WSC – CAM – II A

Quality Assurance and Quality Control Requirements for ***SW-846 Method 8260B, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*** for the Massachusetts Contingency Plan (MCP)

Document Status: Final

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Document Chronology

Revision	Status	Date
0	Public Comment Draft	5 January 01
1	Revised Public Comment Draft	26 June 01
2	Revised Interim Final	12 June 02
3	Final	22 May 03
4	Final	30 April 04

II. Gas Chromatography/Mass Spectrometry (GC/MS) Methods

A. Quality Assurance/Quality Control (QA/QC) Requirements and Performance Standards for SW-846 Method 8260B (Volatile Organics by GC/MS)

Table of Contents

1.0 QA/QC Requirements for SW-846 Method 8260B 3

1.1 Method Overview 3

1.2 Summary of Method 5

1.3 Method Interferences 6

1.4 Alternative Sample Introduction Methods 7

1.5 Quality Control Requirements for SW-846 Method 8260B 7

1.6 Analyte List for SW-846 Method 8260B 13

2.0 Data Usability Assessment for SW-846 Method 8260B 18

3.0 Reporting Requirements for SW-846 Method 8260B 18

3.1 General Reporting Requirements for SW-846 Method 8260B 18

3.2 Specific Reporting Requirements for SW-846 Method 8260B 18

3.3 Tentatively Identified Compounds (TICs) by GC/MS 20

List of Tables and Appendices

Number	Title	Page
Table II A-1	Specific QA/QC Requirements and Performance Standards for SW-846 Method 8260B	10-12
Table II A-2	Analyte List for SW-846 Method 8260B	15-17
Table II A-3	Routine Reporting Requirements for SW-846 Method 8260B	20
Appendix II A-1	Sample Collection, Preservation and Handling Procedures for Volatile Organic Compound (VOC) Analyses	22-24
Appendix II A-2	Guidance for the Evaluation of Tentatively Identified Compounds (TICs) for SW-846 Method 8260B Under the MCP Samples Under the MCP (Including Exhibit II A-1)	25-27

1.0 QA/QC Requirements for SW-846 Method 8260B

1.1 Method Overview

SW-846 Method 8260B is used to determine the presence of volatile organic compounds (VOCs) in a variety of matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling sorbent media, groundwater and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. All references to SW-846 methods in this document refer to the United States Environmental Protection Agency's most recently published version.

1.1.1 Reporting Limits for SW-846 Method 8260B

The reporting limit (RL) using SW-846 Method 8260B for an individual compound is dependent on the concentration of the lowest analytical standard in the initial calibration, choice of sample preparation/introduction method and/or percent (%) solids of the sample. Using standard quadrupole instrumentation and the purge-and-trap technique (operating at ambient temperature), reporting limits should be approximately 5-10 µg/kg (wet weight) for low-level soil/sediment samples, 100-200 µg/kg (wet weight) for high-level soil/sediment samples (based on 1:1 ratio [mL:g] of methanol to soil/sediment and analysis of 100 µL of methanol extract in 5 mL of water), 500 µg/kg (wet weight) for wastes (sample usually requires special pre-treatment and/or dilution prior to analysis), and 5 µg/L for groundwater (based on a 5 mL purge volume). Somewhat lower limits may be achieved using selective ion monitoring, an ion trap mass spectrometer, or other instrumentation of improved design. Regardless of the instrument that is used, reporting limits for SW-846 Method 8260B will be proportionately higher for samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

It should be noted that for some analytes of concern (e.g. 1,2-dichloroethane, *cis*- and *trans*-1,3-dichloropropene, 1,1,2,2-tetrachloroethane, etc.), the aforementioned reporting limits associated with high-level soil/sediment analyses (with methanol preservation) may not be adequate to verify regulatory compliance. If a lower reporting limit is required, a low-level soil/sediment method (freezing (< -7° C), as described in Appendix II A-1, is the preferred preservation option) must be used. In addition, analytes with poor purging efficiency at ambient temperature, designated as "PP" on Table II A-2, may require the heated purge and trap option as described in SW-846 Method 8260B, Section 7.1.2.2. It should be noted that oxygenates and other compounds susceptible to hydrolysis should not be preserved with acid <u>if heated purge and trap</u> is used as the sample introduction method. See Appendix II A-1.

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for VOCs analyzed in support of MCP decision-making are presented in Appendix II A–1 of this document and Appendix VII-A, WSC-CAM-VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of

Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".

1.1.2 General Quality Control Requirements of SW-846 Method 8260B

Each laboratory that uses SW-846 Method 8260B is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and the analysis of laboratory control spikes (LCSs) and LCS duplicates to assess analytical accuracy and precision. Matrix spikes (MS), matrix spike duplicates (MSD) or Matrix duplicates may also be used to evaluate precision when such samples are analyzed either at discretion of the laboratory or at the request of the data-user.

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 II A-1 of this method. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 Method 8000B (Section 8.4) and SW-846 Method 8260B (Section 8.3). The data associated with the Initial Demonstration of Proficiency should be kept on file at the laboratory and made available to potential data users on request. The data associated with the Initial Demonstration of Proficiency for SW-846 Method 8260B must include the following:

QC Element	Performance Criteria
BFB Tuning	WSC-CAM–II A, Table II A-1
Initial Calibration	WSC-CAM–II A, Table II A-1
Continuing Calibration	WSC-CAM-II A, Table II A-1
Method Blanks	WSC-CAM-II A, Table II A-1
Average Recovery	SW-846 Method 8000, Section 8.4
% Relative Standard Deviation	SW-846 Method 8000, Section 8.4
Surrogate Recovery	WSC-CAM–II A, Table II A-1
Internal Standards	WSC-CAM–II A, Table II A-1

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 standard for one or more QC elements. Under these circumstances, the analyst should attempt to locate and correct the problem and repeat the analysis for all non-conforming analytes. All non-conforming analytes along with the laboratory-specific acceptance criteria should be noted in the Initial Demonstration of Proficiency data provided.

It is essential that laboratory-specific performance criteria for LCS, LCS duplicate 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 analytes and/or 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 II A-1 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

For SW-846 Method 8260B, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table II A-1. It should be noted that the performance standards listed in Table II A-1 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory. Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results. . In some cases, the standard laboratory acceptance criteria for the various QC elements may require modification to accommodate more rigorous project-specific data quality objectives prescribed by the data user. The laboratory may be required to modify routine sample introduction and/or analytical conditions to accommodate project-specific data quality objectives.

This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers (GC/MS) as a quantitative tool and skilled in the interpretation of chromatograms and mass spectra.

1.2 Summary of Method

The volatile compounds are introduced into the gas chromatograph by purge-and-trap or by other methods. The analytes are then introduced directly to a capillary column by ballistic heating or cryo-focused onto a capillary pre-column before being flash evaporated to a capillary column for analysis. The GC oven is temperature-programmed to facilitate separation of the analytes of interest which are then detected by a mass spectrometer that is interfaced to the gas chromatograph.

Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing sample electron impact mass spectra with the electron impact mass spectra of standards. Quantitation is accomplished by using the response of a major (quantitation) ion relative to an internal standard and a response factor generated from a five-point calibration curve.

1.3 Method Interferences

1.3.1 Chemical Contaminants

Major contaminant sources for SW-846 Method 8260B include, but are not limited to, volatile materials in the laboratory and impurities in the inert purging gas and the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds that will be concentrated in the trap during the purge operation.

Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should determine the cause of the contamination before re-analysis occurs. Corrective actions may include changing the purge gas source and/or regenerating the molecular sieve purge gas filter. **Subtracting blank values from sample results is not permitted.** If the laboratory determines that the concentration reported in the blank is so high that false positive results are likely in the associated samples, then the laboratory should fully explain this situation in the Environmental Laboratory case narrative.

1.3.2 Cross-contamination/Carryover

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of volatile organic compounds. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for potential cross-contamination/carryover. The concentration of VOCs which can cause cross-contamination/carryover must be determined by the laboratory and will be dependent upon the concentration and level of saturation of the particular analyte. Concentrations of VOCs which exceed the upper limit of calibration should prompt the analyst to check for potential cross-contamination/carryover. In addition, samples containing large amounts of water-soluble materials, suspended solids, or high boiling point compounds may also present potential for cross-contamination/carryover. Laboratories should be aware that carryover from high boiling point compounds may not appear until a later sample run.

Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. Refer to Section 3.0 of SW-846 Method 8260B for a detailed description of approaches to minimize these interferences, as well as other special precautions associated with the analysis of methylene chloride, a common laboratory contaminant.

1.3.3 Other Potential Interferences

Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank carried through sampling and subsequent storage and handling can serve as a check on such contamination.

The use of sodium bisulfate as the low-level preservation method for solid samples with high organic matter or humic material content has been known to result in the formation of acetone and methyl ethyl ketone (MEK) at potentially significant concentrations in samples. Sodium bisulfate preservation must **never** be used when these conditions are either present or suspected. It should be noted that freezing (< -7° C), and not sodium bisulfate addition, is the preferred low-level preservation method for solid samples (see Appendix II A-1).

Use of methanol in the high-level solid preservation method may also result in the detection of MEK at trace levels in samples due to the presence of MEK as a methanol contaminant.

1.4 Alternative Sample Introduction Methods

Various alternatives are provided in SW-846 Method 8260B, Section 7.1 for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Quality control procedures to ensure the proper operation of the various sample introduction techniques may be found in SW-846 Methods 3500 and 5000, respectively.

Some of these alternative sample introduction methods include:

- Direct injection (SW-846 Methods 5000 and 8260B, Section 7.1.1)
- Purge-and-trap for aqueous samples (SW-846 Method 5030)
- Purge-and-trap for solid samples (SW-846 Method 5035A)
- Vacuum distillation (SW-846 Method 5032)
- Azeotropic distillation (SW-846 Method 5031)
- Automated static headspace (SW-846 Method 5021), and
- Cartridge desorption (SW-846 Method 5041)

This guidance document is primarily intended to provide QA/QC requirements and performance standards for SW-846 Method 8260B using conventional purge-and-trap sample introduction via SW-846 Methods 5030 (ambient temperature) and 5035A for aqueous and solid samples, respectively. If other sample introduction methods are required and utilized because of analytical circumstances, the laboratory must provide a full explanation and justification in the Environmental Laboratory case narrative, as well as details and results of the QC samples and calibrations associated with these different sample introduction methods.

1.5 Quality Control Requirements for SW-846 Method 8260B

1.5.1 General Quality Control Requirements for Determinative Chromatographic Methods

Refer to SW-846 Method 8000 for general quality control procedures for all chromatographic methods, including SW-846 Method 8260B. These requirements ensure 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, Sec. 7.0, and include evaluation of calibrations and chromatographic performance of sample analyses. Instrument quality control and method performance requirements for the GC/MS system may be found in SW-846 Method 8260B, Sections 8.0 and 9.0, respectively.

1.5.2 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8260B

Specific QA/QC requirements and performance standards for SW-846 Method 8260B are presented in Table II A-1. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide an LSP with "Presumptive Certainty" regarding the usability of analytical data to support MCP decisions. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty", parties must:

(a) Comply with the procedures described and referenced in WSC-CAM–II A;

(b) Comply with the applicable QC analytical requirements prescribed in Table II A-1 for this test procedure;

(c) Evaluate, and narrate, as necessary, compliance with performance standards prescribed in Table II A-1 for this test method; and

(d) Adopt the reporting formats and elements specified in the CAM

In achieving "Presumptive Certainty" status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad <u>QA/QC requirements</u> of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data;
- ✓ May be used in a <u>data usability</u> assessment, and, if in compliance with all MCP Analytical Method standards, laboratory QC requirements, and field QC recommended limits and action levels, the data set will be considered usable data to support site characterization decisions made pursuant to the MCP; and
- ✓ May be used to support a data representativeness assessment

Widespread adherence to the "Presumptive Certainty" approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and

standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of alternative analytical methods. However, parties who elect not to utilize the "Presumptive Certainty" option have an obligation, pursuant to 310 CMR 40.0017 and 40.0191(2)(c), to demonstrate and document an overall level of (laboratory and field) QA/QC, data usability, and data representativeness that is adequate for and consistent with the intended use of the data.

1.5.3 Recovery of Matrix Spikes (MS) and Matrix Spike Duplicates (MSD) with Methanol-Preserved Soil/Sediment Samples

The recovery of matrix spikes from a soil/sediment sample that has been preserved with methanol cannot be used to directly evaluate matrix-related bias/accuracy in the conventional definition of these terms. Quality Control parameters expressed in terms of these percent recoveries (%R) may be more indicative of the variabilities associated with the analytical system (sample processing, introduction, and/or component separation). Because of this limitation, it is recommended that laboratory analyze standard reference materials and participate in relevant performance evaluation studies as frequently as possible. Recommended practices for additional quality assurance made be found in SW-846 Methods 5000 and 8000, respectively.

This inherent limitation of methanol preservation with respect to the evaluation of matrix spike recoveries is more than compensated for by the marked improvement in sample integrity and conservation/recoveries of the volatile analytes of concern from soil matrices by minimizing volatilization losses.

1.5.4 Recovery of Surrogates with Methanol-Preserved Soil/Sediment Samples

Analytical surrogates as described in Table II A-1 should be spiked directly into the solvent at the time of extraction. Solvent-fortified analytical surrogates provide unresolved or combined percent (%) recovery data dependent on both analytical efficiencies and sample matrix effects. To determine the source of this analytical anomaly, parties may wish and/or otherwise may need to obtain and analyze additional QC samples.

1.5.5 Trip Blanks and Field Duplicates for SW-846 Method 8260B Analyses

As described in WSC-CAM -VII A, Section 2.5, Table VII A-1, a Trip Blank for each cooler and submission of Field Duplicates are recommended for drinking water samples only. However, the Field Duplicates need only be analyzed if one or more analytes are detected in the primary sample above the Reporting Limit (RL). The cooler Trip Blank need only be analyzed if one or more analytes are detected in any sample above the Reporting Limit. Drinking water samples should be identified and specific analytical instruction for the drinking water and associated field quality control samples provided when the samples are submitted to the laboratory for analysis.

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
GC/MS Tunes with BFB	Inter-laboratory consistency and comparability	(1) Criteria listed in Table 4 of SW-846 Method 8260B (the same criteria must be used for all analyses) (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 (2) Low standard must be ≤ Reporting Limit (RL) (3) %RSD should be ≤15 or "r" should be ≥0.99 for all compounds except CCCs which must be ≤30 %RSD or "r" ≥0.99 (4) Must contain all target analytes (5) If regression analysis is used, the curve must not be forced through the origin.	No	Recalibrate as required by method (1) if any of CCC % RSDs >30 or any of CCC "r" <0.99 or (2) if >20% of remaining analytes have % RSDs >30 or "r" <0.99.	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds in Environmental Laboratory case narrative. If the average response factor or linear regression are not used for analyte quantitation (e.g., use of a quadratic equation), this must be noted in the Environmental Laboratory case narrative with a list of the affected analytes.
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	(1) Every 12 hours prior to the analysis of samples (2) Concentration level near midpoint of curve (3) Must contain all target analytes (4) Percent difference or percent drift must be ≤20 for CCCs and should be ≤30 for other compounds	No	Recalibrate as required by method (1) if %D of any of CCCs >20, or (2) if %D of >10% of other analytes >30.	Report non-conforming compounds in Environmental Laboratory case narrative.
Method Blanks	Laboratory Method Sensitivity (contamination evaluation)	(1) Every 20 samples prior to running samples and after calibration standards (2) Matrix and preservative-specific (e.g., water, MeOH, $NaHSO_4$) (3) Target analytes must be <RL except for common laboratory contaminants (such as acetone, methylene chloride, and MEK which must be <5x the RL)	Yes	Locate source of contamination; correct problem; reanalyze method blank.	(1) Report non-conformance in Environmental Laboratory case narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" flag or some other convention, should qualify the sample results. Blank contamination should also be documented in the Environmental Laboratory case narrative.
Laboratory Control Spikes (LCSs)	Laboratory Method Accuracy	(1) Every 20 samples or for each new tune clock, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration (3) Concentration level must be at or near the mid-level (50%) standard (4) Must contain all target analytes (5) Matrix and preservative-specific (e.g., water, MeOH, $NaHSO_4$) (6) Laboratory–determined percent recoveries must be between 70 – 130 for target compounds. (7) Can also be used as CCAL	Yes	Recalculate the percent recoveries; Reanalyze the LCS; Locate source of problem; reanalyze associated samples.	(1) Report non-conformances in Environmental Laboratory case narrative. (2) Individual laboratories must identify and document "difficult" (**) analytes for which laboratory-determined recovery ranges routinely exceed the 100 ± 30% criterion. Exceedances for these "difficult" analytes must be qualified in Environmental Laboratory case narrative. Analytical data to support the "difficult" analyte classification must be available for review during an audit.

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
LCS Duplicate	Laboratory Method Precision	(1) Every 20 samples or for each new tune clock, whichever is more frequent. (2) Prepared using same standard source and concentration as LCS. (3) Must contain all target analytes. (4) Recommended to be run immediately after LCS in analytical sequence. (5) Laboratory–determined percent recoveries must be between 70 – 130 for target compounds (6) Matrix and preservative-specific (e.g., water, MeOH, $NaHSO_4$). (7) Laboratory–determined Relative Percent Difference (RPD) must be ≤ 25 except for "difficult" (**) analytes which must be ≤ 50.	Yes	Recalculate RPD; Locate source of problem; Narrate non-conformances	(1) Locate and rectify source of non-conformance before proceeding with the analyses of subsequent sample batches. (2) Individual laboratories must identify and document "difficult" (**) analytes for which laboratory-determined RPDs routinely exceed the ≤ 25 criterion. (3) Exceedances for these "difficult" analytes must be qualified in Environmental Laboratory case narrative. Analytical data to support the "difficult" analyte classification must be available for review during an audit. (4) Narrate non-conformances
MS/MSDs	Method Accuracy in Sample Matrix Method Precision in Sample Matrix	(1) Every 20 samples (at discretion of laboratory or at request of data-user) (2) Matrix-specific (3) Prepared by fortifying field sample with standard from source different than source used for initial calibration (4) Concentration level - between low (RL) and mid-level (50%) standard (5) Must contain all target analytes. (6) Percent recoveries - between 70 – 130 (7) RPDs should be ≤30 for waters and solids	Yes Only when requested by the data-user	Check LCS; if recoveries acceptable in LCS, narrate non-conformance.	Note exceedances in Environmental Laboratory case narrative.
Surrogates	Accuracy in Sample Matrix	(1) Evaluate surrogate recovery from individual field samples. (2) Minimum of 3 surrogates, at retention times across GC run (3) Percent recoveries must be between 70-130 for individual surrogate compounds. Laboratory-determined surrogate recovery limits that exceed ± 30% are acceptable for some difficult matrices (wastes, sludges, etc.) with appropriate analytical documentation.	Yes	If one or more surrogates are outside limits, reanalyze sample unless one of the following exceptions applies: (1) obvious interference present (e.g., UCM). (2) for methanol-preserved samples, re-analysis is not required if % moisture >25 and recovery is >10%. (3) if one surrogate exhibits high recovery and target analytes are not detected in sample.	(1) Note exceedances in Environmental Laboratory case narrative. (2) If re-analysis yields similar surrogate non-conformances, the laboratory should report results of both analyses. (3) If re-analysis is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both analyses. (5) If sample is not re-analyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Internal Standards (IS)	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) Minimum of 3 at retention times across GC run (2) Area counts in samples must be between 50 – 200% of the area counts in the associated continuing calibration standard (Section 5.10 of 8260B) (3) Retention times of internal standards must be within ±30 seconds of retention times in associated continuing calibration standard	No	If one or more internal standards are outside limits, reanalyze sample unless obvious interference present (e.g., UCM)	(1) Note exceedances in Environmental Laboratory case narrative. (2) if re-analysis yields similar internal standard non-conformances, the laboratory should report both results. (3) If re-analysis is performed within holding time and yields acceptable internal standard recoveries, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of holding time and yields acceptable internal standard recoveries, the laboratory must report results of both analyses. (5) If sample is not re-analyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
Quantitation	NA	(1) Quantitation must be based on IS calibration. (2) The laboratory must use the average response factor or linear regression curve generated from the associated initial calibration for quantitation of each analyte The IS used for quantitation must be the one nearest the retention time of the subject analyte.	NA	NA	(1) If the average response factor or linear regression are not used for analyte quantitation (e.g. quadratic equation), this must be noted in the Environmental Laboratory case narrative with a list of the affected analytes. (2) It is essential that the laboratory clearly document the calculation of analyte concentrations when non-linear calibrations are employed.
General Reporting Issues	NA	(1) The laboratory must only report values ≥ the sample-specific reporting limit; optionally, values below the sample-specific reporting limit can be reported as estimated, if requested. The laboratory must report results for samples and blanks in a consistent manner. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, surrogates, etc) for each analysis must be "reported". (3) Refer to Section 3.3, TIC Compounds by GC/MS for guidance	NA	NA	(1) Qualification of the data is required if reporting values below the sample-specific reporting limit. (2) Complete analytical documentation for diluted and undiluted analyses is to be available for review during an audit. (3) TICs will be evaluated at the discretion of the LSP consistent with the guidelines presented in Appendix II A–4. (4) The performance of dilutions must be documented in the Environmental Laboratory case narrative.

GC/MS = Gas Chromatography/Mass Spectrometry
BFB = 4-Bromofluorobenzene
MS/MSDs = Matrix Spikes/Matrix Spike Duplicates
%RSD = Percent Relative Standard Deviation
UCM = Unresolved Complex Mixture
"r" = Correlation Coefficient
CCC = Calibration Check Compounds
RPDs = Relative Percent Differences
TIC = Tentatively Identified Compound
NA = Not Applicable

**** Potentially "difficult" analytes include: acetone, bromomethane, chloroethane, dichlorodifluoromethane, diethyl ether, dibromochloromethane, hexachlorobutadiene, MEK, 4-methyl-2-pentanone, 1,4-dioxane and trichlorofluoromethane**

1.6 Analyte List for SW-846 Method 8260B

The MCP analyte list for SW-846 Method 8260B presented in Table II A-2 is intended to be protective of human health and the environment. The list is comprised of potential contaminants that are readily-analyzable by SW-846 Method 8260B using conventional purge-and-trap sample introduction (SW-846 Method 5030 (ambient temperature)) for aqueous and closed-system purge-and-trap (SW-846 Method 5035A) for solid samples. Most of the compounded listed have a promulgated compound-specific or hydrocarbon range (e.g., C_9 – C_{10} aromatic hydrocarbons) MCP Method 1 Groundwater/Soil Standard as described in 310 CMR 40.0974 and 40.0975, respectively. The remaining volatile compounds that comprise the SW-846 Method 8260B Analyte List are designated "consensus contaminants". These volatile compounds do not have a promulgated MCP Method 1 Standards but do have MCP Reportable Concentrations (RCs) as described in 310 CMR 40.0360 and 40.1600 and published EPA Integrated Risk Information System (IRIS) toxicity values. Using available toxicity data for these "consensus contaminants", the Department has derived compound-specific MCP Method 2 Groundwater/Soil Standards as described in 310 CMR 40.0983 and 40.0984, respectively. An updated list of the Department-derived MCP Method 2 Standards may be found at the following URL:

http://www.mass.gov/dep/cleanup/laws/method2.htm

The MCP Method 1 Groundwater/Soil Standards used to characterize the risk of harm posed by oil or hazardous materials at a disposal site are described in 310 CMR 40.0974(2), Table 1. This list of groundwater/soil standards, developed by the Department, takes into account a defined set of conservative potential exposure pathways likely to be encountered at most disposal sites. Method 1 Standards have been developed by the Department for over one hundred organic and inorganic contaminants that are commonly encountered at disposal sites. The MCP Method 1 Groundwater/Soil Standards list is periodically reviewed and updated by the Department. When compounds are added to the MCP Method 1 Groundwater/Soil Standards list that are suitable for analysis by SW-846 Method 8260B, the analyte list for this method will be updated accordingly.

MCP Method 2 Groundwater/Soil Standards are developed by the Department (or others) for contaminants of concern for which MCP Method 1 Standards have not been promulgated. The use of Department-developed MCP Method 2 Standards is discretionary. Alternatively, site-specific MCP Method 2 Standards may be developed or a Method 3 risk characterization, as described in 310 CMR 40.0990, may be conducted to evaluate or characterize the risk of harm posed by oil or hazardous materials at a disposal site.

1.6.1 Analysis of 1,4-Dioxane by SW-846 Method 8260B

1,4-Dioxane is included on the analyte list of SW-846 Method 8260B. The analytical sensitivity (i.e., reporting limit) for this compound (200 – 500 µg/L in water) is not adequate to evaluate compliance with some MCP regulatory limits if conventional (ambient temperature) purge-and-trap sample introduction is utilized. Either a heated ($80 \pm 5\ ^{o}$ C) purge-and-trap technique (may require Selective Ion Monitoring) or pre-concentration with Azeotropic Distillation (SW-846 Method 5031) may be employed to satisfactorily evaluate compliance with regulatory limits for this compound. One of these approaches may also be required for other poor purging volatile organic compounds identified in Table II A-2.

If 1,4-Dioxane is **not** a contaminant of concern for the site, conventional purge-and-trap sample introduction (ambient temperature) may be used for sample analysis. Under these circumstances, it is not necessary for the laboratory to meet the performance standards presented in Table II A-1 or the reporting limits indicated on Table II A-2 for this compound. However, the concentration and reporting limit for 1,4-Dioxane must still be reported, along with that for the other VOCs.

1.6.2 Additional Reporting Requirements for SW-846 Method 8260B

While it is not necessary to request and report all the SW-846 Method 8260B analytes listed in Table II A-2 to obtain Presumptive Certainty status, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous materials. These assessment activities may include but are not limited to:

- ✓ Immediate Response Actions (IRAs) performed in accordance with 310 CMR 40.0410;
- ✓ Initial Site Investigation Activities performed in accordance with 310 CMR 40.0405(1);
- ✓ Phase I Initial Site Investigation Activities performed in accordance with 310 CMR 40.0480 through 40.0483; and
- ✓ Phase II Comprehensive Site Investigation Activities performed in accordance with 310 CMR 40.0830

In a limited number of cases, the use of the full analyte list for a chosen analytical method may not be necessary, with respect to data representativeness concerns, including:

- ✓ Uncharacterized sites where substantial site/use history information is available to rule-out all but a limited number of contaminants of concern, and where use of the full analyte list would significantly increase investigative costs; or
- ✓ Well-characterized sites where initial full-analyte list testing efforts have sufficiently narrowed the list of contaminants of concern.

Note that a desire to avoid detection and quantitation of a contaminant that is present or likely present at a site above background levels is <u>not</u> a valid reason to limit an analyte list, and that such an action could constitute a criminal violation of MGL c. 21E.

In cases where a truncated list of method analytes is selected, laboratories must still employ the method-specific quality control requirements and performance standards associated with the requested analytes list to obtain Presumptive Certainty status.

The Reporting Limit (based on the concentration of the lowest calibration standard) for each contaminant of concern must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, RfDs, benchmark values, background, etc.) <u>with the exceptions footnoted in Table II A-2</u>. Meeting “MCP program” reporting limits may require analytical modifications, such as increased sampling weight or volume

or the use of selective ion monitoring, to increase sensitivity. All such modifications must be described in the Environmental Laboratory case narrative.

Analyte	CASN	MCP CLEANUP STANDARDS	
		GW-1 [a]	S-1/GW-1
		µg/L (ppb)	µg/g (ppm)
Table II A-2 (Page 1 of 3)			
Acetone [PP]	67641	3000	3
Amyl Methyl Ether (TAME), *tert-* [OXY]	994058	X[1]	X[1]
Benzene	71432	5	10
Bromobenzene	108861	X[1]	X[1]
Bromochloromethane	74975	X[1]	X[1]
Bromodichloromethane	75274	5	0.1
Bromoform	75252	5	0.1
Bromomethane [SX]	74839	2[2] (GW-2)	3 (S-1/GW-2)
Butylbenzene, sec-	135988	200[3]	100[3]
Butylbenzene	104518	200[3]	100[3]
Butylbenzene, *tert-*	98066	200[3]	100[3]
Carbon Disulfide	75150	X[1]	X[1]
Carbon Tetrachloride	56235	5	1
Chlorobenzene	108907	100	8
Chlorodibromomethane	124481	5	0.09
Chloroethane [SX]	75003	X[1]	X[1]
Chloroform	67663	5	0.1
Chloromethane [SX]	74873	X[1]	X[1]
Chlorotoluene, 2-	95498	X[1]	X[1]
Chlorotoluene, 4-	106434	X[1]	X[1]
Dibromo-3-chloropropane [PP]	96128	X[1]	X[1]
Dibromoethane, 1,2- (EDB)	106934	0.02[2]	0.005
Dibromomethane	74953	X[1]	X[1]
Dichlorobenzene, 1,3- (m-DCB)	541731	600	100
Dichlorobenzene, 1,2- (o-DCB)	95501	600	100
Dichlorobenzene, 1,4- (p-DCB)	106467	5	2
Dichlorodifluoromethane (Freon 12) [SX]	75718	X[1]	X[1]
Dichloroethane, 1,1-	75343	70	3

Analyte	CASN	MCP CLEANUP STANDARDS	
		GW-1 [a]	S-1/GW-1
		µg/L (ppb)	µg/g (ppm)
Table II A-2 (Page 2 of 3)			
Dichloroethane, 1,2-	107062	5	0.05
Dichloroethylene, 1,1-	75354	1[2] (GW-2)	0.1 (S-1/GW-2)
Dichloroethylene, *cis*-	156592	70	2
Dichloroethylene, *trans*-	156605	100	4
Dichloropropane, 1,2-	78875	5	0.1
Dichloropropane, 1,3-	142289	X[1]	X[1]
Dichloropropane, 2,2-	594207	X[1]	X[1]
Dichloropropene, 1,1-	563586	X[1]	X[1]
Dichloropropene, *cis*-1,3-[4 SX,]	10061015	0.5[2]	0.01
Dichloropropene, trans-1,3- [SX, 4]	10061026	0.5[2]	0.01
Diethyl Ether	60297	X[1]	X[1]
Diisopropyl Ether (DIPE) [OXY]	108203	X[1]	X[1]
Dioxane, 1,4- [PP,]	123911	50[2]	0.05[2]
Ethyl Tertiary Butyl Ether (ETBE) [OXY]	637923	X[1]	X[1]
Ethylbenzene	100414	700	80
Hexachlorobutadiene	87683	0.6	3
Hexanone (MNBK), 2- [PP, SX]	591786	X[1]	X[1]
Isopropylbenzene (Cumene)	98828	200[3]	100[3]
Isopropyltoluene, p-	99876	200[3]	100[3]
Methyl Ethyl Ketone (MEK) [PP, SX]	78933	350	0.3
Methyl Isobutyl Ketone (MIBK) [PP]	108101	350	0.5
Methyl Tertiary Butyl Ether (MTBE)	1634044	70	0.3
Methylene Chloride	75092	5	0.1
Naphthalene	91203	20	4
Propylbenzene, n-	103651	200[3]	100[3]
Styrene [SX]	100425	100	2
Tetrachloroethane, 1,1,1,2-	630206	5	0.4
Tetrachloroethane, 1,1,2,2-	79345	2	0.02

Analyte	CASN	MCP CLEANUP STANDARDS	
		GW-1 [a]	S-1/GW-1
		µg/L (ppb)	µg/g (ppm)
Table II A-2 (Page 3 of 3)			
Tetrachloroethylene	127184	5	0.5
Tetrahydrofuran (THF)	109999	X[1]	X[1]
Toluene	108883	1000	90
Trichlorobenzene, 1,2,4-	120821	70	100
Trichlorobenzene, 1,2,3-	87616	X[1]	X[1]
Trichloroethane, 1,1,1-	71556	200	30
Trichloroethane, 1,1,2-	79005	5	0.3
Trichloroethylene (TCE)	79016	5	0.4
Trichlorofluoromethane (Freon 11) [SX]	75694	X[1]	X[1]
Trichloropropane, 1,2,3- [SX]	96184	X[1]	X[1]
Trimethylbenzene, 1,2,4-	95636	200[3]	100[3]
Trimethylbenzene, 1,3,5-	108678	200[3]	100[3]
Vinyl Chloride [SX]	75014	2	0.3
Xylene, o-[5]	95476	10,000	500
Xylene, m-[5]	108383	10,000	500
Xylene, p-[5]	106423	10,000	500

PP – Poor purging efficiency resulting in high estimated quantitation limits (EQLs), as described in SW-846 Method 8260B, Section 1.1. May not meet some CAM- QC performance standards for this Method.

SX - compounds are potentially unstable and susceptible to acid hydrolysis, abiotic degradation and/or loss during storage

OXY - Oxygenate: gasoline additives, indicators of historical gasoline releases.

a. MCP GW-1 Standard unless otherwise specified

1 Department-Developed MCP Method 2 Standard. Use of these Standards is discretionary. See URL: http://www.mass.gov/dep/cleanup/laws/method2.htm.

2 Standard reporting limit for this compound may not be able to achieve regulatory compliance limit

3 Standard for sum of the C_9 – C_{10} Aromatics encountered in sample. If standard exceeded, it may be prudent to conduct an independent VPH analysis (MADEP-VPH-98-1).

4 Regulated as 1,3-Dichloropropene, Mixed Isomers (CAS Number: 542756). Report as the additive sum of the concentrations of *cis*-1,3-Dichloropropene and *trans*-1,3-Dichloropropene

5 Regulated as Xylenes (Mixed Isomers). Report as Total Xylenes or as individual Xylene isomers, if separated chromatographically.

2.0 Data Usability Assessment for SW-846 Method 8260B

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for SW-846 Method 8260B which may be used to directly assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document.

3.0 Reporting Requirements for SW-846 Method 8260B

3.1 General Reporting Requirements for SW-846 Method 8260B

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM VII A, Section 2.4. This guidance document provides recommendations for field QC, as well as the required content of the Environmental Laboratory Report, including:

- Laboratory identification information presented in WSC-CAM-VII A, Section 2.4.1,
- Analytical results and supporting information in WSC-CAM-VII A, Section 2.4.2,
- Sample- and batch-specific QC information in WSC-CAM-VII A, Section 2.4.3,
- Laboratory Report Certification Statement in WSC-CAM-VII A, Section 2.4.4,
- Copy of the Analytical Report Certification Form in WSC-CAM-VII A, Exhibit VII A-1,
- Environmental Laboratory Environmental Laboratory case narrative contents in WSC-CAM-VII A, Section 2.4.5,
- Chain of Custody Form requirements in WSC-CAM-VII A, Section 2.4.6

3.2 Specific Reporting Requirements for SW-846 Method 8260B

Specific Quality Control Requirements and Performance Standards for SW-846 Method 8260B are presented in Table II A-1. Specific reporting requirements for SW-846 Method 8260B are summarized below in Table II A-3 as “Required Analytical Deliverables (**YES**)”. These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as “Required Analytical Deliverables (**NO**)”, these data are to be available for review during an audit and may also be requested on a client-specific basis.

3.2.1 Data Correction for VOC Concentration Calculations for Methanol Preservation Dilution Effect

Based on the requirements of SW-846 Method 8000C, Section 11.10.05, VOC analytical results for soil/sediment samples must be corrected for the Methanol Preservation Dilution Effect. The potential for under reporting volatile organic concentrations is more pronounced as the “as-received” % moisture content of the soil/sediment sample increases, if this correction is neglected.

VOC concentrations and the recovery of matrix spikes and/or surrogates in solid samples preserved with methanol are subject to a systematic negative bias if the potential increase of the total solvent volume during the methanol extraction process is not considered. This increase in extraction solvent volume is a direct result of the solubility of the entrained sample moisture (water) in the methanol. The total solvent volume is the additive sum of the volume of methanol and the entrained sample moisture that partitions into the methanol during extraction. The volume of water partitioned is estimated from the % moisture determination (and the assumption that 1 g of water occupies a volume of 1 mL). This is a conservative correction regarding calculated VOC concentrations because some fraction of the sample's % moisture may not partition into the methanol, due to various physiochemical binding forces. The total solvent/water volume (Vt) is calculated using the following equation:

$$\text{mL solvent/water (Vt)} = \text{mL of methanol} + ((\%\ \text{moisture}/100) \times \text{g of sample})$$

This "corrected" Vt value should be substituted directly for the Vt value in the equation shown in SW-846 Method 8000. Section 7.10.1.2. It should be noted that whether corrected or uncorrected, the Vt value used to calculate VOC concentrations must also take into consideration the volume of any surrogate/spiking solution added to soil/sediment samples

3.2.2 Sample Dilution

Under circumstances that sample dilution is required because either the concentration of one or more of the target analytes exceed the concentration of their respective highest calibration standard or any non-target peak exceeds the dynamic range of the detector (i.e., "off scale"), the Reporting Limit (RL) for each VOA target analyte must be adjusted (increased) in direct proportion to the Dilution Factor (DF). Where:

$$DF = \frac{\text{Sample Aliquot Volume (mL)} + \text{Diluent Volume (mL)}}{\text{Sample Aliquot Volume (mL)}}$$

And the revised RL for the diluted sample, RL_d:

$$RL_d = DF \times \text{Lowest Calibration Standard for Target Analyte}$$

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy "MCP program" reporting limits in some cases if the RL_d is greater than the applicable MCP standard or criterion to which the concentration is being compared. Such increases in RLs are the unavoidable but acceptable consequence of sample dilution that enable quantification of target analytes which exceed the calibration range. All dilutions must be fully documented in the Environmental Laboratory case narrative.

Analytical Note: Over dilution is an unacceptable laboratory practice. The post-dilution concentration of the highest concentration target analyte must be at least 60 to 80% of its highest calibration standard. This will avoid unnecessarily high reporting limits for other target analytes which did not require dilution.

If a sample analysis results in a saturated detector response for any target or non-target compound, the analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank demonstrates the lack of system interferences.

Soil and sediment results must be reported on a dry-weight basis. Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

Table II A-3 Routine Reporting Requirements for SW-846 Method 8260B

Parameter	Required Analytical Deliverable
GC/MS Tunes	***NO***
Initial Calibration	***NO***
Continuing Calibration (CCAL)	***NO***
Method (Preparation) Blank	***YES***
Laboratory Control Spikes (LCSs)	***YES***
LCS Duplicates	***YES***
Field Matrix Spike (MS)	***YES (if requested field MS)***
Field Matrix Spike Duplicate (MSD)	***YES (if requested field MSD)***
Field Matrix Duplicate (MD)	***YES (if requested field MD***
Surrogates	***YES***
Internal Standards (ISs)	***NO***
Tentatively Identified Compounds (TICs)	***YES (if requested by LSP)***
Identification and Quantification	***NO***
General Reporting Issues	***YES***

3.3 Tentatively Identified Compounds (TICs) by GC/MS

The evaluation of Tentatively Identified Compounds (TICs) in conjunction with GC/MS analyses (SW-846 Methods 8260B and 8270C) is a powerful and cost-effective analytical tool that can be utilized by the LSP to support MCP 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 in support of MCP decision-making, an analysis of TICs is:

Always expected when drinking water samples are analyzed,
Not usually expected at petroleum-only sites,
Not usually expected when the contaminants of concern have been previously identified,
Not usually expected when used to determine the extent and magnitude of contamination associated with a "known" release of OHM, and/or
Should be considered, at the discretion of the LSP, in support of site characterization activities for releases at locations with complex and/or uncertain history

It should be noted that TICs only need to be evaluated by the laboratory when specifically requested by the LSP.

3.3.1 Reporting of Tentatively Identified Compounds (TICs)

If evaluated, all TICs that meet the chromatographic criteria presented in Section 1.0 of Appendix II A-2 must be reported by the laboratory either in the Environmental Laboratory Report or in the Environmental Laboratory case narrative. In turn, the LSP must include a discussion regarding the disposition of all reported TICs as part of the MCP submission. Depending on specific site circumstances (e.g., a potentially toxic contaminant is found in a private drinking water supply well, etc.), resampling/re-analysis with analyte-specific calibration and quality control may be required to definitively assess the risk posed by the TIC to human health and the environment. Guidance for the evaluation of TICs for MCP decision-making is presented in Appendix II A-2 of this document.

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for volatile organic compounds analyzed in support of MCP decision-making are summarized below and presented in Appendix VII-A of WSC-WSC-CAM–VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data Conducted in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)". The selection of preservation for samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

Aqueous Samples

Matrix	Analyte	Container [1]	Preservative [2]	Holding Time
Aqueous Samples, with no Residual Chlorine	Most Volatile Organic Compounds	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	Adjust pH to < 2.0 by addition of HCl or $NaHSO_4$. to container before sampling. **Cool 4 ± 2^{O} C.**	14 days
	MTBE or other fuel oxygenates *only* **with heated purge-and-trap sample introduction**	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	0.7 g of trisodium phosphate dodecahydrate (TSP) per 40 ml. **Verify pH > 11.0. Cool 4 ± 2^{O} C.**[3]	14 days
	Reactive[4] volatile organics susceptible to acid hydrolysis, abiotic degradation or loss during storage	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	**Cool 4± 2^{O} C.**	Analyze ASAP but not more 7 days [5,6]
Aqueous, with Residual Chlorine	Presence of chlorine residual is usually associated with drinking water samples. Collect sample in at least two (2) x 40-mL VOC vials w/ Teflon-lined septa screw caps ***containing*** either 25 mg of Ascorbic A cid or 3 mg of Sodium Thiosulfate. **If Residual Chlorine > 5 mg/L additional dechlorination agent may be required** After dechlorination is confirmed, preserve as above based on compound classes			

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 Preservation of samples by acidification to pH < 2.0 and analysis within 14 days is considered a suitable preservation technique for samples not expected to contain reactive contaminants of concern.

3 TSP may also be used to preserve samples for BTEX and/or VPH analysis (i.e., it would not be necessary to obtain samples in separate vials).

4 While there are chemicals that are described as *potentially* reactive on the list of Target Analytes (see Table II A-2), at this time DEP does not consider any chemicals on this list to be "reactive" and requiring special preservation and/or hold times.

5. Every reasonable effort should be made to analyze reactive samples as soon as possible (the goal should be 24 hours or sooner) after the time of collection. In all cases the holding time for reactive samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

6. In the unusual circumstance that contaminants of concern at a disposal site require mutually exclusive preservation techniques (e.g., acid preservation/with cooling for BTEX and no acid preservation/cooling-only for reactive compounds) separate sampling containers to accommodate the different preservation techniques may be required. The selection of preservation technique for samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

Soil, Sediment and Waste Samples

Matrix	Container [a]	Preservation[1,2]	Holding Time[3]
Soil/Sediment Samples ***High-Level Analysis***	Extrude 5 grams of sample directly into a pre-weighed vial* w/ Teflon-lined septa screw caps: Vials must contain 1 mL purge-and-trap grade methanol for every g soil/sediment. *(1) x 60-mL vial or (1) x 40-mL vial	Cool to 4 ± 2° C; protect from light	14 days Up to 1 year for samples frozen within 24 hours of collection
	5 g EnCore samplers[4] or other suitable coring device	Cool to 4 ± 2° C in field and deliver to laboratory within 48 hours of collection for freezing (< -7° C) or methanol preservation.	
Soil/Sediment Samples ***Low-Level Analysis*** by Closed-System Purge-and-Trap Process (SW-846 Method 3035A)	5 g EnCore samplers[4] or other suitable coring device.	Cool to 4 ± 2° C in field and deliver to laboratory for freezing (< -7° C) or analysis within 48 hours of sample collection (see Note 1). Alternatively, samples may be frozen to < -7° C in the field using gel packs	14 days Up to 1 year for samples frozen within 24 hours of collection
	Extrude 5 grams of sample directly into (2) x pre-weighed 40 ml VOC vials containing 5 mL of reagent water (with or without chemical preservation; see Note 1) and a Teflon-coated magnetic stir bar[5].	Cool to 4 ± 2° C in field and deliver to laboratory for freezing (< -7° C) or analysis within 48 hours of sample collection. Alternatively, samples may be frozen to < -7° C in the field using gel packs	
Waste Samples	Collect sample in one (1) x 500 mL amber wide mouth jar with a teflon lined screw cap.	No special preservation required	14 days

a. 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. Caution: samples to be frozen should not be stored vertically. These samples must be stored horizontally or at least at a 45 degree angle to avoid breakage from expansion.

1. For biologically active soils, immediate chemical or freezing preservation is necessary due to the rapid loss of BTEX compounds within the first 48 hours after sample collection.

2 A number of acceptable alternative preservation techniques requiring close communication with the receiving laboratory that require field cooling (4 ± 2°) with subsequent laboratory preservation (freezing, methanol, $NaHSO_4$, etc.) and/or expedited analysis (48 hours) are presented in Appendix A, "Collection and Preservation* of Aqueous and Solid Samples for Volatile Organic Compounds (VOC) Analyses" of the document entitled , "Closed System Purge-and-Trap and Extraction for Volatile Organics In Soil and Waste Systems", an updated version of SW-846 Method 5035A published by US EPA In July 2002. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/5035a_r1.pdf

3 Holding time is calculated from the time of sample collection and only applies to samples that have been frozen and chemically preserved.

4. EnCore Sampler may not be suitable for certain soil types; refer to guidance in SW-846 Method 5035A

5. Not required if Closed-System Purge-and Trap device employs a means of stirring the sample other than a magnetic stirrer

Additional Sample Handling and Preservation Notes:

Aqueous Samples:

1. The most common preservation technique for aqueous samples analyzed for volatile organic compounds is the addition of HCl to the container before sampling (pH to < 2.0) and cooling to 4 + 2^{O} C. As indicated in the table above, some classes of analytes (reactive, MTBE and other fuel oxygenates if heated purge and trap is used for analysis, etc.) may require alternative preservation techniques because of their reactivity or volatility. In the unusual circumstance that contaminants of concern at a disposal site require mutually exclusive preservation techniques (acid preservation/with cooling for BTEX and no acid preservation/with cooling for reactive compounds) separate sampling containers to accommodate the different preservation techniques may be required. In all cases the selection of preservation technique for samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

2. If effervescence occurs upon addition of HCl, samples should be collected without the acid preservative. In these instances, the analysis holding time is seven (7) days from date collected to date analyzed.

Low-Level and High-Level Solid Samples:

An extra aliquot of sample must be collected in a 4 oz. glass jar with no preservative so that the laboratory can perform a percent solids analysis. If the same sample is being submitted to the laboratory for additional analyses which require no preservative, the percent solids analysis can be measured using an aliquot from these bottles. Otherwise, a separate bottle will be needed.

Sample Preparation Prior to Analysis

The sample must be allowed to warm to room temperature. Surrogates, internal standards, and 5 mLs of water are added to the sample vial through the septum seal, and the sample is analyzed on the closed system purge and trap.

The appropriate surrogates must be immediately added to the sample through the septum seal. The sample must be allowed to warm to room temperature. All samples must be shaken for 2 minutes prior to analysis. A 100 microliter (uL) aliquot of the methanol extract must then be removed and injected into 5 mL of purge water and the internal standards added to the 5 mL of purge water.

A logic diagram for the Evaluation of Tentatively Identified Compounds (TICs) for SW-846 Method 8260B Under the MCP is presented in Exhibit II A –2. This exhibit graphically presents a systematic approach to evaluate tentatively identified compounds based on chromatographic, mass spectral, and toxic spectral characteristics criteria.

1.0 Chromatographic Criteria

- Initially include all of the non-target compounds that have a peak area count of $\geq$ 10% of the nearest internal standard.

1.1 Mass Spectral Criteria

- All spectra must be evaluated by a qualified mass spectrometrist.
- The spectral library match must be $\geq$ 85% for a tentative identification to be made.
- The major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within $\pm$ 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or for the presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks.
- 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).
- 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 Environmental Laboratory case narrative to support any “unknown” classification.

- TICs, which are identified as petroleum aliphatic hydrocarbons, do not have to be reported as TICs. However, there must be a statement in the Environmental Laboratory case narrative discussing the presence of these hydrocarbons in the sample(s).

- After the above criteria are met, the top ten (10) compounds, chosen by comparing the area of the TIC to the area of the nearest internal standard, must be tentatively identified, quantitated, and reported.

2.0 Toxic Spectral Characteristics Criteria

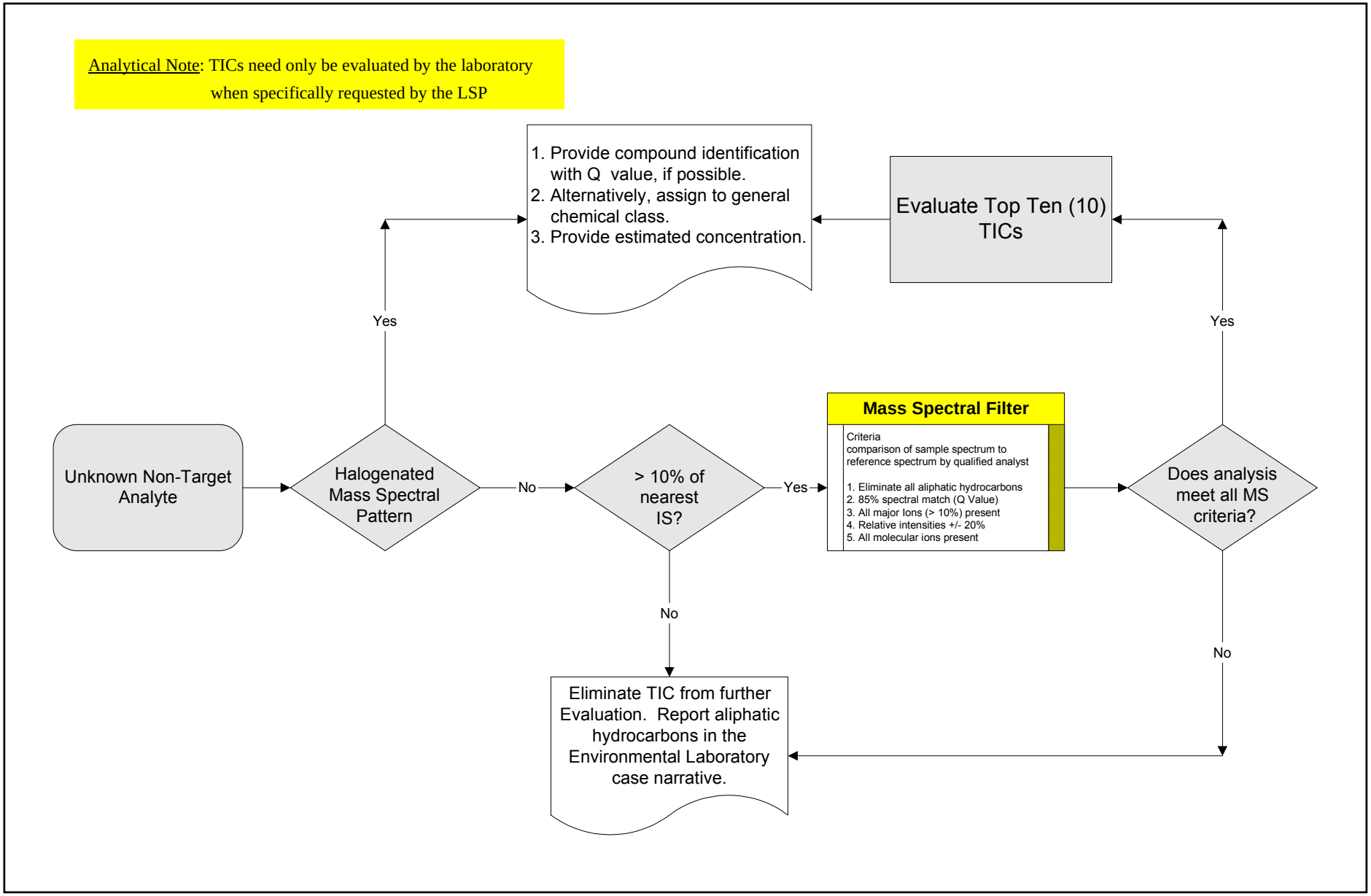
Regardless of the peak area count in relation to the nearest internal standard, the laboratory must evaluate the spectra for any compound if the mass spectrum:

- Exhibits a characteristic chlorine or bromine spectral pattern

3.0 Reporting Criteria

All TICs 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 as discussed in Section 3.3.1. This reporting requirement may be fulfilled by discussion in the Environmental Laboratory case narrative, by using a “J” flag designation, or by some other laboratory reporting convention to qualify the sample results. General environmental laboratory reporting recommendations are presented in WSC-CAM–VII A, Section 2.3.

If an LSP determines that the presence of the TIC at the estimated concentration reported by the laboratory may appreciably increase the overall risk posed by the site or the utility/cost of the potential remedial measures under consideration, additional analytical work is recommended to verify the identification and/or concentration of the reported TIC either by reanalysis or resampling. This contingency will require additional coordination and communication between the laboratory and the LSP.


Analytical Note: TICs need only be evaluated by the laboratory when specifically requested by the LSP
1. Provide compound identification with Q value, if possible.
2. Alternatively, assign to general chemical class.
3. Provide estimated concentration.
Evaluate Top Ten (10) TICs
Yes
Yes
Unknown Non-Target Analyte
Halogenated Mass Spectral Pattern
No
> 10% of nearest IS?
Yes
Mass Spectral Filter
Criteria
comparison of sample spectrum to reference spectrum by qualified analyst
1. Eliminate all aliphatic hydrocarbons
2. 85% spectral match (Q Value)
3. All major Ions (> 10%) present
4. Relative intensities +/- 20%
5. All molecular ions present
Does analysis meet all MS criteria?
No
No
Eliminate TIC from further Evaluation. Report aliphatic hydrocarbons in the Environmental Laboratory case narrative.