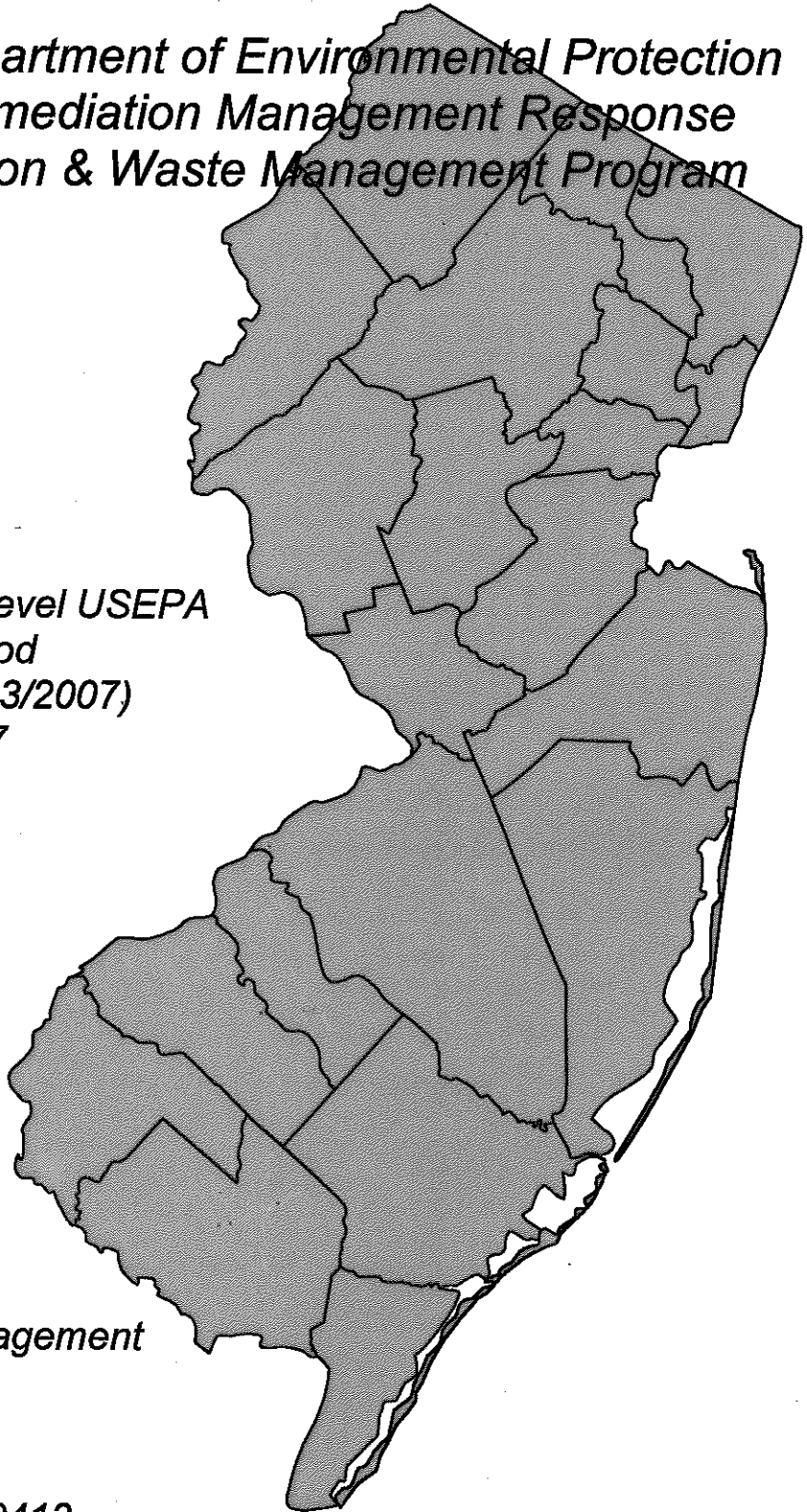


***New Jersey Department of Environmental Protection  
Division of Remediation Management Response  
Site Remediation & Waste Management Program***

***NJDEP- SRWM Low Level USEPA  
TO-15 Method  
(NJDEP-LLTO-15-3/2007)  
March 2007***



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## **A. Purpose**

NJDEP has developed the low level method to address the needs of the various programs of the department. This new method provides for a lower reporting limit and additional quality control requirements as compared to those found in USEPA Method TO-15 "The Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry January 1999".

This Method entitled "NJDEP-SRWM Low Level USEPA Method TO-15 March 2007 (NJDEP-LLTO-15- 3/2007)" requires the laboratory to follow the requirements of USEPA Method TO-15 with the incorporation of the NJDEP modifications listed below. If there is a difference between the USEPA method and the NJDEP requirements, the NJDEP requirements override the method requirements. The method that is being modified by NJDEP is USEPA Method TO-15 "The Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/ Mass Spectrometry".

## **B. NJDEP Modifications**

The modifications to the method include the following:

- Holding times
- Canister types and regulators
- Method detection limits
- Reporting limits
- Clean canister certification levels
- GC/MS tuning and instrument performance check requirements
- GC/MS techniques
- Standard type and concentrations
- Initial and continuing calibration standards
- Laboratory control samples
- Limitation regarding the source of make up air

## **C. Certification Offered**

This Certification is offered by the New Jersey Environmental Laboratory Certification Program (NJ-ELCP) and the National Environmental Laboratory Accreditation Program (NJ-NELAP). The Laboratory's Standard Operating Procedures must specify all operation details of the method. Proprietary statements are not acceptable.

## **D. Analytical Data Package Requirements**

Part of the initial certification requirement of this method is the ability of the Laboratory to submit a compliant analytical data package that can be validated by the NJDEP-SRWM Program. Certification for this method will only be granted to Laboratories who can submit a compliant data package as part of their application for certification.

If after certification has been granted and if laboratory is found to be routinely unable to properly submit a compliant data package, the laboratory may be fined, subject to loss of certification and/or found "ineligible to report data to the NJDEP" Data package requirements are found in

Appendix 1 of this method. The requirements include both hardcopy deliverables and electronic deliverables.

NJDEP-SRWM Program will post any changes required for the deliverable as needed.

#### **E. One Laboratory Requirement for all Analyses**

All analyses required by this method, (which include the clean canister certification and the analysis of the environmental sample collected in the canister) must be conducted by the same laboratory. It is not acceptable under this method to have one laboratory certify the canisters clean and a second laboratory conduct the analysis of the environmental samples.

#### **F. Required Holding Times**

##### **1. Limitations on the Number of Days Canisters can be out of the Laboratory**

All canisters after evacuation to negative thirty (-30) inches of mercury have a finite period before the level of the vacuum pressure loss that occurs naturally will inhibit the use of the canister in sample collection. Due to the loss of vacuum that occurs naturally during the storage of canisters, NJDEP is establishing a fifteen (15) day time limit that canisters can be out of the laboratory. The fifteen-day time limit begins with the shipment of the canisters to the client. The canisters must be returned to the laboratory after 15 days whether they were used for sample collection or not.

##### **2. Samples collected in stainless steel canisters must be analyzed within thirty (30) days of sample collection.**

#### **G. Temperature Requirements for Sample Shipment**

This method does not have temperature requirements for shipment as stainless steel canisters are used for sample collection.

#### **H. Chain of Custody Requirements**

##### **1. Preparation of Canisters**

Chain of Custody commences with the preparation of the canisters at the laboratory for shipment to the client. The laboratory's sample custodian shall initiate the chain of custody on the forms and then transfer the canister and regulators under legal strict chain of custody to the client. The forms used by the laboratory must contain the same information as the forms used by NJDEP. Copies of the forms are provided in Appendix I and II of this method. The laboratory providing empty shipping containers to any client must seal the shipping containers with custody seals.

## 2. Laboratory's Client Responsibility

Upon receipt of the canisters from the laboratory, the client shall open the shipping containers to determine if the correct number of canisters and regulators were received from the laboratory.

The client shall document the condition of the shipping containers and its contents. The client must record the appropriate information on the chain of custody document for each sampling point as well as the Field Test Data Sheets (Appendix III). After sample collection, the client then ships the samples back to the laboratory where an authorized representative from the laboratory accepts custody and annotates with a signature on each chain of custody document.

## 3. NJDEP TO-15 Field Test Data Sheets

The NJDEP TO-15 Field Test Data Sheet (FTDS), as provided in Appendix 1 of this method, must be completed for each canister used in the sampling events. All information must be completed on the FTDS for each canister. This form is required whether the sample is analyzed at a fixed (offsite) laboratory or a mobile laboratory. The FTDS is initiated by the laboratory and accompanies the canisters to and from the field. The laboratory shall fill out the Canister Seal Number at the top of the form in the General Information Section, the Batch Certification Number or File Number (as applicable) and the Date Shipped at the bottom section of the form in the Laboratory Information. The FTDS shall be included in the analytical data package prepared by the laboratory. The FTDS must be located immediately behind the case narrative of the data package and prior to any sample data.

Alternately, laboratories can integrate the FTDS with the External Chain of Custody Form (Appendix 1). The approval for the integration of the two forms must be obtained from the Office of Data Quality, Division of Remediation Management and Response. Upon approval from the Office of Data Quality, the integrated Chain of Custody/FTDS shall be approved as part of the Laboratory's Standard Operating Procedures.

## 4. Internal Chain of Custody Documentation

Internal chain of custody procedures and the associated documentation are required for this method. The laboratory has responsibility for storage and internal distribution of the canisters. A copy of the NJDEP Internal Chain of Custody Form is provided in Appendix I. Each time responsibility for the canister changes from one individual to another, the laboratory shall record the changes on the laboratory's own internal chain of custody form and sign it. On completion of sample analysis, attach all chain of custody documents to the data report and forward to the client. The laboratory must ensure that chain of custody forms are maintained in the laboratory and the forms travel with the canisters throughout the laboratory. The form must bear the name of the person assuming responsibility of the samples and the date/time of transfer. The chain of custody is only acceptable if there is no lapse in the custody. Legible signatures are required on all documentation. The use of initials to document changes in sample custody is not acceptable.

5. Samples of the laboratory's internal and external chain of custody forms must be provided in the Standard Operating Procedures for review and approval of the method documentation by NJDEP.
6. The NJDEP Technical Requirements for Site Remediation NJAC 7:26E Technical Requirements for Site Remediation" N.J.A.C. 7:26 E Appendix A Section C which requires the Chain of Custody to remain with the samples at all times and bear the name of the person assuming responsibility of the samples and the date. Electronic Internal Chain of Custody documentation is not acceptable for this method.

## **I. Canister Flow Controllers and Regulator Requirements**

### **1. Canister Types**

- a. Four canister types shall be acceptable under this method. The canister sizes are 1-liter, 2.7-liter, 3.2 -liter and 6-liter passivated, leak free, stainless steel canisters. These canisters must be equipped with a laboratory-preset flow controller, pressure gauge, critical orifice, and stainless steel frit dust filter over the orifice, and specially prepared interior surfaces for the removal of active sites. The canisters must be equipped with sample inlets or sampling caps to prevent water droplets from accumulating at the edge of the tubing where they could be pulled into the sampling train. Hard seat metal valves are required for the shutoff valves on the canisters. Soft-seated valves are not acceptable.
- b. 6-Liter is the only canister size that is acceptable for the collection of indoor air samples and ambient samples.
- c. All four sizes of the canisters can be used for the collection of soil gas samples.
- d. Canisters are shipped to the clients at subatmospheric pressure approximating negative 30 inches of mercury.
- e. Tedlar bags cannot be used.

### **2. Flow Controller Flow Rate Requirements**

The flow controller flow rate for each type of canister is dependent on the sampling location. It shall be the laboratory's responsibility to preset the regulators for the sample collection periods specified by their clients and to clearly identify each canister's regulator preset sample collection time. The two options are as follows:

- a. *Building Interior Samples*  
Building interior sampling and the accompanying background sample usually occurs over an 8-hour or a 24-hour period.
- b. *Soil Gas Samples*  
The maximum flow rate for the collection of soil gas using a canister is 200 milliliters per minute. The laboratory shall preset the flow rate of the regulator to the required flow rate.

NOTE: A 6-liter canister with a preset flow rate of 200 milliliters per minute and a critical orifice of 0.0060 inches, and not drawing against backpressure constraints, will fill in approximately 30 minutes.

The 2.7-liter and 3.2-liter canisters with a preset flow rate of 200 milliliters per minute and a critical orifice of 0.0060 inches, and not drawing against backpressure constraints, will fill in approximately 15 minutes.

A 1-liter canister with a preset flow rate of 200 milliliters per minute and a critical orifice of 0.0060 inches, and not drawing against backpressure constraints, will fill in approximately 5 minutes.

*c. Landfill Gas Samples and Other Type of Samples*

A copy of the permit's analytical requirements should be submitted to the laboratory which will establish the baseline for the canister preparation.

A 6-liter canisters will usually be required because the volume collected is being analyzed by more than one method,(such as USEPA Methods 3C and 25C). Analysis for volatiles organics is routinely conducted first with the other methods. The permitting agency should specify the order of analysis.

NOTE: The laboratory must be made aware of the collection rates for landfill gas samples, treatment system sampling etc. that are established by a regulatory agency or in a permit issued by a regulatory agency. Flow Controllers and pressure gauges are routinely required to be supplied for these types of samples. Laboratory supplied pressure gauges are routinely used to report the pressure of the canister prior to sample initiation and after the samples are collected. Critical orifices of 0.0060 inches can also be specified.

Most agencies required a 6-liter canisters because the volume collected is being analyzed by more than one method,(such as USEPA Methods 3C and 25C) with the volatiles organics being analyzed first followed by other methods.

**J. Pressure and Temperature Specifications**

In preparing the canisters for sample collection, the laboratory sets the flow rate of the regulators based on the barometric (atmospheric) pressure and temperature inside the laboratory in order to meet the client's needs. The laboratory must record the actual temperature and barometric (atmospheric) pressure of the room at the time the canisters (with the regulators) are prepared for shipment. Canister pressure for shipment from the laboratory must be set at negative 30 inches of mercury.

**K. Pressure of Canisters**

1. Laboratories must check and record pressure of all canisters prior to shipping and upon return receipt. This negative pressure information must be recorded in a laboratory notebook and reported in the data package. The use of "<" or ">" from the standard pressure of 30 inches is not acceptable; the actual numeric reading is required.

2. Only humidified ultra pure zero air shall be used as the source of air that is added to a canister for pressure adjustment. It must be from the same source as the method blank air. The humidified ultra pure zero air that is added to a canister for pressure adjustment is considered a dilution. The NJDEP Reporting Limits must be adjusted for the dilution. The NJDEP Reporting Limits requirements for this method cannot be met if makeup air is added to the canister.
3. The laboratory should make every attempt to analyze the canisters without the addition of make up air. The laboratory must be aware that automatically adding makeup air to canisters does cause a dilution that **must** be taken into account in the determination of the Reporting Limit used by the laboratory. Adjustment of the total sample volume injected on the column to adjust for the addition of makeup air is not acceptable. The volume injected on the column shall not be varied from the initial calibration. The addition of makeup air to canisters may raise the reporting limit used for that individual sample above the acceptable NJDEP Reporting Limits. All non-detected results must be at the NJDEP established Reporting Limit for a sample unless there is a concentration for a particular compound above 40 ppbv that causes a dilution. There are exceptions for the m & p-xylene isomer mixture, isopropanol and ethanol. See Table 2 for the NJDEP Reporting Limits. The laboratory is referred to the Sample Dilution Section for additional information on the specific requirements.
4. The laboratory SOP must clearly describe how the pressure of the canister is determined and how the amount of makeup air to be added to canisters is determined.

**L. Sample Delivery Group**

1. A Sample Delivery Group (SDG) is a unit of no greater than twenty (20) canisters collected at a particular site. The SDG assignment is made upon receipt of the samples at the laboratory's facility. If less than twenty (20) samples are submitted for a particular site, it is considered a single SDG. If more than twenty samples are submitted from a particular site, then the laboratory is required to split those samples into separate SDGs of 20 or less and analyze each SDG with the appropriate number of QC samples.
2. A SDG is a group of 20 or fewer samples received over a period of up to seven (7) calendar days. Data from all samples in a Sample Delivery Group are due concurrently.
3. Laboratory Control Samples, method blanks and instrument blanks (if applicable) are considered QC samples and are not included in the sample count for a SDG.
4. The SDG assignment made by the laboratory may not be related to the analytical sequence. The sample delivery group assignment is strictly used to track the movement of the samples in the laboratory, for defining and the production of the analytical data package.



## **M. Analytical Sequence Requirements**

The laboratory is required to follow the sequence below in the analysis of the samples.

### **1. Initial Calibration Sequence**

GC/ MS Tuning and Instrument Performance Check  
Initial Calibration (minimum of five points)  
Initial Calibration Verification Sample Standard (*Second Source*)  
Method Blank  
Reporting Limit Laboratory Control Sample (*location in sequence optional see Section O.-11*)  
Samples  
Instrument blanks and other blanks (if applicable location optional)  
Closing Continuing Calibration Verification Standard (*within 24 hours of the injection of the GC/MS Tuning and Instrument Performance Check*)

### **2. Daily Calibration Sequence**

GC/ MS Tuning and Instrument Performance Check  
Daily Calibration Verification Standard  
Method Blank  
Reporting Limit Laboratory Control Sample (*location in sequence optional see Section O-11*)  
Samples  
Instrument blanks and other blanks (if applicable location optional)  
Closing Continuing Calibration Verification Standard (*within 24 hours of the injection of the GC/MS Tuning and Instrument Performance Check*)

## **N. General Analytical Standards Requirements**

1. The laboratory must use gas standards (not liquid standards) for any analysis conducted using the NJDEP-LLTO-15 method. Preparation of standard gases from neat liquid standards by the laboratory personnel is not acceptable. The laboratory must purchase commercially prepared gas standards from one of the standard suppliers.
2. The laboratory must use standard mixtures of target gases in high-pressure cylinders certified traceable to a NIST Standard Reference Materials (SRM) or NIST/EPA approved Certified Reference Material (CRM). The laboratory must certify in the case narrative of each data package that gas phase standards have been used. The laboratory must specify their suppliers in the Standard Operating Procedure submitted to the Office of Quality Assurance for certification. The laboratory must document in their Standard Operating Procedures how they handle the second source for standards and document it in the standards logbooks.
3. Original Certificates of Analysis (C of A) from the supplier for each lot must be maintained by the laboratory. Copies of specific lot C of A used in the analysis of the samples for a particular Sample Delivery Group must be included in the analytical data package.

4. The calibration standards and the Reporting Limit Laboratory Control Sample (RLLCS) standard can be from the same lot.
5. The tracer gas standards that are analyzable by this method (isopropanol and n-butane) must meet the same technical criteria compounds as other standards in this method. The tracer gas standards must be in the same cylinders as the target gases.
6. Humidified ultra- pure zero air is the required source for all makeup air, method blanks and instrument blanks.
7. Initial Check Verification Sample Standard
  - a. The Initial Check Verification Sample Standard shall be either from a different commercial supplier or from an independent lot from the same commercial supplier (different from the lot used for the Calibration Standards and the Laboratory Control Sample).
  - b. The standard must contain all the compounds of interest. Tracer gas standards must be included in this standard.
8. Instrument Performance Check Gas Standard
  - a. Bromofluorobenzene (BFB) is the required Instrument Performance Check Gas Standard.
  - b. A 50 ng standard is the required concentration.
  - c. BFB shall not be combined with any calibration standard to create a single mixture injection consisting of a calibration standard and the Instrument Performance Check Gas Standard.
9. Internal Standards
  - a. The required internal standards are bromochloromethane, chlorobenzene-d5 and 1,4-difluorobenzene.
  - b. The same internal standards must be added to all calibration standards, blanks, RLLCSs and samples.
  - c. The same concentration of internal standards must be used for all calibration standards, blanks, LCS and samples.
  - d. The required concentration of each of the internal standards is 10 ppbv.

## 10. Calibration Standard Requirements

### a. GC/MS Initial Calibration Requirements

The laboratory is required to conduct the initial calibration using a minimum of five (5) points for each calibration standard. The laboratory can use more than five calibration standards for any compound. For the majority of the compounds the calibration range must be from 0.20 ppbv to 40 ppbv.

- 1) The allowable exceptions to the 0.2 ppbv to 40 ppbv requirements are acetone, chloroethane, chloromethane, tertiary butyl alcohol, tetrahydrofuran and 1,4-dioxane. These compounds may not be amenable at the lower calibration levels, and the lowest calibration standard can be raised to a higher concentration. The upper calibration standard for these compounds remains the same and shall not exceed 40 ppbv.
- 2) Isopropanol and ethanol can be analyzed at the various concentrations chosen by the laboratory. The only requirement is that the lowest calibration standard be equal to 0.20 ppbv and the highest standard be less than or equal to 40 ppbv.
- 3) For the xylene isomers (m& p), the contribution of both isomers is considered equal in the calibration gas standard. To meet the required concentration of each isomer the calibration range for the mixture calibration range is from 0.40 ppb to 80 ppbv.
- 4) Tracer gas standards must be included in the initial calibration standard and must be at the same concentration as the other standards unless that tracer gas compounds is isopropanol then 2) above must be followed. If n-butane is used the laboratory must define the calibration range and have it approved by the New Jersey Environmental Laboratory Certification Program.
- 5) Each initial calibration standard mixture must be spiked with the same internal standards as the samples and at the same concentration as the samples.
- 6) The required analyte concentration of each compound's lowest and highest initial calibration standards are specified in Table 1 "Required Concentrations of the Low and High Calibration Standards and Reporting Limit Laboratory Control Sample Concentrations".

### b. Initial Calibration Verification Sample Standard

- 1) All the compounds in the initial calibration verification sample standard shall be spiked at 10 ppbv. The only exception is that the xylene (m& p) isomer mixture requires spiking at 20 ppbv.
- 2) Tracer gas standards must be included in the initial calibration verification standard and must be spiked at 10 ppbv.
- 3) The initial calibration verification sample standard mixture must be spiked with the same internal standards as the samples and at the same concentration as the samples.

c. *GC/MS Daily Calibration Verification Standard*

- 1) All the compounds in the daily calibration verification standard shall be spiked at 10 ppbv. The only exception is that the xylene (m& p) isomer mixture requires spiking at 20 ppbv.
- 2) Tracer gas standards must be included in the daily calibration verification standard and must be spiked at 10 ppbv.
- 3) The daily calibration verification standard mixture must be spiked with the same internal standards as the samples and at the same concentration as the samples.

d. *Closing Calibration Verification Standard*

- 1) All the compounds in the closing calibration verification standard shall be spiked at 10 ppbv. The only exception is that the xylene (m& p) isomer mixture requires spiking at 20 ppbv.
- 2) Tracer gas standards must be included in the closing calibration verification standard and must be spiked at 10 ppbv.
- 3) Each closing calibration verification standard mixture must be spiked with the same internal standards as the samples and at the same concentration as the samples.

11. Reporting Limit Laboratory Control Sample (RLLCS)

- a. The reporting limit laboratory control sample (RLLCS) must contain all of the target analytes required in the method.
- b. The required compound concentrations of the RLLCS are specified in Table 1.
- c. Tracer gas standards must be included in the RLLCS and must be spiked at same concentration as the lowest initial calibration standard.
- d. The RLLCS must be prepared with humidified ultra pure zero air and in the same manner as the method blank (Method TO-15 Section 10.7). The difference is that the canister is spiked with all compounds to obtain the concentrations as specified in Table 1.
- e. Each RLLCS must be spiked with the same internal standards as the samples and at the same concentration as the samples.

**O. Sample Analysis Requirements**

1. Gas Chromatography/Time of Flight Mass Spectrometry

The GC/MS Technology known as GC/Time of Flight Mass Spectrometry is acceptable for this method provided that all the requirements of this Method and the NJDEP performance requirements specified herein are met. However only with prior approval of the technique by the Office of Quality Assurance and with the following additional specifications can the technique be used in the laboratory.

- a. Fast Chromatography will not be allowed for NJDEP work.
- b. A separate method detection limit study must be conducted for each instrument using this technique.
- c. If this technique is used for certifying the canisters as clean, the same technique must be used for the analysis of the canisters. This is required so that the experimental conditions such as scan rate, ramp rate etc. are the same for both analysis.
- d. The data must be delivered in the same reporting format as quadropole GC/MS and all labeling requirements of the data package must be met.
- e. A separate Standard Operating Procedure must be provided for this technique.

## 2. Mass Spectrometer (MS)

- a. The MS must be capable of scanning from 35-300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the 4-Bromofluorobenzene (BFB) GC/MS performance check technical acceptance criteria in Table 1 of the USEPA Method TO-15.

NOTE: To ensure sufficient precision of mass spectral data, the MS scan rate must allow acquisition of at least five spectra while a sample compound elutes from the GC. The purge-and-trap GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system, which prevents the release of contaminants into the instrument room.

- b. The laboratory will operate the GC/MS in the full SCAN mode only. Selective Ion Monitoring (SIM) Mode is not acceptable for this method.

## 3. Data System

- a. A computer system must be interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.
- b. The computer must have software that allows searching of any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time and scan number limits.
- c. The NIST (2005 release or later), Wiley (2005 release or later) or equivalent mass spectral library shall be used as the reference library. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel. Proof of software ownership or license agreement from the manufacturer must be provided as part of the SOP documentation.

#### 4. Data Storage Device

- a. Data storage devices must be suitable for long-term, off-line storage of data.
- b. The laboratory shall store all raw data and processed electronic analytical data in the appropriate instrument manufacturer's format, uncompressed and with no security codes. The electronically stored data shall include all data needed to completely reconstruct a hard copy and electronic deliverable. The electronic data files shall include, but are not limited to, blanks, spikes, tunes, calibrations, quality control samples, proficiency testing samples and check samples. The electronic data files shall also include all laboratory generated spectral libraries and quantitation reports as well as the associated raw data files if those files contain data or instrument parameters related to analytical results.
- c. If a request is made by the NJDEP Office of Quality Assurance for the electronic data files, the files must be sent within ten (10) days.
- d. The laboratory shall store GC/MS and other electronic data in a format retrievable on-line to the data system for ten (10) years. The laboratory shall store the data storage medium under secure and appropriate environmental conditions to preclude the loss of data.

#### 5. Raw Data Storage

- a. The laboratory is responsible for storing the raw data collected during the analysis of all samples. Raw data consist of both electronic files and bound laboratory notebooks
- b. The laboratory must maintain bound notebooks to record all raw data. The analyst must sign all entries in this laboratory notebook. The analyst's supervisor MUST also sign entries in this notebook. This information includes but is not limited to instrument run logs, canister certification batch assignments, canister preparation and receipt information, and addition of air to bring up to volume documentation. The laboratory shall maintain a bound paginated laboratory notebook with the analyst's and supervisor's signature for archival storage of all data, except computerized data. The analyst must sign any computerized printout or chromatogram.

#### 6. Instrument Performance Check Requirements

- a. Instrument Performance Check Requirements of this method must meet the requirements of USEPA Method TO-15 Table 3 "Required BFB Key Ions and Ion Abundance Criteria" and Method Sections 10.4.3 and 10.4.4 for the Instrument Performance Check to be considered acceptable. The use of any other criteria must be approved by the Office of Quality Assurance prior to submittal of any data using the procedure.
- b. BFB shall not be combined with any calibration standard to create a single mixture injection consisting of a calibration standard and the Instrument Performance Check Gas Standard.
- c. The Instrument Performance Check Standard must be the first analysis in any 24-hour sequence.

- d. Post acquisition manipulation of the ion abundances using computer software to achieve tuning criteria is unacceptable. Any sample, blank or quality control sample analyzed in conjunction with a failed tune performance check requires a reanalysis. The laboratory shall comply with the requirements of N.J.A.C. 7:18-5.2(a)8, 5.2(a) 13.

#### 7. GC/MS Initial Calibration Requirements

- a. The laboratory is required to conduct the initial calibration using a minimum of five (5) points for each of the calibration standards.
- b. The initial calibration standards must be analyzed immediately after the compliant Instrument Performance Check analysis and prior to the analysis of the associated method blank if samples are analyzed immediately after the initial calibration. Calibration standards associated with different Instrument Performance Check analysis shall not be merged together to create a compliant initial calibration.
- c. The calculated % RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

#### 8. Initial Calibration Verification Sample Requirements

- a. The initial calibration verification standard must be analyzed immediately after the final initial calibration standard is analyzed and prior to the analysis of the field samples if samples are analyzed after the initial calibration. The standard can be analyzed prior to or after the method blank.
- b. All the compounds in the initial calibration verification sample standard shall be spiked at 10 ppbv. For xylene (m& p) isomer mixture, the spiking is at 20 ppbv.
- c. Tracer gas standards must be included in the initial calibration verification standard and must be spiked at 10 ppbv.
- d. The % Recovery of the Initial Calibration Verification Standard from the required concentration of each compound in the standard (see the required concentration in item b. of this section) must be between +/- 30 percent (%) for the Initial Calibration Verification Standard to be acceptable. If the % Recovery of any compound is outside of control limits, the Laboratory shall reinject the Initial Calibration Verification Standard. The reinjection must be the next injection after the failed standard and the one of the following actions shall occur:
  - 1) If the second injection of the Initial Calibration Verification Standard meets the +/- 30% criteria, the laboratory will use the second injection as the compliance standard. The failed first injection must be noted on all run logs and discussed in the case narrative.
  - 2) If the second injection of the Initial Calibration Verification Standard fails to meet the +/- 30% criteria, the laboratory shall halt the analytical sequence and take the required appropriate corrective action that may include reparation of standards. Upon completion of the corrective action, the laboratory shall be required to restart the calibration analytical sequence with an initial calibration sequence.

- 3) If the Laboratory fails to analyze the second Initial Calibration Verification Standard as required due to a failed initial injection of the standard and then continues the analytical sequence (either initial or an associated daily sequence), all associated data shall be unacceptable. The laboratory is required to reanalyze all the associated samples and blanks in another analytical sequence that begins with an acceptable initial tune, calibration sequence and Initial Calibration Verification Standard.

#### 9. GC/MS Daily Calibration Verification Standard

- a. The daily calibration standard must be analyzed in accordance with the method.
- b. All the compounds in the daily calibration verification standard shall be spiked at 10 ppbv. For xylene (m& p) isomer mixture, the spiking is at 20 ppbv.
- c. Tracer gas standards must be included in the daily calibration verification standard and must be spiked at 10 ppbv.
- d. The daily calibration standard must be analyzed immediately after the compliant GC/ MS Tuning and Instrument Performance Check analysis and prior to the analysis of the associated method blank.
- e. Calibration standards obtained with different GC/MS Tuning and Instrument Performance Check Analysis shall not be merged together to create a compliant initial calibration.
- f. The samples associated with the daily calibration standard must be run after the associated method blank and prior to the closing continuing calibration verification standard.
- g. The % Difference for each Relative Response Factor (RRF) of target compound in the daily calibration verification standard must be within +/- 30 percent (%) of the mean Relative Response Factor (mean RRF) in the associated initial calibration in order to proceed with the analysis of samples, blanks and quality control samples.
- h. If the rejection of the Continuing Calibration Verification Standard fails to meet the technical acceptance requirements, laboratory shall halt the analytical sequence. The laboratory is required to restart the analytical sequence beginning with an initial tune and calibration sequence.

#### 10. Closing Continuing Calibration Verification Requirements

- a. In addition to the Daily Calibration standard that is analyzed in accordance with Method Section 10.6 of the method, NJDEP will be requiring the analysis of a Closing Calibration Verification Standard after all samples, blanks and reporting limit Laboratory control samples have been analyzed and before the end of the 24-hour time period.
- b. The concentration of the Closing Calibration Verification Standard must be the same as the Daily Calibration Verification Standard.



- c. The Closing Calibration Verification Standard must meet the same technical requirements as the Daily Calibration Verification Standard with the following exception.
- 1) If the Closing Calibration Verification Standard fails to meet the % Difference of +/- 30 % for all the compounds, the laboratory is required to do the following:
    - a) Immediately reinject the Closing Calibration Verification Standard. The reinjection must be the next injection after the failed standard.
    - b) The reinjection of the Closing Calibration Verification Standard must occur **prior to the expiration of the 24-hour daily period for the analytical sequence.** It is acceptable for the completion of the run to occur after the expiration of the 24-hours. Reinjection that occurs after the expiration of the 24 hours will is not acceptable.
  - 2) The laboratory shall submit both sets closing calibration verification standard and documentation data in the analytical data package. The submittal of both Closing Calibration Verification Standards requires the following action by the laboratory:
    - a) If the reinjection of the Closing Calibration Verification Standard meets all the technical acceptances criteria, the laboratory will use the reinjection as the compliant closing calibration standard.
    - b) If both the initial and reinjection of the Closing Calibration Verification Standard fail to meet all the technical acceptances criteria, the laboratory must fully discuss the failure of the meeting the daily calibration criteria and all corrective action measures taken in the case narrative. The following information must be included in the case narrative of the analytical data package for each failed Closing Calibration Verification Standard,
      - The list of the compounds and the % Differences that failed
      - The affected samples

#### 11. Reporting Limit Laboratory Control Samples (RLLCS)

- a. The reporting Limit laboratory control sample (RLLCS) must contain all the target analytes required in the method. The required compounds and their associated concentrations for the RLLCS are specified in Table 1. Tracer gas standards must be included in the RLLCS and must be spiked at same concentration as the lowest initial calibration standard.
- b. The RLLCS is required to meet the same technical requirements for area response and retention time for the internal standards as for the method blank as provided for in Method TO-15 Section 10.7.5.
- c. The laboratory is required to analyze one RLLCS within the 24-hour Instrument Performance Check and calibration sequence window established by the method. This is the same frequency as the method blank. The RLLCS must be analyzed after the method blank in the analytical sequence and prior to the Closing Calibration Verification Standard.
- d. The RLLCS must be analyzed within the 24 hour window that begins with the injection of the Instrument Performance Check Gas Standard

- e. If a separate Instrument Performance Check and calibration sequence is used for the clean canister certification, a RLLCS is required to be analyzed in the calibration sequence that is used to certify a canister as clean as per the method.
- f. The RLLCS recovery for each of the compounds must be within 60-140 % of the spiked value for 90 % of the compounds for the RLLCS to be considered acceptable. If less than 90% of the RLLCS recoveries are within the control limits, all the compounds (detected and non detected compounds) in the associated sample, a statement must be added to the case narrative qualifying all the data in the affected samples. If greater than 90% of the RLLCS recoveries are within control limits, only the affected compounds and the affected samples are to be listed in the case narrative of the required analytical data package.

## 12. Chromatographic Scaling Requirements

- a. Chromatograms must display all target compound peaks and internal standard peaks normalized to full scale for all samples, standards and QC samples. The chromatogram shall be normalized to full scale based on the highest target or internal standard.
- b. If a water peak or carbon dioxide peak are present in the sample chromatogram, these peaks are not be taken into account for scaling. These peaks must be identified by the analyst on the chromatogram.
- c. When no compounds are identified in a sample, the chromatograms from the analyses of the sample must use the same scaling factor as was used for the low-point standard of the initial calibration associated with those analyses.
- d. If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.
- e. All target compounds and internal standards in the chromatograms shall be labeled with the names of compounds or retention times on the peak.
- f. Reconstructed ion chromatograms shall be normalized to the largest target or internal standard and shall be labeled with following header information:
  - 1) Sample identification number
  - 2) Date and time of analysis
  - 3) GC/MS instrument identification -- exact instrument employed.
  - 4) Lab file Identifier
  - 5) Analyst ID

## 13. Water Management

The laboratory must provide for appropriate or optimized water management procedures during sample analysis.

#### 14. Spectra Acceptability

- a. For comparison of standard and sample component mass spectra, mass spectra obtained on the Laboratory's GC/Mass Spectrometer (MS) are required. Once obtained, these standard spectra may be used for identification purposes, only if the Laboratory's GC/MS meets the daily instrument performance requirements for 4-bromofluorobenzene (BFB). These standard spectra may be obtained from the run used to obtain reference RRTs.
- b. The guidelines for qualitative verification by comparison of mass spectra are as follows:
  - 1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
  - 2) The relative intensities of ions specified in the above paragraph must agree within +/- 20 % between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70%).
  - 3) Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra.
- c. If a compound cannot be verified by all of the spectral identification criteria listed above, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Laboratory shall report that identification and proceed with quantitation.

#### 15. Secondary ion Quantitation

Quantitation based on secondary ion is not allowed. Exceptions are allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, the reasons must be documented in the SDG Narrative. A secondary ion cannot be used unless the Relative Response Factor is calculated using the secondary ion.

#### 16. Manual Integration

- a. It is expected that situations will arise where the automated integration procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the laboratory must perform a manual integration. Manual integrations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific target compound or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall also not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet Quality Control (QC) criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration must be documented in the SDG Narrative.

- b. In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS Operator must identify such edits or manual procedures by signing (full signature) and dating the changes made to the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "M" on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the peak prior to the manual integration and after the manual integration shall be included in the raw data on separate EICP area printouts. The manual integration lines must be clearly distinguishable from the baseline. This applies to all compounds and internal standards compounds. The GC/MS supervisor must review and sign the report.

#### 17. Quantitation Report Presentation

The quantitation report must contain all the compounds required in the analysis. The laboratory shall not delete compounds for the report if they were not detected or if the mass spectral identification was not confirmed. The data system printouts must comply with all any current deliverable requirements specified by the state.

#### 18. Humidified Ultra Pure Zero Air Makeup Air Requirements

Only humidified ultra pure zero air shall be used as the source of air that is added to a canister for pressure adjustment. It must be from the same source as the method blank air. Nitrogen gas is not acceptable.

#### 19. Volume of Sample Used for Analysis

The undiluted volume of sample drawn from the canister for analysis will vary from laboratory to laboratory based on the procedures established by the laboratory and by the instrumentation employed. If dilutions are required due to concentrations in the samples that exceed the upper calibration of the instrument, the volume drawn from the canister must be reduced and ultra pure humidified zero air is to be used as the makeup air. Laboratories shall not automatically add air to the undiluted sample either on the column, in a canister, Tedlar bag, or other options to meet their systems requirements without the sample being reported as diluted.

The laboratory must address the following requirements in the standard operating procedures.

- a. Automatic dilution of samples is not permitted. If none of the target compounds in the sample exceed the required concentration of the highest calibration standard, the sample must be analyzed without the addition of any makeup air and the data reported without any dilution factor adjustment applied.
- b. If dilutions are required due to concentrations in the samples that exceed the highest calibration standard, the volume drawn from the canister must be reduced and ultra pure humidified zero air is to be used as the makeup air. All sample data must be reported with the dilutions factored in and the all the reporting limits must be adjusted for the required dilutions.

- c. Both the undiluted and diluted sample data must be reported on separate data summary reporting forms with all the accompanying documentation.

The laboratory can propose other options for dilution of samples. The specific procedures must be provided for in their standard operating procedures for review and approval. Laboratories should consider establishing a screening procedure for all samples analyzed by this method.

Refer to Section 24 for the Dilution Requirements of this method.

## 20. Method Blanks

- a. The laboratory is required to follow the requirements of Method TO-15 Section 10.7 regarding method blanks. Any method blank that deviates from the preparation and technical acceptance requirements specified in the method is not acceptable and will be rejected. Any analysis that is related to a failed method blank will also be rejected.
- b. The method blank canister is required to be a dedicated canister that has never left the laboratory. The serial number of the method blank canister must be noted on all the clean canister logs and instrument run logs.
- c. A canister that has been used for sample collection out in the field shall not be used as method blank canister.
- d. A canister that has been designated as a canister that is being certified clean as part of the batch certification process shall not be designated as a method blank.

## 21. Instrument Blanks

- a. If the laboratory determines during the analytical sequence that an instrument blank needs to be analyzed for any reason within an analytical sequence, the instrument blank is to meet the requirements of Method TO-15 Section 10.7 to be acceptable. The sample must be labeled as an instrument blank and the reason for analyzing the blank documented in the case narrative and the instrument run log.
- b. The instrument blank canister is required to be a dedicated canister that has never left the laboratory. The serial number of the instrument blank canister must be noted on all applicable instrument run logs.
- c. A canister that has been used for sample collection out in the field shall not be used as instrument blank canister.
- d. A canister that has been designated as a canister that is being certified clean as part of the batch certification process shall not be designated as an instrument blank.
- e. The instrument blank that demonstrates that there was no carryover from the previous sample is to be reported. The laboratory can also report the instrument blank that demonstrates that the system is clean. Instrument blanks analyzed during the instrument decontamination process that exceed the requirements listed in this section do not need to be reported.

## 22. Internal Standards

Internal standard responses and retention times in all samples must be evaluated during, or immediately after, data acquisition. The criteria for evaluation are as follows:

- a. As required by Method TO-15 Section 10.8.5 in the note, the following criteria must be used if the samples are analyzed with the initial calibration.

"If the most recent valid calibration is an initial calibration, internal standard area responses and the retention times in the sample are evaluated against the corresponding internal standard area responses and retention times in the mid level standard (10 ppbv) of the initial calibration."

- b. The retention time for each internal standard must be within +/- 0.33 minutes of the retention time of the internal standard in the most recent valid calibration.
- c. If the retention time for any internal standard changes by more than +/- 0.33 minutes from the latest daily (24 hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS must be inspected for malfunctions, and corrections made as required.
- d. If the area response for any internal standard changes by more than +/- 40 % between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunctions and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.
- e. If after reanalysis, the area responses or the retention times for all internal standards are inside the control limits, then the problem with the first analysis is considered to have been within the control of the laboratory. The laboratory is required to submit the data for the second analysis as the compliant analysis.
- f. If after reanalysis, the area responses or the retention times for all internal standards are still not inside the control limits, a matrix effect may be occurring. This matrix effect shall be considered outside the control of the laboratory. The laboratory must document in the case narrative and the instrument run logs all corrective actions undertaken prior to the reanalysis of the sample. Therefore, the laboratory is required to submit both analyses.

## 23. Qualitative Identification of Targeted and Non Target Compounds by GC/MS

- a. The compounds listed as required for NJDEP-LLTO-15 shall be identified by an analyst experienced in the interpretation of mass spectra by comparison of the sample mass spectrum to the reference mass spectrum. Two criteria must be satisfied to verify the identifications:
  - 1) Elution of the sample component at the same GC relative retention time as the standard component
  - 2) Correspondence of the sample component and standard component mass spectra.

- b. For establishing correspondence of the GC relative retention time (RRT) the sample component RRT must compare within  $\pm 0.06$  RRT units of the RRT of the standard component. If samples are analyzed within the same 24-hour time period as the initial calibration standard, use the RRT values from the 10 ppbv standard (or the middle standard of the initial calibration).
- c. If co-elution of interfering compounds prohibits accurate assignment for the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions used to obtain reference RRTs.
- d. For comparison of standard and sample component mass spectrum, mass spectra obtained on the laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes only if the laboratory's GC/MS meets the daily instrument performance requirements for BFB. These standard spectra may be obtained from the run used to obtain reference RRT.
- e. All ions present in the standard mass spectra at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100.0 percent) must be present in the sample spectrum.
- f. The relative intensities of ions specified above must agree within  $\pm 20$  percent between the standard and sample spectra.
- g. Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra.
- h. Structural isomers that produce very similar mass spectra shall be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height from the baseline to 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.
- i. If a compound cannot be verified by all the criteria above, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the laboratory shall report that identification with comment and proceed with quantitation.
- j. For all compounds detected below the NJDEP Reporting Limits (See Table 2), the concentrations are to be reported with the numeric value of the reporting limit with the "U" qualifier. This indicates that compound was not detected at the NJDEP Reporting Limit.
- k. For all compounds not detected in the sample, the sample result is to be reported as the numeric value of the reporting limit with the "U" qualifier. This indicates that compound was not detected at the NJDEP Reporting Limit.
- l. For samples requiring dilution, the reporting limits for the all compounds must be adjusted for the dilution that was conducted. All detected results between the NJDEP-LLTO-15 undiluted Reporting limits and the dilution adjusted reporting limits must be reported. The laboratory is required to use the "J" qualifier for any compound detected between the NJDEP Reporting Limit and the dilution-adjusted Reporting Limit. For

compounds not detected in the diluted sample, the sample result is to be reported as the numeric value of the dilution adjusted reporting limit with the "U" qualifier. This indicates that compound was not detected at the dilution adjusted reporting limit.

- m. Non-Target Compound identification is required for air analysis. A maximum of 30 Non-Target compounds must be identified.

#### 24. Sample Dilutions

As part of the routine analysis, canisters will be received by the laboratory that will require dilutions to be conducted so that samples results will be within the calibration range of the instrument. As part of the process, this method requires the laboratory to incorporate the following procedures into their screening procedures of the canisters. The laboratory must describe the dilution procedures that they intend to use for this method.

- a. If the laboratory must add air to the sample for the dilution, the air source must be the same as the air source that is used for the preparation of the method blanks, that being humidified, ultra-pure zero air.
- b. All dilutions must be made immediately prior to GC/MS analysis of the sample.
- c. The dilution procedures must be documented in the Case Narrative of the analytical data package.
- d. Laboratory procedural dilution of samples is not permitted. If the sample is reported with all target analyte results at or below the required reporting limits, then the sample must be analyzed without the addition of any makeup air and without any corrections for sample dilutions.
- e. If any target analyte results are less than 40 ppbv in the sample, the sample must be analyzed without the addition of any makeup air and the data reported without any dilution factor adjustment applied. (See item k. in this section below for additional information.)
- f. If dilutions are required due to concentrations in the samples that exceed the upper calibration of the instrument, the volume drawn from the canister must be reduced and ultra pure humidified zero air is to be used as the makeup air. All sample data must be reported with the dilutions factored in and the all the reporting limits must be adjusted for the required dilutions.
- g. Both the undiluted and diluted sample data must be reported on separate data summary reporting forms with all the accompanying documentation.
- h. The laboratory must choose a sample specific dilution factor that is required to keep the concentration of the largest peak for a target compound in the upper half of the initial calibration range.
- i. The screening data must be provided in the analytical data packages as required by the current deliverable requirements established by the NJDEP.



- j. If the screening results indicate that the peak response for any target compound in any sample does not exceed the peak response in the highest standard in the initial calibration, the sample must be analyzed without being diluted.
- k. If the screening results indicates that the peak response for any target compound in any sample does exceed the peak response in the highest standard in the initial calibration, the laboratory shall chose of one two options.
  - 1) The laboratory can analyze the sample as undiluted and then analyze the sample at the correct dilution level. The laboratory can use the results of the original analysis to determine the approximate dilution factor to get the largest analyte peak within calibration range. The laboratory may not submit more than two sets of data. The laboratory must submit both sets of data separately. Both sets of data must meet the requirements of the method.
  - 2) The laboratory must chose the dilution level that will allow the sample can be analyzed at the most concentrated dilution and meet the requirements of the method. The laboratory must demonstrate that it has chosen the appropriate level by analyzing the sample at one further dilution. The laboratory may not submit more than two sets of data. The laboratory must submit both sets of data separately. Both sets of data must meet the requirements of the method.
- l. There are various options available for the dilution of the samples depending on the analytical systems used by the laboratory. The laboratory must provide in their SOP which options they will be using in sample analysis. The options can include the following:
  - 1) Injection of a volume of sample into another certified clean canister and induction of ultra pure humidified zero air.
  - 2) Dilutions conducted directly on the instrument.
  - 3) Tedlar Bags can be used. When tedlar bags are used, absorption and contribution issues must be determined prior to their use. Tedlar bag blanks must be analyzed as part of the analytical sequence. These blanks are in addition to the required method blanks must be clearly identified in the sequence. The blanks must be analyzed after the method blank and prior to the sample.
- m. The laboratory can propose other options for the dilution of the samples. However, approval must be obtained for NJDEP prior to their use.

## 25. Tracer Compounds for Soil Gas

- a. The laboratory must be aware that clients are required to use tracer compounds to determine if the soil gas collection system at the probe level is free of leaks. Two common tracer compounds are isopropanol and n-butane. Prior to the initiation of soil gas sampling, the laboratory must determine from the client which tracer compound they will be using. The laboratory is required to have that compound included in its calibration. In most commercially prepared gas standard cylinders, isopropanol is in the mixture while n-butane may not be in the standard mixture. If the client wants to use n-butane or other recognized compounds as the tracer compound, the laboratory will be required to obtain commercially prepared gas standards that contain n-butane.

- b. The tracer gas standards must meet the same technical criteria compounds as other standards in this method. The tracer gas standards, if analyzable by this method, must be in the same cylinders as the target gases.
- c. If the laboratory wants to use n-butane or any other gas not listed in this method as a tracer gas and report data by this method, the laboratory must request certification for that compound.
- d. If a tracer gas such as helium gas, that is not analyzable by this method, is used by the samplers as the tracer gas, the laboratory must be certified for the method being used for the analysis of the tracer gas. Laboratory Certification is required for both field instrumentation techniques and laboratory instrumentation techniques.
- e. The laboratory is not required to dilute the sample to bring the concentration of the tracer compound within the calibration range of the instrument. The laboratory is to report the data in the same manner as the other target compounds in the method.

## 26. Isopropanol and Ethanol

- a. High concentrations of isopropanol and ethanol in indoor air samples are causing laboratories to conduct unnecessary dilutions of samples. These two alcohols are present in numerous products found in residences and businesses. Ethanol is also a gasoline additive. This is one source of the elevated levels of the alcohols in the samples.
- b. The commercial gas suppliers are routinely adding these two compounds to the standard gas mixtures; therefore, if the compounds are in the standards, the concentrations of the compounds must be reported in the samples. Ethanol has been reported by the standard manufacturers not to be stable within the standard mixtures.
- c. Isopropanol is used as tracer gas compounds for soil gas analysis. The presence of this compound in soil gas samples may be an indication that the seal around the tubing was not tight. However, the presence of these compounds in soil gas when the alcohols were not used as the tracer gas may be indication of another source of contamination.
- d. If these compounds are of concern at site, this method may not be appropriate for the reporting of these compounds and a difference method should be proposed. Laboratory certification will be required for any proposed method.
- e. The laboratory is not required to dilute the sample to bring the concentration of the two alcohols compounds within the calibration range of the instrument.

## P. Method Detection Limit/ Method Detection Limit Verification Requirements for All Canister Types

### 1. Method Detection Limit Requirements

- a. Frequency and Reporting Requirements

- 1) There are specific criteria that the laboratory must meet regarding the Method Detection Limit (MDL). The MDL is a statistical determination based on the requirements of the Method.
- 2) The MDL study must be conducted annually for each instrument used in the clean canister certification and/or analysis of the samples.
- 3) Separate MDL studies must be submitted for each instrument used in the sample analysis and clean canister certification must be submitted in any analytical data package.
- 4) Copies of the MDL studies must be submitted upon request to the Office of Quality Assurance.

b. Required Spiking Levels

The laboratory shall calculate all Method Detection Limits (MDLs) in accordance Method TO-15. Section 11.2 requires the use of the procedures stated in Appendix B of 40 CFR 136 for performing the MDL study. For the majority of the compounds, the MDL determination must be conducted using a spiking solution at 0.20 ppbv concentration. For the other compounds listed below, the MDL determination can be conducted at a higher concentration and they are listed below. The laboratory has the option of using a lower concentration of spiking solution for these compounds. However, it shall not be less than 0.20 ppbv. All data shall be reported in ppbv.

<b>Compound</b>	<b>Spiking Level for the MDL Determination</b>
Acetone	0.50 ppbv
Carbon Disulfide	0.50 ppbv
Methylene Chloride	0.50 ppbv
Xylenes (m& p)	0.40 ppbv (equal amount of each isomer)

c. Derived MDL Requirements

The derived MDL must be less than the Clean Canister Certification Level of 0.20 ppbv as specified by the method for all compounds except for acetone (2-propanone) and *tert*-butyl alcohol (see below). The maximum MDL for acetone (2-propanone) and *tert*-butyl alcohol have been elevated to address various concerns within the laboratory community. Laboratories may use lower MDLs for these compounds.

<b>Compound</b>	<b>Maximum MDL Exceptions</b>
Acetone	1.0 ppbv
<i>tert</i> -Butyl Alcohol	3.0 ppbv

**d. Method Detection Limit Summary Format**

Method Detection Limit Summary submitted by the laboratory must contain the following information for each compound in a tabular format. All information except for signatures must be computer generated or typed.

Laboratory Name  
Laboratory Location  
Matrix Type  
Effective Date/Expiration date of MDL Study  
Instrument ID and Column ID  
Indication if Instrument is used for Clean Canister Certification  
Compound name  
Data for seven replicates  
Mean value  
True Value  
Percent recovery  
Standard deviation  
Method Detection Limits (ppbv)  
Reporting Limits (ppbv)  
True Value/MDL  
Analyst name and date analyzed  
Reviewed by name and date  
Report preparer's name and date prepared  
QA Officer name and date signed

**2. Method Detection Limit Verification (MDLV)**

- a. The Method Detection Limit Verification Study (MDLV) must be completed after the Method Detection Limit Study is completed.
- b. The MDLV must be conducted for each analyte in the MDL Study. The required concentration for each compound is between 2-5 times the reported compound specific MDL values. The MDLV results must be compared against the MDL and the entire study reported in the format specified below.
- c. The MDLV study must be conducted annually for each instrument used in the clean canister certification and/or analysis of the samples. Separate MDLV reports must be submitted for each instrument.
- d. Copies of the MDLV studies for all the instruments used in the sample analysis and clean canister certification must be submitted in any analytical data package.
- e. Copies of the MDLV studies must be submitted upon request to the Office of Quality Assurance.
- f. Method Detection Limit Summary Verification (MDLV)

The Method Detection Limit Verification Summary (MDLV Summary) must be submitted with the Method Detection Limit Study. The required format of the Summary is as follows:

#### Header Information

- Date of verification study
- Analysis method
- Cleanup method (if applicable)
- Study Identification file name:
- Matrix
- Analysis level
- Analyst name
- Approval by QA Officer (name and date)

#### Required Columns

- Analyte name
- CAS number
- MDLV source
- Source study
- Source instrument
- Source analysis date
- MDLV (ppbv)
- Reporting Limit (ppbv)
- QL/MDLV ratio
- Reporting limit (ppbv)

#### **Q. Clean Canister Certification Requirements**

1. The canister used for batch certification must be certified clean prior to the shipment of any canisters to the field for sample collection.
2. Canisters used for clean canister certification shall not be used as a method blank in an analytical sequence.
3. The laboratory must document and track which canisters are associated with each batch certification. A separate logbook page must be generated documenting the canisters associated with each batch certification. The logbook page must include the start and stop date/time of cleaning, heating unit type, number of cycles, analyst's name and signature and canister serial numbers. In addition, the laboratory file number from the GC/MS analysis associated with the canister being cleaned must be listed.
4. The laboratory must specify the canister cleaning procedures that are used in their SOP. For each type of canister cleaning procedure (bands, ovens or heating jacket) a separate canister must be used to demonstrate that the cleaning procedure meets the requirement of the method.
5. NJDEP has not established a batch maximum for canisters cleaned by a particular cleaning technique. All the canisters in a batch must be cleaned under the same conditions

(temperature, time, cycles etc.). The laboratory in their SOP must specify the maximum number of canisters in a cleaning batch. The laboratory is required to follow the requirements of Method TO-15, Section 8.3 regarding cleaning and certifying canisters.

6. The laboratory must utilize the same reporting limits for the clean canister certification as for the sample data. Clean canister data less than 0.2 ppbv shall not be reported. The reporting criteria is provided in the section below entitled "**SAMPLE REPORTING LIMITS FOR ALL OF THE CANISTER TYPES**".
7. Tracer gas compounds must meet the same clean canister requirements as the target compounds in this method.
8. Clean Canister Certification for 6-Liter Canisters for Building Interiors, Soil Gas Sampling and other types of sampling (as specified)

The canisters must be batch cleaned and certified with the majority of Method NJDEP-LLTO-15 target analytes at a less than 0.20 ppbv Reporting Limit. Exceptions to the required clean canister certification limit are detailed below.

<b>Compound</b>	<b>Clean Canister Certification Level (Maximum)</b>
Acetone	2.0 ppbv
Tetrahydrofuran	2.0 ppbv
1,4-Dioxane	2.0 ppbv
Tert-Butyl Alcohol	2.0 ppbv
Xylenes (m& p)	0.5 ppbv

9. Clean Canister Certification for 1- Liter, 2.7-Liter and 3.2-Liter Canisters used for Soil Gas Sampling
  - a. The laboratory is required to follow the requirements of Method TO-15, Section 8.3 regarding cleaning and certifying canisters.
  - b. The canisters must be batch cleaned and certified with the majority of Method NJDEP-LLTO-15 target analytes at a  $\leq 0.20$  ppbv Reporting Limit. Exceptions to the required clean canister certification limit are detailed below.

<b>Compound</b>	<b>Clean Canister Certification Level (Maximum)</b>
Acetone	5.0 ppbv
Carbon Disulfide	0.50 ppbv
Methylene Chloride	0.50 ppbv
Methyl Ethyl Ketone	0.50 ppbv

1,2,4-Trichlorobenzene	0.50 ppbv
Tetrahydrofuran	2.0 ppbv
Dichlorodifluoromethane	0.50 ppbv
Methyl Methacrylate	0.50 ppbv
1,4-Dioxane	5.0 ppbv
Methyl Isobutyl Ketone	0.50 ppbv
Tert-Butyl Alcohol	5.0 ppbv
Xylenes (m& p)	0.50 ppbv

**R. Sample Reporting Limits for all of the Canister Types**

1. The laboratory shall not report any target data lower than the reporting limits established by this method. The reporting limits are found at the end of this method in Table 2 *"List of Required Compounds, Molecular Weights and CAS Numbers and NJDEP Required Reporting Limits"*.
2. For all compounds detected below the NJDEP Reporting Limits, the concentrations are to be reported with the numeric value of the reporting limit with the "U" qualifier. This indicates that the compound was not detected at the NJDEP Reporting Limit.
3. For all compounds not detected in the sample, the sample result is to be reported as the numeric value of the reporting limit with the "U" qualifier. This indicates that the compound was not detected at the NJDEP Reporting Limit.
4. For samples requiring dilution, the reporting limits for the all compounds must be adjusted for the dilution that was conducted. All detected results between the NJDEP-LLTO-15 undiluted Reporting limits and the dilution adjusted reporting limits must be reported. The laboratory is required to use the "D" qualifier for any compound detected between the NJDEP Reporting Limit and the dilution-adjusted Reporting Limit. For compounds not detected in the diluted sample, the sample result is to be reported as the numeric value of the dilution adjusted reporting limit with the "U" qualifier. This indicates that compound was not detected at the dilution adjusted reporting limit.
5. If the laboratory is using lower reporting limits for the compounds that NJDEP has indicated that higher reporting limits are acceptable, replace the wording "NJDEP" with "Laboratory" and use the same criteria.
6. Reporting Limits for 6 Liter Canisters (Building Interiors, Soil Gas Sampling and other types of sampling (as specified))

For the majority of the compounds, the Reporting Limits (RL) have been set at 0.20 ppbv. For the compounds listed below, the reporting limits have been set at a higher level due to the type of compound. The laboratory can use a lower reporting limit for these compounds, however, they cannot be lower than 0.20 ppbv.

<b>Compound</b>	<b>Reporting Limit (Maximum)</b>
Acetone	5.0 ppbv
Carbon Disulfide	0.50 ppbv
Chloroethane	0.50 ppbv
Chloromethane	0.50 ppbv
Methylene Chloride	0.50 ppbv
Methyl Ethyl Ketone	0.50 ppbv
1,2,4-Trichlorobenzene	0.50 ppbv
Tetrahydrofuran	5.0 ppbv
Dichlorodifluoromethane	0.50 ppbv
Methyl Methacrylate	0.50 ppbv
1,4-Dioxane	5.0 ppbv
Methyl Isobutyl Ketone	0.50 ppbv
tert-Butyl Alcohol	5.0 ppbv
Xylenes (m & p)	0.50 ppbv

7. Reporting Limits for 1-Liter, 2.7-Liter and 3.2-Liter Canisters (Soil Gas Canisters)

For the majority of the compounds, the Reporting Limits (RL) have been set at 2.0 ppbv. The higher reporting limits factor in the automatic dilution that occurs when 1-liter canisters are used. The dilution must be conducted with ultra pure humidified zero air. This makeup air is required to be the volume of air for introduction into the instrument. For the compounds listed below, the reporting limits have been set at a higher level due to the type of compound. The laboratory can use a lower reporting limit for these compounds. However, they cannot be lower than 2.0 ppbv.

<b>Compound</b>	<b>Reporting Limit (Maximum)</b>
Acetone	50.0 ppbv
Carbon Disulfide	5.0 ppbv
Chloroethane	5.0 ppbv
Chloromethane	50 ppbv
Methylene Chloride	5.0 ppbv
Methyl Ethyl Ketone	5.0 ppbv
1,2,4-Trichlorobenzene	5.0 ppbv
Tetrahydrofuran	50.0 ppbv
Dichlorodifluoromethane	5.0 ppbv
Methyl Methacrylate	5.0 ppbv
1,4-Dioxane	50.0 ppbv
Methyl Isobutyl Ketone	5.0 ppbv
tert-Butyl Alcohol	50.0 ppbv
Xylenes (m & p)	5.0 ppbv



## S. Tables

**Table 1**  
**Required Concentrations of the Low and High Calibration Standards and Laboratory Control Sample Concentrations**

<b>Chemical Compound</b>	<b>Low Calibration Standard (ppbv)</b>	<b>High Calibration Standard (ppbv)</b>	<b>RLLCS Required Conc. (ppbv)</b>
Acetone	0.20 <sup>4</sup>	40	0.20 <sup>5</sup>
Allyl chloride	0.20	40	0.20
Benzene	0.20	40	0.20
Bromodichloromethane	0.20	40	0.20
Bromoform	0.20	40	0.20
Bromomethane	0.20	40	0.20
1,3-Butadiene	0.20	40	0.20
Chlorobenzene	0.20	40	0.20
Chloroethane	0.20 <sup>4</sup>	40	0.20 <sup>5</sup>
Chloroform	0.20	40	0.20
Chloromethane	0.20 <sup>4</sup>	40	0.20 <sup>5</sup>
Carbon disulfide	0.20	40	0.20
Carbon tetrachloride	0.20	40	0.20
2-Chlorotoluene	0.20	40	0.20
Cyclohexane	0.20	40	0.20
Dibromochloromethane	0.20	40	0.20
1,2-Dibromoethane	0.20	40	0.20
1,2-Dichlorobenzene	0.20	40	0.20
1,3-Dichlorobenzene	0.20	40	0.20
1,4-Dichlorobenzene	0.20	40	0.20
Dichlorodifluoromethane	0.20	40	0.20
1,1-Dichloroethane	0.20	40	0.20
1,2-Dichloroethane	0.20	40	0.20
1,1-Dichloroethene	0.20	40	0.20
1,2-Dichloroethene (cis)	0.20	40	0.20
1,2-Dichloroethene (trans)	0.20	40	0.20
1,2-Dichloropropane	0.20	40	0.20
1,3-Dichloropropene (cis)	0.20	40	0.20
1,3-Dichloropropene (trans)	0.20	40	0.20
1,2-Dichlorotetrafluoroethane	0.20	40	0.20
1,4-Dioxane	0.20 <sup>4</sup>	40	0.20 <sup>5</sup>
Ethanol	0.20	40	0.20
Ethylbenzene	0.20	40	0.20
4-Ethyltoluene	0.20	40	0.20

<b>Chemical Compound</b>	<b>Low Calibration Standard (ppbv)</b>	<b>High Calibration Standard (ppbv)</b>	<b>LCS Required Conc. (ppbv)</b>
N-Heptane	0.20	40	0.20
1,3- Hexachlorobutadiene	0.20	40	0.20
n-Hexane	0.20	40	0.20
Isopropanol	0.20 <sup>1</sup>	40 <sup>2</sup>	0.20
Methylene chloride	0.20	40	0.20
Methyl ethyl ketone	0.20	40	0.20
Methyl isobutyl ketone	0.20	40	0.20
Methyl methacrylate	0.20	40	0.20
Methyl tert-butyl ether	0.20	40	0.20
Styrene	0.20	40	0.20
Tert-butyl alcohol	0.20 <sup>4</sup>	40	0.20 <sup>5</sup>
1,1,2,2-Tetrachloroethane	0.20	40	0.20
Tetrachloroethene	0.20	40	0.20
Tetrahydrofuran	0.20 <sup>4</sup>	40	0.20 <sup>5</sup>
Toluene	0.20	40	0.20
1,2,4-Trichlorobenzene	0.20	40	0.20
1,1,1-Trichloroethane	0.20	40	0.20
1,1,2-Trichloroethane	0.20	40	0.20
Trichloroethene	0.20	40	0.20
Trichlorofluoromethane	0.20	40	0.20
1,1,2-Trichloro-1,2,2-trifluoroethane	0.20	40	0.20
1,2,4-Trimethylbenzene	0.20	40	0.20
1,3,5-Trimethylbenzene	0.20	40	0.20
2,2,4-Trimethylpentane	0.20	40	0.20
Vinyl bromide	0.20	40	0.20
Vinyl chloride	0.20	40	0.20
Xylenes (m&p)	0.40 <sup>1</sup>	80 <sup>2</sup>	0.40 <sup>3</sup>
Xylenes (o)	0.20	40	0.20

**Notes:**

1. The low standard concentration is based on the equal contribution of both the m&p isomers of xylene.
2. The high standard concentration is based on the equal contribution of both the m&p isomers of xylene.
3. The laboratory control standard concentration is based on the equal contribution of both the m&p isomers of xylene.
4. The low calibration standard can exceed 0.20 ppbv.
5. The laboratory control sample spiking level for this compound must be equal to the low calibration standard used in the initial calibration.

**Table 2**  
**List of Required Compounds, Molecular Weights and CAS Numbers and NJDEP Required Reporting Limits**

This Table contains the required compounds and their associated molecular weights and CAS numbers. The information in this table must be used for the reporting of the analytical data to NJDEP. Changes to the compound names, CAS numbers and molecular weights are not allowed for reporting of the data to the State of New Jersey.

<b>Required Compound Name</b>	<b>CAS Number</b>	<b>Molecular Weight</b>	<b>6- Liter Canister Reporting Limits (ppbv)</b>	<b>1, 2.7 &amp; 3.2- Liter Canister Reporting Limits (ppbv)</b>
Acetone	67-64-1	58.08	5.0	50.0
Allyl chloride	107-05-1	76.53	0.20	2.0
Benzene	71-43-2	78.11	0.20	2.0
Bromodichloromethane	75-27-4	163.8	0.20	2.0
Bromoform	75-25-2	252.8	0.20	2.0
Bromomethane	74-83-9	94.94	0.20	2.0
1,3-Butadiene	106-99-0	54.09	0.20	2.0
Chlorobenzene	108-90-7	112.6	0.20	2.0
Chloroethane	75-00-3	64.52	0.50	50.0
Chloroform	67-66-3	119.4	0.20	2.0
Chloromethane	74-87-3	50.49	0.50	50.0
Carbon disulfide	75-15-0	76.14	0.50	5.0
Carbon tetrachloride	56-23-5	153.8	0.20	2.0
2-Chlorotoluene	95-49-8	126.6	0.20	2.0
Cyclohexane	110-82-7	84.16	0.20	2.0
Dibromochloromethane	124-48-1	208.3	0.20	2.0
1,2-Dibromoethane	106-93-4	187.9	0.20	2.0
1,2-Dichlorobenzene	95-50-1	147.0	0.20	2.0
1,3-Dichlorobenzene	541-73-1	147.0	0.20	2.0
1,4-Dichlorobenzene	106-46-7	147.0	0.20	2.0
Dichlorodifluoromethane	75-71-8	120.9	0.50	5.0
1,1-Dichloroethane	75-34-3	98.96	0.20	2.0
1,2-Dichloroethane	107-06-2	98.96	0.20	2.0
1,1-Dichloroethene	75-35-4	96.94	0.20	2.0
1,2-Dichloroethene (cis)	156-59-2	96.94	0.20	2.0
1,2-Dichloroethene (trans)	156-60-5	96.94	0.20	2.0
1,2-Dichloropropane	78-87-5	113.0	0.20	2.0
1,3-Dichloropropene (cis)	10061-01-5	111.0	0.20	2.0
1,3-Dichloropropene (trans)	10061-02-6	111.0	0.20	2.0
1,2-Dichlorotetrafluoroethane	76-14-2	170.9	0.20	2.0
1,4-Dioxane	123-91-1	88.12	5.0	50.0

<b>Required Compound Name</b>	<b>CAS Number</b>	<b>Molecular Weight</b>	<b>6- Liter Canister Reporting Limits (ppbv)</b>	<b>1, 2.7 &amp; 3.2- Liter Canister Reporting Limits (ppbv)</b>
Ethanol*	64-17-5	46.07	0.20	2.0
Ethylbenzene	100-41-4	106.2	0.20	2.0
4-Ethyltoluene	622-96-8	120.2	0.20	2.0
n-Heptane	142-82-5	100.2	0.20	2.0
1,3-Hexachlorobutadiene	87-68-3	260.8	0.20	2.0
n-Hexane	110-54-3	86.17	0.20	2.0
Isopropanol*	67-63-0	60.10	0.20	2.0
Methylene chloride	75-09-2	84.94	0.50	5.0
Methyl ethyl ketone	78-93-3	72.11	0.50	5.0
Methyl isobutyl ketone	108-10-1	100.2	0.50	5.0
Methyl methacrylate	80-62-6	100.12	0.50	5.0
Methyl tert-butyl ether	1634-04-4	88.15	0.20	2.0
Styrene	100-42-5	104.1	0.20	2.0
Tert-butyl alcohol	75-65-0	74.12	5.0	50.0
1,1,2,2-Tetrachloroethane	79-34-5	167.9	0.20	2.0
Tetrachloroethene	127-18-4	165.8	0.20	2.0
Tetrahydrofuran	109-99-9	72.11	5.0	50.0
Toluene	108-88-3	92.14	0.20	2.0
1,2,4-Trichlorobenzene	120-82-1	181.5	0.50	5.0
1,1,1-Trichloroethane	71-55-6	133.4	0.20	2.0
1,1,2-Trichloroethane	79-00-5	133.4	0.20	2.0
Trichloroethene	79-01-6	131.4	0.20	2.0
Trichlorofluoromethane	75-69-4	137.4	0.20	2.0
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	187.4	0.20	2.0
1,2,4-Trimethylbenzene	95-63-6	120.2	0.20	2.0
1,3,5-Trimethylbenzene	108-67-8	120.2	0.20	2.0
2,2,4-Trimethylpentane	540-84-1	114.2	0.20	2.0
Vinyl bromide	593-60-2	106.9	0.20	2.0
Vinyl chloride	75-01-4	62.50	0.20	2.0
Xylenes (m&p)	1330-20-7	106.2	0.50	5.0
Xylenes (o)	95-47-6	106.2	0.20	2.0

\* Ethanol and Isopropyl alcohol is listed only because labs report data for these compounds, but dilutions are not required. If looking for these compounds, other methods may be required.