State of Connecticut

Department of Energy and Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Extractable Petroleum Hydrocarbons

by the State of Connecticut, Department of Public Health

ETPH Method

Version 3.0

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Written by the Connecticut DEEP QA/QC Workgroup

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1.0	First version for publication	7/05
2.0	Final version based upon public comments	July 2006
3.0	Updated formatting and updated language to reflect updates to overall RCP language	May 2024

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Acronym List

ACRONYM	DEFINITION
CASN	Chemical Abstracts Service Number
CCV	Continuing calibration verification
CF	Calibration Factor
%D	Percent difference or percent drift
DEEP	CT Department of Energy and Environmental Protection
DF	Dilution factor
EP	Environmental Professional
ETPH	Extractable Total Petroleum Hydrocarbons
FID	Flame Ionization Detector
g	grams
GC	Gas chromatograph
GC/MS	Gas chromatography/mass spectrometry
HCl	Hydrochloric acid
ICV	Initial calibration verification
LCS	Laboratory control sample
LLOQ	Lower Limit of Quantitation
mL	Milliliters
MS	Matrix spike
MSD	Matrix spike duplicate
MSE	Microscale Solvent Extraction
NA	Not applicable
PFE	Pressurized Fluid Extraction
QA	Quality assurance
QC	Quality control
r/r^2	Correlation coefficient
%R	Percent recovery
%RSD	Percent relative standard deviation
RCP	Reasonable Confidence Protocol
RF	Response factor
RL	Reporting limit
RPD	Relative percent difference
RSR/RSRs	Remediation Standard Regulations
RT	Retention Time
UCM	Unresolved complex mixture
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
µL	microliters

1.0 QA/QC Requirements for the CT-ETPH Method

1.1 Method Overview

The CT-ETPH Method published by the University of Connecticut Environmental Research Institute (1999) is a gas chromatography ("GC") procedure used to determine petroleum hydrocarbons, range C9 through C36, in soils, sediments, and aqueous samples. This procedure requires an experienced GC analyst familiar with the quality assurance and quality control ("QA/QC") requirements of the method. The sample introduction procedure requires the use of a solvent extraction procedure, see Table 1.0 for suggested extraction methods.

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.

1.2 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.

Table 1.0: Extraction Methods for Sample Preparation for ETPH Analysis

SW-846 Method	Matrix	Description
3510	Aqueous	Separatory Funnel Liquid-Liquid Extraction
3520	Aqueous	Continuous Liquid-Liquid Extraction
3511	Aqueous	Organic Compounds in Water by Microextraction
3535	Aqueous	Solid-Phase Extraction ("SPE")[1]
3540	Soil/Sediment	Soxhlet Extraction
3541	Soil/Sediment	Automated Soxhlet Extraction
3545	Soil/Sediment	Pressurized Fluid Extraction ("PFE")
3546	Soil/Sediment	Microwave Extraction
3550	Soil/Sediment	Ultrasonic Extraction
3570	Soil/Sediment	Microscale Solvent Extraction ("MSE")
3580	NAPL	Waste Dilution[1]

[1]Not formally published in the CT ETPH Method, but these extraction methods have been established and employed by laboratories since the Method was promulgated. Laboratories may employ these extraction methods as long as they provide the necessary QA/QC to demonstrate Reasonable Confidence.

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 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, 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 FID 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).

Analysis of blanks provides information about the presence of contaminants. When potential interfering peaks or high levels of target compounds are detected in blanks, the laboratory should try and find the source of the contamination and eliminate it. **Subtracting blank concentrations from sample results is not permitted.** Any method blank exceedances should be fully documented in the laboratory report narrative.

1.4 Quality Control Requirements for the CT-ETPH Method

1.4.1 Reporting Limits/Lower Limits of Quantitation for the CT-ETPH Method

The reporting limit (“RL”), or lower limit of quantitation (“LLOQ”), for a compound is dependent on the concentration of the lowest non-zero standard in the initial calibration, sample weight/volume, sample introduction method, and moisture content. Table 2.0 lists approximate RL/LLOQs for various matrices utilizing GC with an FID. Solid matrices in this table assume 100% solids.

Table 2.0: Typical Reporting Limits / Lower Limits of Quantitation[1]

Matrix	Typical Reporting Limit
Water	150 µg/L
Soil/sediment	100 mg/kg

[1]Note these values are intended to serve as guidance to EPs when planning analytical needs to achieve the data quality objectives to meet project-specific goals. These tables are not intended to dictate what RL/LLOQs laboratories must report.

Moisture content of soils and sediments will also raise the RL/LLOQ, 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 RLs/LLOQs to be raised. It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL/LLOQ for the target analytes to meet the project Data Quality Objectives (“DQOs”). To meet the RLs/LLOQs applicable to project DQOs, it may be necessary to modify the analytical method by using

increased sample volume or mass or employing selective ion monitoring. In such cases the modifications must be noted in the laboratory report narrative.

1.4.2 General Quality Control Requirements

This protocol is restricted to use by, or under the supervision of, analysts experienced in the use of GC/FID instrumentation as a quantitative tool and skilled in the interpretation of chromatograms for semivolatile organics.

Refer to SW-846 Method 8000 for general quality control requirements for all chromatographic methods, and CT ETPH method for specific QA/QC requirements. These requirements ensure that each laboratory maintain a formal QA program and records to document the quality of all chromatographic data and be certified by the Connecticut Department of Public Health for the analysis performed. QC procedures necessary to evaluate the GC system operation may be found in SW-846 Method 8000. Instrument QC and method performance requirements for the GC system may be found in CT ETPH Method including initial and continuing verification of instrument calibrations and chromatographic performance of sample analyses.

The minimum requirements for a formal QA program include Initial Demonstration of Laboratory Capability (“IDOC”), ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples (“LCS”) and/ or matrix spikes (“MS”) to assess accuracy and LCS duplicates (“LCSD”) and matrix spike duplicates (“MSD”) to assess precision. The use of site-specific MS/MSD’s is highly recommended. Evaluation of sample matrix effects on compound recovery is key to making informed decisions. Percent recovery data from site-specific samples allow the environmental professional (“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. Field, rinsate, or other blanks should not be used for MS/MSD’s.

Laboratories must document and have on file an IDOC for each combination of sample preparation and determinative method being used. An IDOC must be completed and documented when a method is initially started up, whenever a method is substantially modified, or new laboratory staff is trained to perform this method. These data must meet or fall within the performance standards as presented in Section 1.4 and Table 1A of this RCP and presented in SW-846 Method 8000. The IDOC must include the following elements provided in Table 3.0:

Table 3.0: 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, MS/MSD compound recovery and relative percent difference (“RPD”) limits, and surrogate recovery limits. These limits must be equal to or fall within the limits specified in Table 1A.

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

Specific QA/QC requirements and performance standards for 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 EP with “Reasonable Confidence” regarding the usability of analytical data to support environmental decisions. The concept of "Reasonable Confidence" is explained on the CT Department of Energy and Environmental Protection (“DEEP”) website.

While optional, parties electing to utilize these protocols will be assured that agency reviewers will, generally accept “Reasonable Confidence” data. 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 all protocol non-compliances and implement, as necessary, required corrective actions and analytical response actions for all non-conforming analytical performance standards; and

3. Retain reported and unreported analytical data and information for a period of 5 years or as required under applicable accreditation criteria.

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

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required 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 Demonstration of Capability ("IDOC")	Laboratory Analytical Accuracy& Precision	(1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must contain all target analytes. (4) Must follow procedure in the ETPH method.	No	Refer to the ETPH method and Section 1.4.2 of this RCP.	
Initial Calibration ("ICAL")	Laboratory Analytical Accuracy	(1) Minimum of 5 standards per ETPH method. (2) Low std at RL/LLOQ (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 check.	Sample analysis cannot proceed without a valid initial calibration. Report non-conformances in laboratory report narrative.
Initial Calibration Verification ("ICV")	Laboratory Analytical Accuracy	(1) Immediately after each initial calibration. (2) Second source standard. (3) Concentration level near midpoint of curve. (4) Must contain all alkanes listed in the CT ETPH Method. (5) Percent recoveries must be between 70-130% for all alkanes.	No	Locate source of problem; recalibrate if >10% of all analytes are outside of criteria.	If recovery is outside of 70-130% for any alkanes, report non-conforming compounds in laboratory report narrative. Sample analysis may not proceed without a valid ICV.
Continuing Calibration Verification ("CCV")	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 CCV and/or recalibrate. Labs are allowed one compound out of criteria for the discrimination check.	Report non-conformances in laboratory report narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
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 the CT ETPH method.	Yes	(1) Perform instrument maintenance, reanalyze CCV and/or recalibrate. (2) One compound can be out as long as %D ≤50%.	Report non-conformances in laboratory report narrative.
Method Blanks ("MB")	Laboratory Contamination Evaluation	(1) Extracted every ≤20 field samples or every batch, whichever is more frequent. (2) Matrix specific (3) Target analytes must be <RL/LLOQ	Yes	(1) Locate source of contamination and correct problem. Reanalyze method blank. Re-extract samples if method blank contaminated. (2) No corrective action required if concentration of contaminant in sample is >10x concentration in blank or if contaminant not detected in sample.	(1) Report non-conformances in laboratory report narrative. (2) All results for compounds present in method blank above RL/LLOQ 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 field 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	(1) Recalculate the percent recoveries (2) Reanalyze the LCS (3) If MS/MSD in same batch, compare to determine if problem isolated to LCS (4) Locate & correct problem, reanalyze associated samples	(1) Report non-conformances in laboratory report narrative. (2) If re-extraction performed within holding time, report only compliant data. If re-extraction performed outside holding time report all data.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
LCS Duplicate ("LCSD")	Laboratory Method Accuracy & Precision	(1) Every ≤20 field 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%. (6) RPD must be ≤20% for waters and ≤30% for solids.	Yes	(1) Recalculate the percent recoveries (2) Reanalyze the LCS (3) If MS/MSD in same batch, compare to determine if problem isolated to LCS (4) Locate & correct problem, reanalyze associated samples	(1) Report non-conformances in laboratory report narrative. (2) If re-extraction performed within holding time, report only compliant data. If re-extraction performed outside holding time report all data. (3) If RPD >30% report non-conformances in laboratory report narrative.
Matrix Spike/Matrix Spike Duplicate ("MS"/"MSD") (Site specific)	Precision and Accuracy in Sample Matrix	(1) Every ≤20 field samples per matrix (2) Spike concentration in lower part of calibration curve. (3) Laboratory determined percent recovery limits must be between 50-150% (4) RPD's ≤ 30%	Yes (If requested by data user)	If compounds out, compare to LCS; if LCS recoveries in note in narrative; if LCS compounds out note in narrative probable lab error	Note non-conformances in laboratory report narrative.
Surrogates	Accuracy in Sample Matrix	(1) Minimum 1 surrogate (2) Recovery limits lab generated and within 50-150%.	Yes	(1) If surrogate diluted out below lowest calibration std, no recovery criteria. (2) If obvious matrix interference, note in narrative	Note non-conformances in laboratory report narrative.
General Reporting Issues	N/A	(1) The laboratory should report only concentrations detected above the sample specific RL/LLOQ. (2) Concentrations below the RL/LLOQ should be reported as "ND" with the sample specific RL/LLOQ 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	Performance of dilutions must be documented in the laboratory report narrative.

1.5 Special Analytical Considerations for the CT-ETPH Method

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 8000. 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

1.6 Routine Reporting Deliverables for the CT-ETPH Method

The following table (Table 4.0) 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.

Table 4.0: Report Deliverables

Parameter	Deliverable	Comments
Retention Time Windows	NO	
Initial Calibration	NO	Note non-conformances in laboratory report narrative
Continuing Calibration Verification	NO	Note non-conformances in laboratory report narrative
Method Blanks	YES	Note non-conformances in laboratory report narrative. Flag all positive sample results above RL/LLOQ with “B” flag.
Discrimination Check	YES	Note non-conformances in laboratory report narrative
Lab Control Sample / Lab Control Sample Duplicate	YES	Note non-conformances in laboratory report narrative
Site Specific Matrix Spike/ Matrix Spike Duplicate	YES (If analyzed)	Note non-conformances in laboratory report narrative
Surrogate Recoveries	YES	Note non-conformances in laboratory report narrative
General Reporting Issues	YES	Note non-conformances in laboratory report narrative
QA/QC Certification Form	YES	Signed by laboratory director or their designee.
Chain-of-Custody Form	YES	Signed by sample collector, courier, and laboratory.

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 RL/LLOQ). The RL/LLOQ for each compound in each sample must be listed on the report,

based upon the lowest calibration standard, the exact sample mass, any dilution factors, percent moisture, etc.

- Compounds detected above the RL/LLOQ in blanks and in samples shall be flagged with a "B" suffix (e.g., 25B).
-
- All soil/sediment results shall be reported on a dry weight basis.

1.7 Sample Containers, Preservation, and Holding Times

Table 5.0 identifies the type of containers, preservation requirements, and holding times dependent upon analyte and matrix.

Table 5.0: Sample Containers, Preservations, and Holding Times

Matrix	Container[1]	Preservative[2]	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.[3]

[1]The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

[2]If samples were received by the laboratory on the same day of collection and were stored and transported to the laboratory on ice, cooler temperatures above 6ºC are acceptable.

[3]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.