State Of Connecticut
Department of Environmental Protection

Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements For Extractable Petroleum Hydrocarbons by the State Of Connecticut, Department of Public Health ETPH Method

Version 2.0
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Written by the Connecticut DEP QA/QC Workgroup

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1.0	First version for publication	7/05
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1.0 QA/QC Requirements for the CT-ETPH Method

1.1 Method Overview

The CT-ETPH Method is gas chromatography procedure used to determine diesel range (C9 thru C36) petroleum hydrocarbons in soils, sediments and aqueous samples. This procedure requires an experienced GC analyst familiar with the QA/QC requirements of the method. The sample introduction procedure requires the use of a solvent extraction procedure.

Open-tubular, capillary columns are employed with a flame ionization detector (FID). When compared to packed columns, these fused-silica, open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis.

1.1.1 Reporting Limits for the CT-ETPH Method

The reporting limit (RL) for the ETPH is dependent on the concentration of the lowest standard in the initial calibration, sample weight/volume, extraction procedure, and moisture content. The following table lists approximate reporting limits for various matrices utilizing a gas chromatograph with a FID. Solid matrices in this table assume 100% solids.

Table 1.0 Typical Reporting Limits

Matrix	Typical Reporting Limit
Water	100 ug/L
Soil/sediment	100 mg/Kg

Moisture content of soils and sediments will raise the RL, as all results must be reported on a dry weight basis for these two matrices. Sample dilution or lower sample weight/volume will also cause the RL's to be raised.

Sample container type, preservation requirements, and holding times for waters, soils, and sediments are presented in Table 2A of this document.

1.1.2 General Quality Control Requirements

Each laboratory is required to operate a formal quality assurance program and be certified by the Connecticut Department of Public Health for the analysis performed. 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. The use of site specific matrix spikes and matrix spike duplicates is highly recommended. Evaluation of sample matrix effects on compound recovery is key to making good decisions.

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 Section 1.5 and Table 1A. See Section 8.4 of Method 8000 in SW-846 for the procedure. The Initial Demonstration of Proficiency must include the following elements:

Table 1.1 IDOC Requirements

QC Element	Performance Criteria
Initial Calibration	Table 1A
Continuing Calibration	Table 1A
Discrimination Check	Table 1A
Method Blanks	Table 1A
Average Recovery	Table 1A
% Relative Standard Deviation	Table 1A
Surrogate Recovery	Table 1A

Laboratories are required to generate laboratory specific performance criteria for LCS compound recovery limits, matrix spike/matrix spike duplicate compound recovery and precision (RPD) limits, and surrogate recovery limits. These limits must meet or exceed the limits specified in Table 1A.

1.2 Summary of the CT-ETPH Method

1.2.1 Sample Extraction and Cleanup

Samples for analysis by the CT-ETPH Method require extraction by one of the following methods.

SW-846 Method	Matrix	Description
3510C	Aqueous	Separatory Funnel liquid-Liquid Extraction
3520C	Aqueous	Continuous Liquid-Liquid Extraction
3511	Aqueous	Organic Compounds in Water by Microextraction
3540C	Soil/Sediment	Soxhlet Extraction
3541	Soil/Sediment	Automated Soxhlet Extraction
3545A	Soil/Sediment	Pressurized Fluid Extraction (PFE)
3546	Soil/Sediment	Microwave Extraction
3570	Soil/Sediment	Microscale Solvent Extraction (MSE)
3550C	Soil/Sediment	Ultrasonic Extraction

1.2.2 GC Analysis

The hydrocarbons are extracted from the sample using the appropriate procedure. The solvent extract is treated with silica gel to remove any polar compounds. The silica gel is removed via filtration or centrifuging, followed by final concentration of the sample extract. Aliquots of the extract are injected onto the GC column in the gas chromatograph. The gas chromatograph (GC) oven is temperature programmed to facilitate separation of the analytes which are then detected by the FID.

Identification of retention time window is accomplished by comparing the retention times of the chromatographic peaks of the standards. Confirmation is not required for this method. Quantitation is accomplished by integrating all peaks which elute in the retention time window. If the surrogate elutes in the retention time window, the area of the surrogate peak is subtracted from the total area for quantitation.

1.3 Method Interferences

Refer to SW-846 Methods 3500 (Sec. 3.0, in particular), 3600, and 8000 for a detailed discussion of interferences. Interferences co-extracted from the samples will vary considerably from matrix to matrix. Dirty glassware, especially at ground glass joints, is the most common form of contamination leading to high method blank results. Analysts must ensure that all glassware is clean prior to sample processing.

The flame ionization detector will respond to any compound which combusts in an air/hydrogen flame. As such many classes of compounds besides petroleum hydrocarbons will be included in the ETPH concentration. The use of silica gel to remove polar compounds (e.g. fatty acids, tannins, etc.) is critical to the analysis. Samples highly contaminated may require additional silica gel treatments to remove these type compounds.

1.3.1 Cross-contamination/ Carryover

Cross-contamination can occur when any sample is analyzed immediately after a sample containing high concentrations of compounds which cause a detector response. Syringes on the autosampler may also become contaminated in the same manner. If a high sample is inadvertently analyzed, the system must be demonstrated to be clean by analysis of solvent blanks. Laboratories should be aware that carryover from high boiling point compounds may not appear until a later run (ghost peaks).

1.4 Quality Control Requirements for SW-846 the CT-ETPH Method

1.4.1 General Quality Control Requirements for Determinative Chromatography Methods

Refer to SW-846 Method 8000 for general quality control requirements for all chromatographic methods, and Section 8.0 of the Connecticut ETPH method for specific QA/QC 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 SW-846 Method 8000, Section 7.0, and include initial and continuing verification of instrument calibrations and chromatographic performance of sample analyses

1.4.2 Specific QA/QC Requirements and Performance Standards for SW-846 the CT-ETPH Method

Specific QA/QC requirements and performance standards for SW-846 the CT-ETPH Method 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.

While optional, parties electing to utilize these protocols will be assured that agency reviewers will, generally accept "Reasonable Confidence" data. 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 in Section 1.6 of this method.

1.4.3 Site Specific Matrix Spike (MS), Matrix Spike Duplicate (MSD) Samples

It is strongly recommended that site specific MS/MSD samples be analyzed from each site, and each matrix type sampled. Percent recovery data from site specific samples allow the EP to make informed decisions regarding contamination levels at the site. Batch MS/MSD results do not give any indication of site specific matrix interferences or analytical problems related to the specific site matrices and are in general discouraged. Non-site specific MS/MSD's should not be reported for the RCP's. Additionally trip blanks, field blanks, rinsate blanks, etc. should not be used for MS/MSD's.

1.4.4 Special Analytical Considerations for ETPH

Because of the variable solubility, extraction efficiency and analytical sensitivity of the different compounds that are potentially analyzable by the CT-ETPH Method, the recovery ranges presented in Table 1A for laboratory control samples, matrix spikes, and surrogates should be considered general upper/lower acceptance limits when a single extraction procedure is utilized to prepare the extract for subsequent analysis. It is essential that laboratory-specific performance criteria for LCS and surrogate recoveries also be calculated and documented as described in SW-846 Method 8000B, Section 8.7. When experience indicates that the criteria recommended in specific methods are frequently not met for some matrices, the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards described in Table 1A to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

Table 1A Specific QA/QC Requirements and Performance Standards for the CT-ETPH Method*

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Retention Time Windows	Accurate identification of ETPH	1) Use the average RT of the C9 and C36 peaks of the initial calibration to establish the RT window.	NO	N/A	N/A
Initial Calibration	Laboratory Analytical Accuracy	1) Minimum of 5 standards per ETPH method. 2) Low std at reporting limit 3) % RSD must be ≤30% or if linear regression used "r" ≥ 0.990 4) Quantitation by average CF/RF or by linear regression. 5) Curves must be verified with independent ICV prior to sample analysis. 6) Must perform discrimination check.	NO	Recalibrate as required by the method. Perform injection port maintenance if discrimination check fails. Labs are allowed one compound out of criteria for the discrimination chk.	Sample analysis cannot proceed without a valid initial calibration. Report non-conformances in narrative.
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	1) Prior to sample analysis and every 12-hours 2) Concentration near mid-point of curve. 3) Percent difference or drift ±30%. 4) Verify all analytes fall in retention time windows. 5) Perform discrimination check	NO	1) Perform instrument maintenance, reanalyze CCAL and/or recalibrate. Labs are allowed one compound out of criteria for the discrimination chk.	Report exceedances in narrative.
Discrimination check	Laboratory Analytical Accuracy & Instrument Performance	1) After initial calibration and at beginning of 12-hour sequence prior to any sample analysis. 2) As per Section 7.2.3 of the ETPH method.	YES	1) Perform instrument maintenance, reanalyze CCAL and/or recalibrate. 2) One compound can be out as long as %D ≤50%.	Report exceedances in narrative.

Table 1A Specific QA/QC Requirements and Performance Standards for the CT-ETPH Method*

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Method Blanks	Laboratory Contamination Evaluation	1) Extracted every 20 samples or every batch, whichever is greater. 2) Matrix specific 3) Target analytes must be <RL	YES	Locate source of contamination and correct problem. Reanalyze method blank. Re-extract samples if method blank contaminated	1) Report non-conformances in case narrative. 2) All results for compounds present in method blank above RL must be "B" flagged if detected in samples associated with the method blank. 3) If re-extraction performed within holding time, report only compliant data. If re-extraction performed outside holding time report all data.
Laboratory Control Sample LCS)	Laboratory Method Accuracy	1) Every 20 samples or each batch, whichever is more frequent. 2) Standard source different from initial calibration source. 3) Concentration level must be near or at the mid-point of the initial calibration. 4) Matrix specific. 5) Laboratory determined percent recovery limits must be between 60-120% .	YES	Recalculate the percent recoveries Reanalyze the LCS If MS/MSD in same batch compare to determine if problem isolated to LCS Locate & correct problem, reanalyze associated samples	1) Report non-conformances in case narrative. 2) If re-extraction performed within holding time, report only compliant data. If re-extraction performed outside holding time report all data.

Table 1A Specific QA/QC Requirements and Performance Standards for the CT-ETPH Method*

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Site Specific Matrix Spike/Matrix Spike Duplicate	Precision and Accuracy in Sample Matrix	1) Every 20 samples per matrix* 2) Spike concentration in lower part of calibration curve. 3) Laboratory determined percent recovery limits must be between 50-150% 5) RPD's ≤ 30%	Yes* (*If requested by EP)	If compounds out compare to LCS; if LCS recoveries in note in narrative; if LCS compounds out note in narrative probable lab error	Note outliers in narrative
Surrogates	Accuracy in Sample Matrix	1) Minimum 1 surrogate 2) Recovery limits lab generated and within 50-150%. 3) Labs must develop own in-house limits which fall within 50-150% limits.	Yes	1) If surrogate diluted out below lowest calibration std, no recovery criteria. 2) If obvious matrix interference, note in narrative	1) Note exceedances in narrative.
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) should be reported as "ND" with the sample specific RL also reported 3) If a dilution is performed, the ETPH concentration must be in the upper 60% of the calibration curve, unless there are non-target analytes whose concentrations are so high as to cause damage to the instrumentation	N/A	N/A	1) Performance of dilutions must be documented in the case narrative

Notes for Table 1A

* Refers to latest published version of the CT-ETPH Method. r = Correlation Coefficent N/A = Not Applicable
RPD = Relative Percent Difference %RSD = Relative Percent Standard Deviation CF = Calibration Factor
EP= Environmental Professional

1.5 Additional Reporting Requirements for SW-846 the CT-ETPH Method

The Reporting Limit (RL) is based upon the lowest standard in the initial calibration. Taking into account exact sample weight/volume, dilutions, percent solids, etc. Soil/sediment samples must be reported on a dry weight basis.

1.6 Routine Reporting Deliverables for the CT-ETPH Method

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

1.6.1 Reporting and Flagging of Results

The following rules apply to reporting results:

Non-Detects: Report all non-detects and results below the reporting limit as “ND” (Not Detected at the specified Reporting Limit). The reporting limit for each compound in each sample must be listed on the report and take into account the exact sample mass, any dilution factors, percent moisture, 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).

All soil/sediment results shall be reported on a dry weight basis.

Table 1.2 Report Deliverables

PARAMETER	DELIVERABLE	COMMENTS
Retention Time Windows	NO	
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 sample results above RL with "B" flag.
Discrimination Check	YES	Note non-conformances in narrative
Lab Control Sample (LCS)	YES	Note non-conformances in narrative
Site Specific Matrix Spike/ Matrix Spike Duplicate	YES (If analyzed)	Note non-conformances in narrative
Surrogate Recoveries	YES	Note non-conformances in narrative
General Reporting Issues	YES	Note non-conformances in narrative
QA/QC Certification Form	YES	Signed by laboratory director or his/her designee.

Table 2A Sample Containers, Preservation and Holding Times

MATRIX	CONTAINER	PRESERVATIVE	HOLDING TIME
Aqueous with no chlorine present	1-liter amber glass bottle with Teflon line cap	Store at 4 ± 2º C.	7 days to extraction. 40 days from extraction to analysis.
Aqueous with chlorine present	(1-liter amber glass bottle with Teflon line cap	Neutralize chlorine with either 25 mg ascorbic acid or 3 mg sodium thiosulfate. Store at 4 ± 2º C.	7 days to extraction. 40 days from extraction to analysis.
Soil/Sediment samples.	250 mL amber glass jar with Teflon lined cap.	Cool to 4 ± 2º C	14 days to extraction. 40 days from extraction to analysis. Up to one year for samples frozen within 48 hours of collection. (Note 1)

Notes:

Note 1: If the freezing option is selected, the sample must be frozen within 48 hours of collection. The holding time recommences when thawing begins. The total holding time is calculated from the time of collection to freezing plus the time allowed for thawing. The total elapsed time must be less than 14 days.

The number of sample containers is optional. Laboratories should supply enough containers to allow for any reanalysis or breakage.