 point initial calibration for all analytes	Initial calibration prior to sample analysis. Instrument must be recalibrated after failed DFTPP, failed CCV, major instrument changes. Curve valid for 6 weeks, max valid time is 3 months.	All compounds with minimum average RRF as specified in Table 8.2.2.1.1, and %RSD ≤ 30%, each calibration level must be ±30% of nominal. For quadratic or linear regression r≥0.995, each calibration level must be ±30% of nominal. Targets and surrogates within ±0.06RRT of Curve's mean RRT. ($\overline{RRT}$) Each Int Std RT with ±0.33 min (20sec) of curve average.	Correct problem then repeat initial calibration	
		Second-source calibration verification	Once per 5 point initial calibration	Analytes within ± 30% of nominal..	Correct problem and then repeat initial calibration.	

Table 14.2 Summary of Calibration and QC Procedures for Method EPA TO13A

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA TO13A	**PAHs**	Continuing Calibration Verification	Daily, after DFTPP and before sample analysis and at the conclusion of each sequence.	Analytes within ± 30% of nominal or RRF within 30% of initial calibration.	Rerun CCC once, if passes use sample result. If not, correct problem then repeat calibration verification once. If passes continue sample analysis. If fails, recalibrate.	
		Initial Demonstration and Continuing: ability to generate acceptable accuracy and precision using four replicate analysis of a QC check sample	Once per analyst for IDC Every Six months for CDC	Intial: Build Curve. All analytes in 4 LCS replicates must have recoveries of (60-120%), Precision ≤30% RPD. Blind sample must also meet same limits. CDF: 4 replicates, 2 sets of LCS/LCSD or blind, meet QC above	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Check of mass spectral ion intensities using 50ng DFTPP	Every 12 hours	Refer to criteria listed in the SOP	Retune instrument and verify with DFTPP tune check again.	
		Internal Standards	Immediately after or during data acquisition of calibration check standard	Internal standards area within 50-200% of initial calibration midpoint response areas. All Int Stds RT with ±0.33 min of most recent CCV.	Inspect mass spectrometry or GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning.	
		Method Blank extracted using a certified clean PUF cartridge and a clean quartz filter	Every analytical extraction batch of ≤20 samples. Must run with every field sample analysis sequence	All analytes ≤ 2x MDL	Ensure no contamination then reanalyze method blank	Flag with "LB"
		Solvent Extraction Blank (500ml extraction fluid only, no PUF no surrogates)	Every analytical extraction cycle of 18 hours for samples	5ml sample analyzed, all target compounds each <0.01ug/ml	Add appropriate qualifier(s) to report.	
		Solvent Method Blank (not extracted)	Every extraction batch of 20 or fewer field samples	1ml of the extraction solvent fluid is fortified with Int Std. All target compounds must be ≤ MDL	Add appropriate qualifier(s) to report.	
		Field Blank	One per month	All target compounds ≤ 5x MDL	Add appropriate qualifier(s) to report.	
		Instrument Solvent Blank	Prior to any instrument DFTPP tune check	1ml Solvent, NOT fortified with Int Std, all compounds must be qualitatively Not Detected	Correct problem then reanalyze the solvent blank.	
		LCS/LCSD for target analytes	One LCS/LCSD per analytical batch of ≤20 samples.	QC acceptance criteria Is 60 – 120%. Precision ≤ 20%RPD for all compounds	Correct problem then reanalyze the LCS/LCSD. During an extraction week re-extract the LCS/LCSD.	

Table 14.2 Summary of Calibration and QC Procedures for Method EPA TO13A

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
EPA TO13A	**PAHs**	Retention Time	All QC and Field Samples	Target analytes within ±0.06RRT of mean Initial Curve RRT. All Int Stds RT with ±0.33 min of most recent CCV.	Correct problem then reanalyze. If fails add appropriate qualifier(s) to report.	
		Field Sample Replicate Analysis	One for every sequence of field samples	QC acceptance criteria Is Precision ≤ 10%RPD for all compounds with concentration ≥0.5ug/ml/PUF	Correct problem then reanalyze. If fails add appropriate qualifier(s) to report.	
		Field and Laboratory Surrogate spike	Every field , QC spiked sample, method blank	Recovery acceptance criteria is between 60-120%	Add appropriate qualifier(s) to report.	
		MDL Study	Once per year	Detection limits established shall be list in Appendix A.		
		Analytes above the 5- pt calibration curve	none	Within Curve Limits	Sample must be diluted and appropriate amount of Int Std added and dilution analyzed.	Apply DI to dilution results, apply EH to analytes out of range.
		Sample Receipt Temperature Check	Every Field Sample	Must be ≤4°C unless delivered to the lab within 4hrs of removal from field sampler.	Add appropriate qualifier(s) to report.	
		Field Sample Holding Time after collection	Every Field Sample	Extract 14 days from sample collection (store ≤4°C, sealed jar, no light)	Add appropriate qualifier(s) to report.	
		Extracted Sample Holding time	Every Extracted Sample	Analysis 40 days from extraction (store ≤4°C)	Add appropriate qualifier(s) to report.	
		Collocated Samples	10% of primary samples	QC acceptance criteria Is Precision ≤ 20%RPD for all compounds with concentration ≥0.5ug/ml	Add appropriate qualifier(s) to report.	
		Compound Identification	Every target PAH in each standard, blank, QC sample, and field collected sample.	Signal-to-noise ≥3:1 RT within prescribed window At least one qualifier ion abundance within 15% of ICAL. Peak apexes co-maximized within 1 scan for quantitation and qualifier ions.	Do not report compound if criteria not met. However, analyst experience may over-ride Acceptance Criteria and must be documented on report paperwork.	

Updates

Combined 4 separate TO13AGCMS SOPs into one unified SOP for Online Access.