State of Connecticut

Department of Energy and Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Volatile Organics in Air by Method TO-17

Version 3.0

May 2024

Written by the Connecticut DEEP QA/QC Workgroup

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1.0	First version for publication	2/3/2006
2.0	Edited version based on comments, Final Guidance	December 2006
3.0	Updates to reflect CAM method updates to improve consistency between different states.	May 2024

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Acronym List

ACRONYM	DEFINITION
BFB	Bromofluorobenzene
CASN	Chemical Abstracts Service Number
CCV	Continuing calibration verification
%D	Percent difference or percent drift
DEEP	CT Department of Energy and Environmental Protection
DF	Dilution factor
EP	Environmental professional
GC	Gas chromatograph
GC/MS	Gas chromatography/mass spectrometry
ICV	Initial calibration verification
In. Hg	Inches of mercury
LCS	Laboratory control sample
LCSD	Laboratory control sample duplicate
LLOQ	Lower Limit of Quantitation
MD	Matrix duplicate
MS	Mass spectrometer
NA	Not applicable
PAH	Polyaromatic hydrocarbons
ppbV	Parts per billion (volume)
PUF	Polyurethane foam
QA	Quality assurance
QC	Quality control
%R	Percent recovery
%RSD	Percent relative standard deviation
r/r^2	Correlation coefficient
RCP	Reasonable Confidence Protocols
RL	Reporting limit
RPD	Relative percent difference
RSR/RSRs	Remediation Standard Regulations
SIM	Selective ion monitoring
SSV	Safe sampling volumes
TAD	Technical Assistance Document
TCL	Target compound list
UCM	Unresolved complex mixture
$\mu g/m^3$	micrograms per cubic meter
VOCs	Volatile organic compounds

1.0 Quality Assurance and Quality Control Requirements for Method TO-17

1.1 Method Overview

Method TO-17 is a sorbent tube/thermal desorption/ gas chromatography/mass spectrometry ("GC/MS") procedure used to determine volatile organic compounds ("VOCs") in air. This procedure requires an experienced GC/MS analyst familiar with air analysis using sorbent tubes and the Quality Assurance/Quality Control ("QA/QC") requirements of the method. Since the original publication methods TO-1 and TO-2, the technology of the solid absorbents has dramatically improved. New absorbents are commercially available, either singularly or in multi-sorbent packings. The Connecticut Reasonable Confidence Protocols ("RCPs") for this method does not allow any detector except 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 Summary of Method TO-17

The monitoring procedure involves pulling a volume of air through a sorbent packing to collect VOCs, over a wide volatility range, followed by a thermal desorption-capillary GC/MS analytical procedure.

Conventional detectors are not allowed under this modification to achieve "Reasonable Confidence".

Key steps of this method are listed below:

- Selection of a sorbent or sorbent mix tailored for a target compound list, data quality objectives and sampling environment.
- Screening the sampling location for VOCs by taking single tube samples to allow estimates of the nature and amount of sample gases.
- Initial sampling sequences with two tubes at nominally 1- and 4-liter total sample volumes (or appropriate proportional scaling of these volumes to fit the target list and monitoring objectives).
- Analysis of the samples and comparison to performance criteria.
- Acceptance or rejection of the data.
- If rejection, then review of the experimental arrangement including repeat analysis or repeat analysis with backup tubes and/or other quality control ("QC") features.

The EPA requires the use of distributed volume pairs for monitoring to ensure high quality data. However, in situations where acceptable data have been routinely obtained through use of distributed volume pairs and the ambient air is considered well characterized, cost considerations may warrant single tube sampling. Any attendant risk to data quality objectives is the responsibility of the data user.

Key steps in sample analysis are listed below:

- Dry purge of the sorbent tube with dry, inert gas before analysis to remove water vapor and air. The sorbent tube can be held at temperatures above ambient for the dry purge.
- Thermal desorption of the sorbent tube (primary desorption).
- Analyte refocusing on a secondary trap.

- Rapid desorption of the trap and injection/transfer of target analytes into the gas chromatograph (secondary desorption).

- Separation of compounds by high resolution capillary GC and molecular mass measurements by MS.

The target compound list ("TCL") is the same as listed in Compendium Method TO-15 (i.e., subsets of the 97 VOCs listed as hazardous pollutants in Title III of the Clean Air Act Amendments of 1990). Only a portion of these compounds has been monitored using solid adsorbents. This method provides performance criteria to demonstrate acceptable performance of the method (or modifications of the method) for monitoring a given compound or set of compounds.

1.3 Method Interferences

1.3.1 Interference from Sorbent Artifacts

1.3.1.1 Minimizing Artifact Interference

Stringent tube conditioning and careful tube capping and storage procedures (see Method TO-17 are essential for minimizing artifacts. System and sorbent tube conditioning must be carried out using more stringent conditions of temperature, gas flow and time than those required for sample analysis.

A reasonable objective is to **reduce artifacts to 10% or less of individual analyte** masses retained during sampling. A summary of VOC levels present in a range of different atmospheric environments and the masses of individual components collected from 1, 2 or 10 L samples of air in each case is presented in Method TO-17.

Given that most ambient air monitoring is carried out in areas of poor air quality, for example in urban, indoor and factory fence line environments where VOC concentrations are typically above 1 ppb, Method TO-17 demonstrates that the mass of each analyte retained will, therefore, range from ~5 ng to ~10 µg in most monitoring situations. Even when monitoring 'ultraclean' environments, analyte masses retained will usually exceed 0.1 ng.

Typical artifact levels for ¼ inch O.D. tubes of 3.5" length range from 0.01 ng and 0.1 ng for carbonaceous sorbents and Tenax® respectively. These levels compare well with the masses of analytes collected - even from sub-ppb atmospheric concentrations (see Method TO-1(7). Artifact levels are around 10 ng for Chromosorb® Century series and other porous polymer sorbents. However, these types of sorbents can still be used for air monitoring at low ppb levels if selective or mass spectrometer detectors are used or if the blank profile of the tube demonstrates that none of the sorbent artifacts interfere analytically with the compounds of interest.

Some varieties of charcoal contain metals which will catalyze the degradation of some organic analytes during thermal desorption at elevated temperatures thus producing artifacts and resulting in low analyte recoveries.

1.3.1.2 Artifacts from Long-term Storage of Blank Tube

Literature reports of the levels of artifacts on (a) Carbotrap/pack™ C, Carbotrap/pack™ B and Carbosieve™ SIII multi-bed tubes and (b) Tenax® GR tubes, by workers sealing the tubes using metal Swagelok®-type caps and PTFE ferrules with multi-tube, glass storage jars are reported to be between 0.01 ng [after 1-2 months] and 0.1 ng [after 6 months] for (a) and (b) respectively.

Artifact levels reported for other porous polymers are higher - for example 5 ng for Chromosorb 106 after 1 week. More information is given in the Technical Assistance Document ("TAD") referred to in Method TO-17.

1.3.1.3 Artifacts Generated During Sampling and Sample Storage

Benzaldehyde, phenol and acetophenone artifacts are reported to be formed via oxidation of the polymer Tenax® when sampling high concentration (100-500 ppb) ozone atmospheres.

Tenax® should thus be used with an ozone scrubber when sampling low levels (<10 ppb) of these analytes in areas with appreciable ozone concentrations. Carbotrap™/pack type sorbents have not been reported to produce

this level of artifact formation. Once retained on a sorbent tube, chemically stable VOCs, loaded in laboratory conditions, have been shown to give good recoveries, even under high ozone concentrations for storage of a year or more.

1.3.2 Minimizing Interference from Water

1.3.2.1 Selection of Hydrophobic Sorbents

There are three preferred approaches to reducing water interference during air monitoring using sorbent tubes. The first is to minimize water collection by selecting, where possible, a hydrophobic sorbent for the sample tube.

This is possible for compounds ranging in volatility from n-C5 (see safe sampling volumes ["SSVs"] listed in Method TO-17). Tenax®, Carbotrap™ or one of the other hydrophobic sorbents listed in Method TO-17 should be used.

It is essential to ensure that the temperature of the sorbent tube is the same and certainly not lower than ambient temperature at the start of sampling or moisture will be retained via condensation, however hydrophobic the sorbent.

1.3.2.2 Sample Splitting

If the sample loading is high, it is usually possible to eliminate sufficient water to prevent analytical interference by using sample splitting.

Samples may be split either (1) between the focusing trap and the capillary column (single splitting) during trap (secondary) desorption or (2) between both the tube and the focusing trap during primary (tube) desorption and between the focusing trap and the column during secondary (trap) desorption (see Method TO-17) (double splitting). It may, in fact, be necessary to split the sample in some cases to prevent overloading the analytical column or detector.

1.3.2.3 Dry Purge

The third water management method is to "dry purge" either the sorbent tube itself or the focusing trap or both. Dry purging the sample tube or focusing trap simply involves passing a volume of pure, dry, inert gas through the tube from the sampling end, prior to analysis.

The tube can be heated while dry purging at slightly elevated temperatures. A trap packing combination and a near ambient trapping temperature must be chosen such that target analytes are quantitatively retained while water is purged to vent from either the tube or trap.

1.3.3 Atmospheric Pollutants not Suitable for Analysis by this Method

Inorganic gases not suitable for analysis by this method are oxides of carbon, nitrogen and sulfur, ozone, and other permanent gases. Exceptions include carbon disulfide (CS_2) and nitrogen dioxide (NO_2).

Other pollutants not suitable are particulate pollutants, (i.e., fumes, aerosols, and dusts) and compounds too labile (reactive) for conventional GC analysis.

1.3.4 Suitable Atmospheric Conditions

1.3.4.1 Thermal Range

The normal working range for sorbent packing is 0-40º C. In general, an increase in temperature of 10º C will reduce the breakthrough volume for sorbent packings by a factor of 2.

The capacity of the analytical instrumentation to accommodate the amount of water vapor collected on tubes is usually the limitation in obtaining successful results, particularly for GC/MS applications. This limitation can be extreme, requiring the use of a combination of water management procedures (see Method TO-17).

The SSVs of VOCs on hydrophobic adsorbents such as Tenax®, other porous polymers, Carbotrap™ and Carbopack™ are relatively unaffected by atmospheric humidity. Spherocarb® or carbonized molecular sieve type sorbents such as Carbosieve™ SIII and the Carboxens® are affected by high humidity, however, and SSVs should typically be reduced by a factor of 10 at 90-95% relative humidity ("RH"). Hydrophilic zeolite molecular sieves cannot be used at all at high humidity.

1.3.4.2 Wind speeds

Air movement is not a factor indoors or outdoors at wind speeds below 10 miles per hour (<20 km per hour).

Above this speed, tubes should be orientated perpendicular to the prevailing wind direction and should be sheltered from the direct draft if wind speeds exceed 20 miles per hour (30-40 km per hour) (see Method TO-17).

1.3.4.3 High concentrations of particulates

It may be necessary to connect a particulate filter (e.g., a 2-micron Teflon® filter or short clean tube containing a loose plug of clean glass wool) to the sampling end of the tube in areas of extremely high particulate concentrations.

Some compounds of interest may, however, be trapped on the Teflon® or on the glass wool. Particulates trapped on the sorbent tube have the potential to act as a source or sink for volatiles and may remain on the tube through several cycles of sampling and desorption. Frequent replacement of the particulate filter is therefore recommended.

1.4 Quality Control Requirements for Method TO-17

1.4.1 Reporting Limits/Lower Limits of Quantitation for Method TO-17

The reporting limit ("RL")/Lower Limit of Quantitation ("LLOQ") for a compound is dependent on the concentration of the lowest non-zero standard in the initial calibration, analyzed under identical conditions as the samples, with adjustments made for sample volume, sample introduction method, and any dilution factors, etc., as required. Table 1.0 lists approximate RL/LLOQs for air utilizing GC/MS.

Table 1.0: Typical Reporting Limits / Lower Limit of Quantitation[1]

Matrix	Typical Reporting Limit
Air	0.01 µg
[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.	

Sample dilution or lower sample 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 such as the use of SIM, an ion trap mass spectrometer, or other instrumentation of improved design to improve sensitivity. All such modifications must be described in the laboratory report narrative. In such cases the modifications must be noted in the laboratory report narrative.

RL/LLOQ limits for atmospheric monitoring vary depending on two key factors including minimizing artifact levels and volume of air sampled. The volume of air sampled is in turn dependent upon a series of variables including SSVs (see Method TO-1(7), pump flow rate limitations and timeweighted- average monitoring time constraints. RL/LLOQs can be as low as sub-ppb for volatile hydrocarbons in 1 L air samples using the GC/MS operated in the full SCAN mode.

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/MS instrumentation as a quantitative tool and skilled in the interpretation of chromatograms for volatile organics.

Refer to the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* for general QC requirements. These requirements ensure that each laboratory maintain a formal quality assurance ("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/MS system operation may be found in the published method and include evaluation of calibrations and chromatographic performance of sample analyses, instrument QC and method performance requirements for the GC/MS system.

The minimum requirements for a formal QA program include an Initial Demonstration of Capability ("IDOC"), ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples ("LCS") to assess accuracy and matrix duplicates ("MD") to assess precision. Percent recovery data from site-specific samples allow the environmental professional ("EP") to make informed decisions regarding contamination levels at the site. Batch MD results do not give any indication of site-specific matrix interferences or analytical problems related to the specific site matrices. Blanks should not be used for MDs.

Laboratories must document and have on file an IDOC for each combination of sample preparation and determinative method being used. These data must meet, or fall within, the performance standards as presented in Section 1.4 and Table 1A of this RCP. 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 Method TO-17. The IDOC must include the elements provided in Table 2.0.

Table 2.0: IDOC Requirements

QC Element	Performance Criteria
BFB Tuning	Method TO-17
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

Because of the extensive analyte list and number of QC elements associated with the IDOC 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 IDOC data. This information should be kept on-file at the laboratory.

Laboratories are required to generate laboratory specific performance criteria for LCS compound recovery limits, 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.

1.4.3 Specific Quality Control Requirements for Method TO-17

Specific QA/QC requirements and performance standards for Method TO-17 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 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 Method TO-17

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Sorbent Tube Cleaning and Certification	Assure tubes are free from contamination	Per Method TO-17 tubes must be identified. One tube per batch must be analyzed for contamination and results documented.	No Data kept on file in lab.	Do not use contaminated or tubes of unknown history without cleaning.	Reclean as necessary.
Sampling System Components	Assure sampling system free from contamination	Pump calibrations must be documented. Tubes must be stored to prevent contamination as per Method TO-17.	No Records kept on file in lab	N/A	N/A
GC/MS Tunes with BFB	Inter-laboratory consistency and comparability	(1) Analyze every 24 hours	No	Perform instrument maintenance as necessary; retune instrument.	Suspend all analyses until tuning non-compliance is rectified.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Initial Calibration ("ICAL")	Laboratory Analytical Accuracy	(1) Minimum of 5 standards. Standards must be prepared per Method TO-17. (2) Low standard must be ≤ RL/LLOQ (3) Must meet technical acceptance criteria as per Method TO-17. (4) Must contain all target analytes (5) %RSD for RRF of each compound must be < 30% with at most two exceptions up to a limit of 40%. (6) RRT for each target compound must be within 0.06 RRT units of mean RRT for the compound. (7) Calibration must be performed under the same conditions as the samples. (8) If linear or non-linear regression used, verify the RL/LLOQ by recalculating concentrations in lowest calibration standard using the final calibration curve, recoveries must be 70-130%. (9) Quantitation ions for the target compounds are shown in Table 2. The primary ion should be used unless interferences are present, in which case a secondary ion is used.	No	Recalibrate as required by method.	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds in laboratory report narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Initial Calibration Verification Standard ("ICV")	Laboratory Analytical Accuracy	(1) Analyzed immediately after initial calibration. (2) Must use a second source standard (3) Standard should be at mid-point of the curve (4) Must contain all target analytes. (5) Recovery must fall within 70-130%. (6) Laboratories are allowed to have 20% of compounds out, as long as all compounds within recover 65-135% (7) %RSD for RRF of each compound must be < 30% with at most two exceptions up to a limit of 40%. (8) RRT for each target compound must be within 0.06 RRT units of mean RRT for the compound. (9) %D for each target analyte must be within 70-130%.	No	(1) Reanalyze ICV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze ICV	(1) Perform maintenance as needed, recalibrate. (2) Note non-conformances in laboratory report narrative.
Continuing Calibration Std ("CCV")	Laboratory Analytical Accuracy	(1) Every 24 hrs prior to analysis of samples per Method TO-17. (2) Can be same source standard as calibration. (3) Must contain all target analytes. (4) %RSD for RRF of each compound must be < 30% with at most two exceptions up to a limit of 40%. (5) RRT for each target compound must be within 0.06 RRT units of mean RRT for the compound. (6) Recovery must fall within 70-130%.	NO	Recalibrate as required by method.	Report non-conforming compounds in laboratory report narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Method Blanks ("MB")	Laboratory Contamination Evaluation	(1) Analyze with every batch, or ≤20 field samples, whichever is more frequent, prior to sample analysis and at the end of the analytical sequence. (2) All target compounds must be <RL/LLOQ (not the MDL as specified in the method)	Yes	Narrate non-conformances.	(1) Report non-conformances in laboratory report 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) Frequency - every batch or ≤20 field samples whichever is more frequent. (2) Second source standard. (3) Concentration level near or at the mid-point of the initial calibration. (4) Must contain all target analytes (5) Recovery must fall within 50-150%.	Yes	(1) Recalculate the percent recoveries (2) Reanalyze the LCS (3) If LCS still falls outside acceptable criteria, narrate non-conformances.	Report non-conformances in laboratory report narrative.
Laboratory Control Sample Duplicate ("LCSD") May be used in lieu of MD	Method Precision	(1) Frequency- one per digestion batch of ≤ 20 field samples (2) Concentration level must be same as LCS. Analyze immediately following LCS. (3) Concentration level near or at the mid-point of the initial calibration. (4) Must contain all target analytes (5) RPD ≤30%	Yes	1) Reanalyze LCSD; if acceptable, no further action required. (2) If reanalysis is still outside of recovery criteria and LCS is in-control for target analytes, no corrective action required. (3) If LCSD and LCS are both outside of recovery criteria, re-digest and reanalyze LCS/LCSD and all associated field samples in batch.	Report recovery and RPD non-conformances in laboratory report narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Matrix duplicates ("MD")	Method Precision	(1) Frequency- every ≤20 samples analyze one sample duplicate. (2) RPD's must be ≤ 25% for compounds present above the concentration of the low calibration standard.	Yes	If more than 10% of analytes present above the concentration of the low std fail the RPD criteria, investigate system. Reanalyze CCV to verify system performance.	Report non-conformances in laboratory report narrative
Internal Standards ("IS")	Laboratory Analytical Accuracy and Method Accuracy in Sample	(1) Laboratory must use a minimum of 3 IS at retention times across the GC run. (2) Must be prepared in accordance with Method TO-17. (3) RT for each IS must be within ± 0.33 minutes of RT of IS in most recent, valid calibration.	No	(1) If RT for any IS changes by more than 20 seconds from latest daily calibration standard, evaluate the analytical system for malfunctions and correct. (2) If area response of any IS changes by more than ± 40%, inspect instrument and reanalyze samples. (3) If IS RT's fall within criteria after reanalysis, only submit data for reanalysis.	(1) Note non-conformances in laboratory report narrative

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Quantitation	N/A	(1) Quantitation must be based on IS calibration. The IS's used for target compounds are ones nearest the RT of a given analyte. (2) The RRF from daily continuing cal is used to calculate concentration of sample. Secondary ion quantitation is allowed ***only*** when there are sample interferences with primary ion. (3) Area of secondary ion cannot be substituted for area of a primary ion unless a RRF is calculated using the secondary ion. (4) A retention time window is calculated for each single component analyte and surrogate. Windows are established as ± RRT units of the retention time for analyte of mid-point of cal curve of initial calibration or the continuing calibration standard.	No	N/A	Note any non-conformances in laboratory report narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
General Reporting Issues	N/A	(1) The laboratory should report only concentrations detected above the sample specific RL/LLOQ. (2) Report concentrations below the RL/LLOQ as "ND" with the reporting limit. (3) Compounds, which exceed the linear range, should be flagged ("E" flag).	N/A	N/A	(1) Qualification of results reported below the RL/LLOQ is required. (2) Performance of dilutions must be documented in the laboratory report narrative (3) If samples are not received with an acceptable cooler temperature, note the non-conformances in the laboratory report laboratory report narrative. (4) If samples are extracted and/or analyzed outside of the holding time, note the non-conformances in the laboratory report narrative.

1.7 Analyte List for Method TO-17

The DEEP analyte list for Method TO-17 is presented in Table 1B. The compounds listed are readily analyzable by Method TO-17.

Table 1B Analyte List for Method TO-17

Analyte	CAS No.	Analyte	CAS No.
Acetone	67641	1,3-Dichloropropane	142289
Acrylonitrile	107131	cis-1,3-Dichloropropene	10061015
Benzene	71432	trans-1,3-Dichloropropene	10061026
n-Butylbenzene	104518	Ethylbenzene	100414
Sec-Butylbenzene	135988	Isopropylbenzene (Cumene)	98828
Bromodichloromethane	75274	4-Isopropyltoluene	99876
Bromoform	75252	Methylene Chloride	75092
2-Butanone (MEK)	78933	4-Methyl-2-pentanone (MIBK)	108101
Carbon Tetrachloride	56235	Methyl tert-butyl ether (MTBE)	1634044
Chlorobenzene	108907	Styrene	100425
Chloroethane	75003	1,1,1,2-Tetrachloroethane	630206
Chloroform	67663	1,1,2,2-Tetrachloroethane	79345
Chloromethane	74873	Tetrachloroethene (Perc)	127184
Dibromochloromethane	124481	Toluene	108883
1,2-Dibromoethane (EDB)	106934	1,1,1-Trichloroethane	71556
1,2-Dichlorobenzene	95501	1,1,2-Trichloroethane	79005
1,3-Dichlorobenzene	541731	Trichloroethene (TCE)	79016
1,4-Dichlorobenzene	106467	Trichlorofluoromethane	75694
Dichlorodifluoromethane	75718	1,2,4-Trimethylbenzene	95636
1,1-Dichloroethane	75343	1,3,5-Trimethylbenzene	108678
1,2-Dichloroethane	107062	Vinyl Chloride	75014
1,1-Dichloroethene	75354	o-Xylene[1]	95476
cis-1,2-Dichloroethene	156592	m-Xylene[1]	108383
trans-1,2-Dichloroethene	156605	p-Xylene[1]	106423
1,2-Dichloropropane	78875		

[1]May be reported as total xylenes or any combination of the three isomers

1.7.1 Additional Reporting Requirements for Method TO-17

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. DEEP 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.

1.8 Routine Reporting Deliverables for Method TO-17

The following table (Table 3.0) 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.

Table 3.0: Report Deliverables

Parameter	Deliverable	Comments
GC/MS Tunes	NO	Analysis cannot proceed without meeting tuning criteria.
Initial Calibration	NO	Note non-conformances in laboratory report narrative
Continuing Calibration	NO	Note non-conformances in laboratory report narrative
Method Blanks	YES	Note non-conformances in laboratory report narrative. Flag all positive results above RL/LLOQ with “B” flag.
Lab Control Sample	YES	Note non-conformances in laboratory report narrative
Sample Replicate	YES	Note non-conformances in laboratory report narrative
Internal Standard Areas	NO	Note non-conformances in laboratory report narrative
General Reporting Issues	YES	Note non-conformances in laboratory report narrative
Identification and Quantitation	NO	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.

1.8.1 Additional Reporting Requirements for the Method TO-17

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 specific 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 volume, any dilution factors, percent moisture, etc.

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

- Report results for any library search compounds as estimated using a “J” suffix (e.g., 25J).

1.9 Sample Collection, Storage and Holding Times

Table 4.0 identifies the type of containers, storage requirements, and holding times.

Table 4.0: Sample Collection, Storage, and Holding Times

Container	Storage	Holding Time
Stainless steel sampling tube, capped, and wrapped in aluminum foil	Refrigerate at ≤4° C	30 days to desorb into can; Desorb to analysis 30 days

1.10 Tentatively Identified Compounds

The evaluation of Tentatively Identified Compounds ("TICs") in conjunction with GC/MS analyses is a powerful and cost-effective analytical tool that can be utilized by the EP to support RSR due diligence requirements. This analytical approach is particularly effective at locations with suspect disposal practices, complex or uncertain site history, and/or sites that require detailed evaluation of critical exposure pathways. When GC/MS analytical methods are utilized an analysis of TICs is not usually expected but should be considered, at the discretion of the EP, in support of site characterization activities for releases at locations with complex and/or uncertain history.

1.10.1 Reporting of Tentatively Identified Compounds ("TICs")

If evaluated, all TICs that meet the chromatographic criteria presented in Appendix A of this RCP must be reported by the laboratory either in the Environmental Laboratory Report or in the Environmental Laboratory's laboratory report narrative. In turn, the EP must include a discussion regarding the disposition of all reported TICs as part of the RSR submission to DEEP. Depending on specific site circumstances (e.g., a potentially toxic contaminant is found in adjacent to a building, etc.), re-sampling/re-analysis with analyte-specific calibration and QC may be required to definitively assess the risk posed by the TIC to human health and the environment. No regulatory judgments or remedial decisions should be made without re-analysis of samples for the TICs using a five-point analyte specific calibration and appropriate QC. This may require re-sampling to meet analytical holding times.

Appendix A: Laboratory Requirements for Evaluation of Tentatively Identified Compounds Method TO-17

A-1. Chromatographic Criteria

A-1.1 Initially include all the non-target compounds that have a peak area count of 10% of the nearest internal standard. The EP may request evaluation of unknown peaks before the first internal standard based on site-specific information.

A-2. Mass Spectral Criteria

A-2.1 All spectra must be evaluated by a qualified mass spectrometrist and the Organic Supervisor/Laboratory Director.

A-2.2 The spectral library match must be ≥ 85% for a tentative identification to be made.

A-2.3 The major ions in the reference spectrum (ions greater than 10% of the most abundant ion) must be present in the sample spectrum.

A-2.4 The relative intensities of the major ions must agree within ± 20%.

A-2.5 Molecular ions present in the reference spectrum should be present in the sample spectrum.

A-2.6 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks.

A-2.7 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different chromatographic retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs (as a mixture of two isomers).

A-2.8 Spectra identified as “unknown” should be assigned to a general chemical class, if possible. Classification as a halogenated hydrocarbon, aldehydes/ketone, carboxylic acid, or cyano compound, etc. is acceptable. An explanation as to why more specific identification cannot be made (e.g., truncated spectra due to insufficient mass scanning range) must be provided in the analytical laboratory report narrative to support any “unknown” classification.

A-2.9 TICs which are identified as petroleum aliphatic hydrocarbons should not be reported as TICs. TICs identified as aromatics or other hydrocarbons should be reported. However, there must be a statement in the laboratory report narrative discussing the presence of these hydrocarbons in the sample(s).

A-2.10 After the above criteria are met, the top ten (10) compounds for VOCs, chosen by comparing the area of the TIC to the area of the nearest internal standard, must be tentatively identified, quantitated, and reported. All TIC concentrations should be flagged as estimated by using a “J” suffix.

A-3. Toxic Spectral Characteristics Criteria

A-3.1 Regardless of the number of peaks present, the laboratory must evaluate any peak where the mass spectrum exhibits a characteristic chlorine or bromine spectral pattern. This only applies to peaks having an area >10% of the nearest internal standard.

A-4. Semi-Quantitative Analysis

A-4.1 Once a TIC has been identified, the semi-quantitation of that compound will be based on the integrated abundance of the TIC and internal standard total ion chromatogram. The response factor for all TICs will be assumed to be 1.0. The internal standard used shall be the one with the nearest retention time to a given TIC and that is interference free.

A-4.2 The resulting semi-quantitative concentration must be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine the concentration.

A-5. Reporting Criteria

A-5.1 All TICs eluting after the first internal standard and 3 minutes after the last target compound meeting the requirements in A-2 must be reported by the laboratory with the clear indication that the reported concentration is an estimated value unless analyte-specific calibration and QA/QC were performed. This reporting requirement may be fulfilled by discussion in the laboratory report narrative or by using a “J” flag designation.

In most circumstances the laboratory must order standards to be able to run a calibration curve and the appropriate QA/QC. The EP should be prepared to expect longer analytical turn-around-times to attain TIC results that are scientifically defensible.