State of Connecticut

Department of Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

PAHs by Method TO-13

Version 2.0

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Written by the Connecticut DEP QA/QC Workgroup

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1.0	Posted on EPOC website	February 2006
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1.0 Overview of Method TO-13

1.1 Method TO-13 is a gas chromatography/mass spectrometry procedure used to determine polynuclear (or polycyclic) organic compounds (PAHs) in air. This procedure requires an experienced GC/MS analyst familiar with sampling and analysis of PAHs using XAD resin and polyurethane foam (PUF) and the QA/QC requirements of the method. Although other detectors may be listed in the EPA method, the Connecticut Reasonable Confidence Protocols require the use of a mass spectrometer. All method references are to the latest published version of the method found in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, published by the US EPA.

1.2 This method is generally applicable to the determination of PAHs involving three member rings or higher. Naphthalene, acenaphthylene, and acenaphthene have only ~35 percent recovery when using PUF alone as the collection medium. This procedure calls for using XAD-2® resin in conjunction with PUF so as to determine these important compounds. Nitro-PAHs have *not* been fully evaluated using this procedure; therefore, they are not included in this method.

1.3 With optimization to reagent purity and analytical conditions, the detection limits for the GC/MS method range from 1 ng to 10 pg based on field experience.

2.0 Summary of Method

2.1 Filters and sorbent cartridges (containing PUF and XAD-2®) are cleaned in solvents and vacuum dried. The filters and sorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler.

2.2 Approximately 300 m of air is drawn through the filter and sorbent cartridge using a high-volume flow rate air sampler or equivalent.

2.3 The amount of air sampled through the filter and sorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and sorbent cartridges to the analytical laboratory for analysis.

2.4 The filters and sorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by Kuderna-Danish (K-D) evaporator, followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by GC/MS.

2.5 The extract is further concentrated by K-D evaporation, then analyzed by GC/MS. The analytical system is verified to be operating properly and calibrated using a five point calibration.

2.6 A preliminary analysis of the sample extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If the preliminary analysis indicates nonperformance, then recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc.

2.7 The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculate the concentration of PAHs in the air sample.

2.8 See Method TO-13A for additional publications and analytical approaches to determine PAHs in air.

2.9 Because of the relatively low levels of common PAHs in the environment, the methodology suggest the use of high volume (0.22 m /min) sampling technique to acquire sufficient sample for analysis. However, the volatility of certain PAHs prevents efficient collection on filter media alone. Consequently, this method utilizes both a filter and a backup sorbent cartridge, which provides for efficient collection of most PAHs involving three member rings or higher.

3.0 Reporting Limits for Method TO-13

3.1 The reporting limit (RL) for a compound is dependent on the concentration of the lowest standard in the initial calibration, the sample volume, the sample introduction method, and any dilution of the sample.

3.2 Lower reporting limits may be achieved using select ion monitoring, an ion trap mass spectrometer, or newer instrumentation.

4.0 Interferences and Contamination

4.1 PAHs span a broad spectrum of vapor pressures (e.g., from 1.1 x 10^{-2} kPa for naphthalene to 2 x -10^{-13} kPa for coronene at 25º C). PAHs that are frequently found in ambient air are listed in Table 1. Those with vapor pressures above approximately 10^{-8} kPa will be present in the ambient air substantially distributed between the gas and particulate phases. This method will permit the collection of both phases.

4.2 Particulate-phase PAHs will tend to be lost from the particle filter during sampling due to volatilization. Therefore, separate analysis of the filter will not reflect the concentrations of the PAHs originally associated with particles, nor will analysis of the sorbent provide an accurate measure of the gas phase. Consequently, this method calls for *extraction of the filter and sorbent together* to permit accurate measurement of total PAH air concentrations.

4.3 Naphthalene, acenaphthylene, and acenaphthene possess relatively high vapor pressures and may not be efficiently trapped by this method when using PUF as the sorbent. The sampling efficiency for naphthalene has been determined to be about 35 percent for PUF. The user must use XAD-2® as the sorbent if these analytes are part of the target compound list (TCL).

4.4 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.

4.5 Glassware must be scrupulously cleaned . All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used in it and then high-purity acetone and hexane. These rinses should be followed by detergent washing with hot water and rinsing with copious amounts of tap water and several portions of reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400º C for four hours. Volumetric glassware must not be heated in a

muffle furnace; rather it should be solvent rinsed with acetone and spectrographic grade hexane. After drying and rinsing, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Glassware should be stored inverted or capped with aluminum foil.
[Note: The glassware may be further cleaned by placing in a muffle furnace at 450º C for 8 hours to remove trace organics.]

4.6 The use of high purity water, reagents, and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

4.7 Matrix interferences may be caused by contaminants that are co-extracted from the sample. Additional clean-up by column chromatography may be required (see Section 12.3).

4.8 During sample transport and analysis, heat, ozone, NO_2, and ultraviolet (UV) light may cause sample degradation. Incandescent or UV-shielded fluorescent lighting in the laboratory should be used during analysis.

4.9 The extent of interferences that may be encountered using GC/MS techniques has not been fully assessed. Although GC conditions described allow for unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere. The use of column chromatography for sample clean-up prior to GC analysis will eliminate most of these interferences. The analytical system must, however, be routinely demonstrated to be free of internal contaminants such as contaminated solvents, glassware, or other reagents which may lead to method interferences. A laboratory reagent blank should be analyzed for each reagent used to determine if reagents are contaminant-free.

4.10 Concern about sample degradation during sample transport and analysis was mentioned above. Heat, ozone, NO_2, and ultraviolet (UV) light also may cause sample degradation. These problems should be addressed as part of the user-prepared standard operating procedure (SOP) manual. Where possible, incandescent or UV-shielded fluorescent lighting should be used during analysis. During transport, field samples should be shipped back to the laboratory chilled (~4º C) using ice.

5.0 Equipment and Supplies

5.1 Refer to Sections 8, 9 and 10 for needed equipment and supplies. Note that the use of XAD-2 ® resin and a GC/MS system are required for sampling and analysis of PAHs. The amount of XAD-2® resin may not be decreased soley for the purpose of using ASE/ Pressurized Fluid Extraction – the resin bed and associated PUF plugs must fill the cartridge.

5.2 The sampling cartridge should consist of the glass cartridge with a stainless steel or nickel screen on one end. To the cartridge a PUF plug is placed over the screen (approximately ½" thick), followed by approximately 200 grams XAD-2® resin, and then an additional PUF plug to hold the resin in place. The PUF plugs should fit securely into the cartridge.

5.3 Field surrogates must be added to the cartridges prior to sampling. Alternate surrogate compounds (minimum of two) may be used.

5.4 Alternative XAD-2® cleanup procedures may be used as long as the method blank criteria listed is Section 10 of the method are met.

6.0 Sampling and Analysis

6.1 Follow the procedure outlined in Section 11 of EPA Method TO-13A. Document all calibration and sample collection data.

6.2 Samples should be extracted using the Soxhlet procedure. Sonication is not allowed. Follow the procedure outlined in Section 12 of the method. ASE/ Pressurized Fluid Extraction is allowed provided the entire amount of XAD resin is extracted in one cartridge. The PUF may be extracted separately, and the extracts concentrated together.

6.3 Laboratory surrogates (minimum of two) must be added to the samples after receipt from the field and prior to extraction. Alternate compounds may be used.

6.4 The use of the silica gel column cleanup is optional. However if interferences are present, the extract must be put through the silica gel cleanup as described in Section 12.3 of the method.

6.5 See Table 1A for specific QA/QC requirements.

6.6 The instrumentation should be calibrated following Section 13 of the method. See Tables 1A and 1-3 for specific QA/QC requirements.

6.7 The laboratory must use the internal standards listed in Section 12.3.6 of the method for quantitation. The laboratory should follow the method recommended internal standard/PAH's listed in Section 13.2.1.8 of the method.

6.8 The mass spectrometer must be tuned using DFTPP. The suggested criteria is listed in Table 2. Alternative referenced criteria may be used, but all samples, standards, blanks, etc. must be analysed under the same tune criteria.

6.9 The laboratory may utilize 1 µl injections if the sensitivity required is still met.

7.0 Specific Quality Control Requirements for Method TO-13

7.1 Refer to the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* for general quality control requirements. These requirements insure that each laboratory maintain a formal quality assurance program and records to document the quality of all chromatographic data. Quality Control procedures necessary to evaluate the GC system operation may be found in the published method and include evaluation of calibrations and chromatographic performance of sample analyses, instrument quality control and method performance requirements for the GC/MS system.

7.2 The minimum requirements include initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples (LCS) to assess precision and accuracy.

7.3 Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Table 1A. The Initial Demonstration of Proficiency must include the elements listed in Table 1.0. Records of this must be kept on file by the laboratory and available for inspection.

Table 1.0 IDOC Requirements

QC Element	Performance Criteria
DFTPP Tuning	Table 1-3
Initial Calibration	Table 1A
Continuing Calibration	Table 1A
Method Blanks	Table 1A
Average Recovery	Table 1A
% Relative Standard Deviation	Table 1A
Surrogate Recovery	Table 1A
Internal Standards	Table 1A

Note: Because of the extensive analyte list and number of QC elements associated with the Initial Demonstration of Proficiency, it should be expected that one or more analytes may not meet the performance standards for one or more QC elements. The laboratory should make every effort to find and correct the problem, and repeat the analysis. All non-conforming analytes along with the laboratory acceptance criteria should be noted in the Initial Demonstration of Proficiency data.

Laboratories are required to generate laboratory specific performance criteria for LCS compound recovery limits and surrogate recovery limits. These limits must meet or exceed the limits specified in Table 1A.

7.2 Specific QA/QC requirements and performance standards for Method TO-13 are presented in Table 1A. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide the environmental professional ("EP") with "Reasonable Confidence" regarding the usability of analytical data to support DEP decisions

7.3 While optional, parties electing to utilize these protocols will be assured that "Reasonable Confidence" data, will be generally accepted by agency reviewers. In order to achieve "Reasonable Confidence" parties must:

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;

2. Evaluate and narrate, as necessary, compliance with performance standards prescribed in Table 1A for this test method; and

3. Adopt the reporting formats and elements specified herein.

7.4 The laboratory must perform a method detection limit study at least annually. At least seven blank cartridges must be spiked with the PAH compounds and put through the entire extraction/analytical procedure. Calculate the MDL in nanograms/cartridge as per Appendix B to 40 CFR Part 136.

8.0 Tentatively Identified Compounds

8.1 Due to the high levels of background contamination associated with the XAD resin and polyurethane foam, it is recommended that tentatively identifed compounds **NOT** be determined using this method.

9.0 Reporting Requirements for Method TO-13

9.1 The analyte List for Method TO-13 is presented in Table 1B. The compounds listed are readily determined by Method TO-13. Additional PAH and other semivolatile compounds may be determined by this procedure, but have not been validated by the US EPA. It is up to the laboratory and/or environmental professional to justify the inclusion of additional compounds. It is noted that polychlorinated biphenyls and certain pesticides may be collected using the same procedure as described in method TO-13. These compounds would require determination using an alternate analytical scheme such as gas chromatography coupled with an electron capture detector (GC/ECD).

9.2 While it is not necessary to request and report all the analytes listed in Table 1B to obtain Reasonable Confidence status, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEP strongly recommends that full list of analytes be reported during the initial stages of a site investigation and/or at sites with an unknown or complicated history of chemical usage or storage.

In cases where a shortened list of analytes is selected, the laboratory must still meet the method specific quality control requirements and performance standards associated with the requested analytes list to obtain Reasonable Confidence.

The Reporting Limit (RL) is based upon the lowest standard in the initial calibration. In order to meet the reporting limit for some compounds, it may be necessary to use select ion monitoring (SIM).

9.3 The following table (Table 1.2) lists the routine report deliverables. Note that while laboratories are not required to report certain items, they must keep the data on file and may be required to report these items in special circumstances.

9.4 The following rules apply to reporting results:

Non-Detects: Report all non-detects and results below the reporting limit as “ND” (Below Quantitation Limit). The reporting limit for each compound in each sample must be ppbv and take into account the exact sample volume, any dilution factors, etc.

Compounds detected above the reporting limit in blanks and found in samples, also above the reporting limit, shall be flagged with a “B” suffix (e.g. 25B).

Table 1.1 Report Deliverables for Method TO-13

Parameter	Deliverable	Comments
GC/MS Tunes	NO	Analysis cannot proceed without meeting tuning criteria.
Initial Calibration	NO	Note non-conformances in narrative
Continuing Calibration	NO	Note non-conformances in narrative
Method Blanks	YES	Note non-conformances in narrative. Flag all positive results above RL with "B" flag.
Lab Control Sample (LCS)	YES	Note non-conformances in narrative
Sample Replicate (If Analyzed)	YES	Note non-conformances in narrative
Internal Standard Areas	NO	Note non-conformances in narrative
General Reporting Issues	YES	Note non-conformances in narrative

Table 1.2 Analyte List for Method TO-13

Analyte	CAS Number	Notes
Acenaphthene	83329	
Acenaphthylene	208968	
Anthracene	120127	
Benzo(a)anthracene	56553	
Benzo(a)pyrene	50328	
Benzo(b)fluoranthene	205992	
Benzo(ghi)perylene	191242	
Benzo(k)fluoranthene	207089	
Chrysene	218019	
Dibenzo(a,h)anthracene	53703	
Fluoranthene	206440	
Fluorene	86737	
Indeno(1,2,3-cd)pyrene	193395	
2-Methylnaphthalene	91576	
Naphthalene	91203	
Phenanthrene	85018	
Pyrene	129000	

Table 1A Specific QA/QC Requirements and Performance Standards for Method TO-13*

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
PUF and XAD-2® Resin Cleaning and Certification	Assure cartridges are free from contamination	Per Section 10 of the method. Alternative cleanup procedures may be used as long as method blank criteria are met.	NO - Data kept on file in lab.	Do not use contaminated cartridges.	Reclean as necessary.
GC/MS Tunes with DFTPP	Inter-laboratory consistency and comparability	1) Criteria listed in Table 3 of Method TO-13 (the same criteria must be used for all analyses). See Section 6.3.3 of this method. 2) Every 12 hours	NO	Perform instrument maintenance as necessary; retune instrument	Suspend all analyses until tuning non-compliance is rectified.
Initial Calibration	Laboratory Analytical Accuracy	1) Minimum of 5 standards. Standards must be prepared per Section 13.3.4 of the method. 2) Low standard must be ≤ reporting limit (RL) 3) Must meet technical acceptance criteria as per Section 13.3.4.5 of method. 4) Must contain all target analytes.	NO	Recalibrate as required by method. 1 compound may fail RSD criteria as long as min RF criteria met and % RSD <50%.	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds in case narrative.
Daily Calibration Std (CCAL)	Laboratory Analytical Accuracy	1) Every 12 hrs prior to analysis of samples per Section 13.3.5 of method.	NO	Recalibrate as required by method. 2 compounds may fail %D criteria as long as min RF criteria met and % D <40%.	Report non-conforming compounds in case narrative.
ICAL Verification Standard	Laboratory Analytical Accuracy	1) Each ICAL must be verified against a second source standard. 2) Std should be at mid-point 3) All target analytes present	NO	1) Compounds must recover within 80-120% 2) Laboratories are allowed to have 20% of compounds out, as long as all compounds within recover 65-135%	1) Perform maintenance as needed, recalibrate. 2) Note outliers in narrative.

Table 1A Specific QA/QC Requirements and Performance Standards for Method TO-13*

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Method Blanks	Laboratory Contamination Evaluation	1) Per Section 13.3.6 of the method. 2) All target compounds must be < RL (not the MDL as specified in the method).	YES	Locate source of contamination and correct problem. Reanalyze method blank.	1) Report non-conformances in case narrative. 2) All results for compounds present in method blank must be "B" flagged if detected in samples associated with the method blank.
Laboratory Control Sample (LCS)	Laboratory Method Accuracy	1) Every 20 samples, per Section 13.3.7 of the method. 2) Standard source should be the same as initial calibration source. 3) Concentration level near or at the mid-point of the initial calibration. 4) Must contain all target analytes 5) Must meet the criteria of Section 13.3.7.4 of the method.	YES	Recalculate the percent recoveries Reanalyze the LCS Locate & correct problem, reanalyze associated samples	1) Report non-conformances in case narrative.
Method Detection Limit Study	System sensitivity	1) Performed annually. 2) See Section 7.2.3 of this method.	NO – Data kept on file in lab	N/A	N/A
Sample Analysis	Valid Results	1) Analyze per Section 13.4 of the method. 2) Must meet technical acceptance criteria of Section 13.4.7. 3) Do not report below lowest std in calibration curve unless instructed by the data user.	YES	If technical criteria not met: 1) Evaluate the analytical system for malfunctions and correct 2) Reanalyze the sample	Note any analytical problems in the narrative.

Table 1A Specific QA/QC Requirements and Performance Standards for Method TO-13*

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Surrogates	Insure data quality and integrity	1) All surrogates should recover 60-120%. 2) Use both field and laboratory surrogates. See Sections 10.4.1 and 12.2.1 of the method.		If surrogate out reanalyze to verify.	Note non-conformances in the narrative. Note which surrogates are field and laboratory.
Internal Standards (IS)	Laboratory Analytical Accuracy and Method Accuracy in Sample	1) Laboratory must IS specified in method. See Sections 12.3.6 and 13.2.1.8 of the method. 2) Must meet technical acceptance criteria as stated in the method.	NO	1) Evaluate the analytical system for malfunctions and correct 2) Reanalyze the sample	1) Note exceedances in narrative 2) If reanalysis confirms matrix interference, report initial analysis and note in narrative 3) If reanalysis in criteria, report only compliant analysis
Quantitation	N/A	1) Quantitation must be based on IS calibration using daily RF from cal chk. 2) Quantitation based on Section 13.4.5 of the method. 3) the IS used for quantitation must be the IS nearest to the retention time of the target analyte, unless there is a matrix interference.	N/A	N/A	Note any problems in narrative.

Table 1A Specific QA/QC Requirements and Performance Standards for Method TO-13*

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
General Reporting Issues	N/A	1) The laboratory should report only concentrations detected above the sample specific RL. 2) Concentrations below the reporting limit (RL) as "ND" with the reporting limit. 3) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for both sets of data. Compounds which exceed the linear range should be flagged ("E" flag). 6) If a dilution is performed, the highest detected analyte must be in the upper half of the calibration curve, unless there are non-target analytes whose concentrations are so high as to cause damage to the instrumentation or saturate the mass spectrometer.	N/A	N/A	1) Qualification of results reported below the RL is required. 2) Performance of dilutions must be documented in the case narrative

* Refers to latest published version of Method TO-13.

GC/MS = Gas Chromatography/Mass Spectrometry RPD = Relative Percent Difference N/A = Not Applicable

DFTPP = Decafluorotriphenylphosphine CCC = Calibration Check Compound

%RSD = Relative Percent Standard Deviation

Table 1.3 GC/MS Tune Criteria for DFTPP

m/z	Required Intensity (relative abundance)
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% 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

The mass spectrum of DFTPP should be acquired in the following manner. Three scans (the peak apex and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and may be accomplished using a single scan no more than 20 scans prior to the elution of DFTPP. Do not subtract part of the DFTPP peak. Alternative DFTPP criteria, such as the Method 525 or CLP criteria, can be utilized provided all samples, standards, blanks, etc. are analyzed using the same GC/MS tuning criteria is. If alternative approaches are utilized, the approach must be documented in the laboratory standard operating procedure. The laboratory is not allowed to vary its approach from day to day in order to in order to pass a tune on an instrument requiring maintenance.