

# **Method TO-15 Supplement**

## **Analysis of 1,1-DCE at pptv Concentrations**

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## **Notice**

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## Abstract

The Supplement to EPA Compendium Method TO-15 provides guidance for reducing the method detection limit (MDL) for the compound 1,1-dichloroethene (1,1-DCE) and for other volatile organic compounds (VOCs) from 0.5 ppbv, as cited in Method TO-15, to much lower concentrations. Revisions to the original wording of Method TO-15 were made where the original language proved limiting to the goal of extending Method TO-15 to low pptv levels or where omissions or errors were observed. Also, recommendations in the form of additions were made on aspects of laboratory procedure deemed critical to low-pptv-level analysis. Specifically, the MDL for 1,1-DCE was determined to be 6 pptv. During this effort, a capability for preparing 1,1-DCE sample concentrations of 30 pptv and 60 ppbv in ambient air was developed. Using this capability and the capability to prepare samples of humidified zero air, samples were prepared in canisters and sent to three contract laboratories as unknowns. Subsequent comparison of results indicated close agreement among the laboratories while maintaining the performance standards for replicate precision (25%) and audit accuracy (30%) originally specified in Method TO-15. The following compounds were also detected at low pptv levels in canisters filled with spiked ambient air: chloroethene, dichloromethane, *cis*-1,2-dichloroethene, trichloromethane, 1,2-dichloroethane, benzene, 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene. Since the different laboratories employed different analytical procedures, the use of a performance-based method appears justified. Specific guidance on analytical procedures from the Colorado Department of Public Health and Environment (CDPHE) is provided. These procedures have proven useful for CDPHE's contract laboratories in analyzing pptv-level samples of VOCs. The procedures followed by the EPA on-site contractor, ManTech Environmental Technology, Inc., in preparing and analyzing low-level concentrations of 1,1-DCE as well as other aspects of their work on this project are provided as Appendix A.

## Foreword

The National Exposure Research Laboratory (NERL), Research Triangle Park, NC, performs research and development to characterize, predict, and diagnose human and ecosystem exposure, giving priority to that research which most significantly reduces the uncertainty in risk assessment and most improves the tools to assess and manage risk or to characterize compliance with regulations. The Laboratory seeks opportunities for research collaboration to integrate the work of the Office of Research and Development's (ORD) scientific partners and provides leadership to address emerging environmental issues and advance the science and technology essential for understanding human and ecosystem exposures. One aspect of the Laboratory's mission is to work with the U.S. Environmental Protection Agency's (EPA) regional and state offices.

EPA was asked by William P. Yellowtail, the Regional Administrator of Region 8, to review protocols from the Colorado Department of Public Health and Environment (CDPHE) for determining low parts per trillion by volume (pptv) concentrations of 1,1-dichloroethene (1,1-DCE) in ambient air in support of vapor intrusion monitoring. Tom Aalto of Region 8 coordinated the effort with EPA, and technical input on the CDPHE method was provided by Ken Niswonger and Edgar Ethington of CDPHE. The effort was funded under EPA's Regional Monitoring Initiative. In response to this request, NERL developed a work assignment for ManTech Environmental Technology, Inc., the current on-site contractor to NERL at the EPA facility in Research Triangle Park, NC. The task consisted of (1) developing a capability to support monitoring of 1,1-DCE at low-pptv concentrations at the EPA laboratory facilities, (2) documenting the existence of similar capabilities at representative contract laboratories, and (3) providing a TO-15 supplement that contains guidance for meeting the enhanced performance criteria.

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## Acronyms and Abbreviations

µm	micrometer	NIST	National Institute of Standards and Technology
1,1-DCE	1,1-dichloroethene	ORD	Office of Research and Development
1,2-DCA	1,2-dichloroethane	PFTBA	perfluorotributylamine
CDPHE	Colorado Department of Public Health and Environment	ppbv	parts per billion by volume
CH <sub>2</sub> Cl <sub>2</sub>	dichloromethane	pptv	parts per trillion by volume
DQO	data quality objective	PQL	practical quantitation limit
EM	electron multiplier	RL	reporting limit
EPA	Environmental Protection Agency	RRT	relative retention time
FTDS	field test data sheet	RSD	relative standard deviation
L/min	liters per minute	SIM	selected ion monitoring
MDL	method detection limit	TAMS	Toxics Air Monitoring System
mL/min	milliliters per minute	TCE	trichloroethene
MS	mass spectrometry	UATMP	Urban Air Toxics Monitoring Program
NATA	National Air Toxics Assessment	VOC	volatile organic compound
NERL	National Exposure Research Laboratory	°C	degrees Celsius

## **Acknowledgments**

The authors thank Tom Aalto of Region 8 for his assistance in starting this research and the scientists at the Colorado Department of Public Health and Environment (CDPHE), particularly Ken Niswonger and Edgar Ethington, for providing their input in the form of Appendix B to this report. Also, thanks to Bill Lonneman, an experienced senior scientist now working with the U.S. Environmental Protection Agency (EPA) as part of the Senior Environmental Employment program, for providing advice on analytical procedures and helping with the substantiation of target compound concentration levels in gas standards. The authors would like to acknowledge the efforts of Stacy Henkle of KulTech, Inc., in editing and formatting this document.

# Chapter 1 Introduction

This document is a supplement to Method TO-15 in the EPA Compendium of Methods for Air Toxics. It addresses the use of specially prepared canisters for monitoring a single, specific chlorinated compound, 1,1-dichloroethene (1,1-DCE), with implications for the monitoring of other compounds and for multiple compounds in samples containing compound mixtures. Recent reevaluation of risk levels specifically for 1,1-DCE indicates a lowered risk level compared to that established earlier. However, the guidance presented in this document remains relevant to other compounds for which 1,1-DCE can be considered a surrogate.

TO-15 is a performance-based method prepared by EPA as a guidance document for monitoring subsets of those volatile organic compounds (VOCs) that are mentioned in Title III of the Clean Air Act Amendments of 1990. The TO-15 performance criteria are based on data from existing databases compiled in national monitoring programs (e.g., the Toxics Air Monitoring System [TAMS] and Urban Air Toxics Monitoring Program [UATMP]) using canister-based sampling and benchtop quadrupole mass spectrometers. These performance criteria

provide a method detection limit (MDL), a method replicate precision, and a method audit accuracy. The sampling and analytical approaches are not restricted in any sense as long as the performance criteria are met. Examples of possible approaches to analysis, generation of calibration mixtures, and use of quality control measures (technical acceptance criteria) are provided in the text of TO-15. These examples are intended to be instructive, not prescriptive.

The TO-15 Supplement is currently restricted to canister-based systems for monitoring target compound concentrations lower than the 0.5 parts per billion by volume (ppbv) stated as one of the TO-15 performance criteria. This enhancement of monitoring capability is typically required if monitoring at  $10^{-6}$  risk levels of high-risk compounds must be done. These levels can be quite low as noted in Table 1, which lists the cancer risk levels of the National Air Toxics Assessment (NATA) compounds. The approach taken in the Supplement is to retain the performance criteria of precision and accuracy while reducing the MDLs to meet more stringent data quality objectives (DQOs). An example of an analytical approach taken by CDPHE

**Table 1.** Risk Levels for NATA Compounds (from [www.epa.gov/iris/](http://www.epa.gov/iris/))

#	TO-14 Compounds	TO-14 #	NATA List	E-6 (1 in 1,000,000) Risk Level mg/m <sup>3</sup>	Molecular Weight	Risk Level Pptv
1	Vinyl chloride	4	Yes	$2.3 \times 10^{-4}$	62.50	90.0
2	1,1-Dichloroethene*	8		$2 \times 10^{-5}$	96.94	5.0
3	Dichloromethane	9	Yes	$2 \times 10^{-3}$	84.93	575.8
4	Trichloromethane	14	Yes	$4 \times 10^{-5}$	119.38	8.2
5	1,2-Dichloroethane	15	Yes	$4 \times 10^{-5}$	98.96	9.9
6	Benzene	17	Yes	$1.3 \times 10^{-4}$	78.12	40.7
7	Carbon tetrachloride	18	Yes	$7 \times 10^{-5}$	153.82	11.1
8	1,2-Dichloropropane	19	Yes	Not established	112.99	Not established
9	Trichloroethene	20	Yes	Not established	131.29	Not established
10	<i>cis</i> -1,3-Dichloropropene	21	Yes	$2 \times 10^{-4}$	110.97	44.1
11	<i>trans</i> -1,3-Dichloropropene	22	Yes	$2 \times 10^{-4}$	110.97	44.1
12	1,1,2-Trichloroethane	23		$6 \times 10^{-5}$	133.41	11.0
13	1,2-Dibromoethane	25	Yes	$5 \times 10^{-6}$	187.87	0.7
14	Tetrachloroethene	26	Yes	Not established	165.83	Not established
15	1,1,2,2-Tetrachloroethane	31	Yes	$2 \times 10^{-5}$	167.85	2.9
16	Hexachlorobutadiene	41		$5 \times 10^{-5}$	260.76	4.7
#	Other Compounds	TO-14 #	NATA List	E-6 (1 in 1,000,000) Risk Level mg/m <sup>3</sup>	Molecular Weight	Risk Level pptv
17	Acrylonitrile		Yes	$1 \times 10^{-5}$	53.06	4.6
18	1,3-Butadiene		Yes	$4 \times 10^{-6}$	54.09	1.8
19	Ethylene oxide		Yes	Not established	44.05	Not established

\*Risk level prior to reevaluation.



is presented along with an analytical approach taken by EPA in-house contractor ManTech Environmental Technology, Inc. CDPHE has developed a set of specifications that are used in purchasing analytical services from contract laboratories. These analytical specifications provide practical guidance in achieving the enhanced performance required for high-risk compounds.

EPA, through its in-house contractor, prepared a set of canisters filled with various levels of 1,1-DCE in a mixture and as a single compound in ambient air, as well as canisters filled with humidified zero air. These samples have been analyzed by four laboratories to obtain an idea of the agreement expected and to verify that low concentration levels corresponding to  $10^{-6}$  risk levels can actually be quantified. While these tests provide an example of how well such samples are likely to be analyzed, it does not mean that other laboratories would do better or

worse, or that a non-canister approach to sampling would not do as well or better.

In summary, the Supplement acknowledges the need for sampling and analytical protocols that reduce the MDLs for certain types of measurements and provides examples of achieving this reduction. The analytical guidelines developed by CDPHE for use by their contract laboratories, for example, provide a useful and practical approach for current monitoring applications. The agreement among the four laboratories (see Appendix A) establishes that more than one analytical approach is viable and, furthermore, that the preparation of canisters and standards for sampling 1,1-DCE is possible at low parts per trillion by volume (pptv) levels. The extension to other single compounds and to multiple compounds should be straightforward.

## Chapter 2 Conclusions

1. The TO-15 Supplement provides guidance for sampling and analysis of 1,1-DCE, and by implication other VOCs, in air at levels lower than the TO-15 MDL of 0.5 ppbv, with the specific level depending on the DQOs for the project at hand. The performance criteria are an MDL at the customized DQO levels, replicate precision of at least 25%, and audit accuracy of 30%.
2. The Supplement includes revisions and additions by section to the original TO-15 Method. As an addition to section 10.2.3, two examples of technical approaches to meet the performance criteria are provided. One is the guidance developed during this project by EPA on-site contractor ManTech Environmental Technology, Inc. (Appendix A); the other is a concise restatement of the guidance developed by CDPHE for the analysis of high-risk compounds associated with vapor intrusion (Appendix B).
3. Samples of 30 and 60 pptv of 1,1-DCE in ambient air prepared by ManTech Environmental Technology, Inc., were analyzed by four laboratories, and the results showed that the TO-15 Supplement performance criteria could be met at concentrations as low as 30 pptv. One of the laboratories was the EPA on-site laboratory operated by ManTech, and at least one of the other contract laboratories used the CDPHE guidance.

## Chapter 3 Recommendations

1. The technical acceptance criteria provided in the original TO-15 and in the TO-15 Supplement must be recognized as guidance. Other technical acceptance criteria can be used for meeting the performance criteria of TO-15 and the TO-15 Supplement. This point is evidenced by the close agreement of results obtained by four independent laboratories analyzing identical samples, each using their own standard operating procedures.
2. Laboratories wishing to perform analyses of VOCs at low-pptv levels must exercise diligence in all aspects related to cleanliness (canister cleanup and certification, carryover issues, instrument background levels, etc.). In addition, accurate calibration standards at the appropriate concentrations must be obtained or generated. Finally, the MS method will need to be optimized according to the specific analytical system used and the analyte(s) chosen.
3. Agreement on the audit standards to be used in monitoring low-level VOCs is necessary whether the audit standard is to be the average of analysis results from different laboratories, diluted National Institute of Standards and Technology (NIST)–traceable standards from commercial suppliers, or fundamentally derived standards. For the TO-15 recommendations see section 9.2.
4. Caution should be exercised when working at low-pptv levels due in part to the need for a more rigorous investigation of storage stability and sample integrity issues as well as a general need for more laboratory tests in the low-pptv range of sample concentrations. Extreme conditions of humidity (<15% RH for any sample and high humidity for positive pressure samples) and of co-collected reactive compounds may complicate the sampling and analytical conditions. More experience is needed in monitoring at low-pptv levels.
5. To confirm consistent sampling technique, a number of replicate samples should be collected and analyzed.

## Chapter 4

### Method TO-15 Supplement

### Correspondence to TO-15 Section Numbers

The Method TO-15 supplementary material that applies to the determination of 1,1-DCE at low-pptv concentrations is enumerated below by Method TO-15 section number. Each section is labeled as either a revision or an addition. When a revision is noted, the italicized text is the text that has been revised. The supplementary material is presented in this format to provide clarity for the reader by consolidating the relevant Method TO-15 sections into a concise text.

**1.2 [REVISION]** This method applies to *low-pptv-level* ambient concentrations of 1,1-DCE and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a  $10^{-6}$  or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at  $10^{-6}$  risk concentrations, the total risk may be significantly greater.

#### **3.1 (last bullet) [REVISION]**

- Finally, Compendium Method TO-15 includes enhanced provisions for inherent quality control. *Recommendations for the method include* internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control *should result in* a higher percentage of good data.

**6.2.4 [REVISION]** Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (*a suggested rule of thumb is 100 times the MDL*) sample is encountered, it should be followed by an analysis of humid zero air to check for carryover contamination.

**6.2.5 [REVISION]** In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents should be tested to identify artifact formation (see Compendium Method TO-17 for more information on artifacts *and sorbents*).

**7.3.3 Electronic Mass Flow Controllers. [REVISION]** One 0 to 5 L/min unit *for air* and one or more 0 to 10 mL/min or 0 to 100 mL/min units for *nitrogen (standard cylinder make-up gas)*, depending on the number of cylinders in use for calibration and the dilution requirements.

**8.3.5 [REVISION]** To verify correct sample flow, a “practice” (evacuated) canister is used in the sampling system.

[**Note:** For a subatmospheric sampler, a flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.]

A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is *observed*. The value should *be* within  $\pm 10\%$  of the *correct value*. If not, the sampler mass flow controller control unit should *be adjusted to give the correct sample flow rate*. *If an unusually large adjustment of the mass flow controller control unit is necessary to obtain the correct flow, then other problems such as leaks in the system should be investigated and corrected.*

[**Note:** Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate to compensate for any zero drift.]

Record final flow under “CANISTER FLOW RATE” on the field test data sheet (FTDS).

#### **8.4 Cleaning and Certification Program [ADDITION]**

- Extremely clean and leak-free canisters are key to meeting the TO-15 acceptance criteria at low-pptv levels.
- Temperatures at or above 100 °C, when combined with alternating high vacuum and humidified ultra-clean air purges, are an excellent way to remove contaminants from the canister. Commercially manufactured canister cleaners which incorporate all these features are currently available.

[**Note:** Check with the manufacturer of the canister valve for information on the temperature limits of the valve so as to prevent any damage to the valve.]

- Canisters known to contain high levels of contaminants may be alternately “rough pumped” to moderate vacuum and vented to ambient pressure under a hood for several cycles before the canisters are placed in the cleaning system if there is a possibility that the canister cleaning system itself might become contaminated by the high levels of contaminants in the canisters.
- Canisters filled with humidified ultra-clean air and awaiting cleanliness certification should be allowed to “age” or equilibrate for a minimum of 24 hours, with several days being recommended.
- A canister should be considered clean if the analysis of humidified ultra-clean air reveals no target VOCs above the MDL for those target VOCs. The number of cleaning cycles required to achieve this stringent goal will vary depending on the type and concentration of analytes previously sampled and on the capabilities of the particular cleaning system used.
- A canister should be considered relatively leak-free if after being evacuated to <25 µm Hg, there is a 20 µm Hg or less increase in pressure after a 24-hour or longer period. However, to eliminate the possibility of contamination of cleaned canisters by influx of ambient air prior to sampling, a “zero tolerance” leak policy is recommended.

## 9.2 Preparation of Standards [ADDITION]

- The concentration of a primary standard chosen by a laboratory should be based on the ability of that laboratory to consistently and accurately reproduce working calibration standards over the specific calibration range of that laboratory.
- Certain vendors now offer cylinder standards for specific VOCs at 10-ppb levels and TO-14 mixtures as low as 100 ppbv. Primary standards at these concentrations allow preparation of working standards at the low-pptv level.

[**Note:** Pay close attention to the linear range of the mass flow controllers used to create the standard dilutions.]

### 9.2.2.2 Calibration Standards [ADDITION]

- Working calibration standards should be prepared in a range of concentrations that reflect the entire reporting range for the analytes of interest.

## 10.2.3 [ADDITION 1 – Suggestions for optimization of a mass spectrometry scan method for detection at low-pptv levels]

- Based on the molecular weight of the VOC or VOCs of interest, the scan range for the mass spectrometry (MS) method may be narrowed. For ion trap instruments in particular, the background mass as well as the segment radio-frequency value and the automatic gain control prescan storage level may be increased.
- The scan time for the MS method may be reduced in order to provide better resolution of peaks. However, most systems will have a minimum scan time threshold below which sensitivity decreases in response to shorter scan times. Optimization is the key word.
- The above adjustments to a working MS method to enhance sensitivity (i.e., lower the MDL) should only be implemented after a thorough investigation of their individual and collective effects on system response to the target analytes.
- An example of an enhanced MS scan method for the specific detection of 1,1-DCE at low-pptv levels is given in Appendix A of this report.

## [ADDITION 2 – Suggestions for optimization of MS-selected ion monitoring (SIM) and MS scan methods for detection at low-pptv levels]

- An example of guidance developed by CDPHE for use in the analysis of canister-based samples for high-risk VOCs is given in Appendix B.

## 10.5 Initial Calibration [ADDITION]

- If the analytical range of interest is 20 to 500 pptv, then the five calibration concentrations chosen might be 10, 25, 50, 200, and 500 pptv. For calibrations over a large range, more than five calibration concentrations may be selected.

[**Note:** Levels as high as or higher than 500 pptv may present carryover problems in some systems for subsequent analyses at low-pptv levels. It is suggested that a humidified ultra-clean air blank be run following any analysis in which the level of any target analyte is 100 times its MDL or greater.]

- One of the calibration points from the initial calibration curve should be at the same concentration as the daily calibration standard (e.g., 50 pptv).

### 10.6 Daily Calibration [ADDITION]

- The daily calibration standard (e.g., 50 pptv) should contain all the target compounds.

### 10.7 Blank Analyses [ADDITION]

- The sorbents used in sorbent preconcentrators will often introduce a background into each analysis upon thermal desorption. It is also possible that there could be a certain amount of outgassing from components in the analytical system. When running ppbv-level analyses, these levels should be negligible. However, at low-pptv levels this background contamination can become significant. It is important to characterize this system background through identification and quantification of the specific contaminants. This could be accomplished by analyzing a series of 10 canisters filled with humidified ultra-clean air or by 10 consecutive analyses of humidified ultra-clean air from a continuously purged clean manifold. The results would be compiled into a spreadsheet and any outliers (high results implying a true background in the canister) could be eliminated. From the remaining results an average background level for each contaminant could be calculated. This background level for each contaminant could then be subtracted from the analytical results of actual samples in order to provide the most accurate data.
- A daily laboratory method blank should still be run as a way to check for any new contamination possibly

introduced through the sample analysis process. In addition, the daily laboratory method blank acts as a humid purge of the analytical system.

**11.1.3 [ADDITION]** The recommendation for extending the MDL for 1,1-DCE to a low-pptv concentration while maintaining the standard Method TO-15 requirements for replicate precision and audit accuracy is based on an EPA-sponsored assessment of the capabilities of laboratories that are currently analyzing ambient air samples containing 1,1-DCE at pptv concentrations. The data supporting replicate precision within 25% have been extracted from the Appendix A report and reproduced for the reader's convenience in Tables 2 through 5. As a measure of audit precision, the excellent agreement among four laboratories analyzing replicate samples of ambient air containing low-pptv levels of 1,1-DCE (Tables 2–5) was considered. For the 30-pptv samples (Tables 2 and 3), the relative standard deviation (RSD) of 18 measurements was 5.5%. For the 60-pptv samples (Tables 4 and 5), the RSD of 12 measurements was 6.8%. Obviously, there exists a need in the VOC analysis community for a NIST-certified gaseous audit standard of 1,1-DCE at low-pptv concentrations so that a true audit may be conducted to ensure that a laboratory meets the Method TO-15 performance criteria for audit accuracy. Despite the fact that a true audit could not be conducted, the agreement among the four laboratories, each of which used varying approaches to instrument calibration, is a measure of audit accuracy. Taking the mean of all measurements made by the laboratories as the “true” concentration, the percent differences between each of the measurements made by the four laboratories and the “true” concentration for 1,1-DCE ranged from 0 to 17%.

**Table 2.** Low-Level Method TO-15 SIM Analytical Results for Ambient Air Spiked with 1,1-DCE (results in pptv)

Compound	CANISTER		A-701	785	GA-B	RSD	RL	120	01578	MTC-22	RSD	RL	208	013	454	RSD	PQL
	LAB																
1,1-Dichloroethene	30	30	30	0.0	10	28	29	27	3.6	10	27	29	29	4.2	10		

RSD = relative standard deviation  
 RL = reporting limit  
 PQL = practical quantitation limit

**Table 3.** Low-Level Method TO-15 Scan Analytical Results for Ambient Air Spiked with 1,1-DCE (results in pptv)

Compound	CANISTER		A-701	785	GA-B	120	01578	MTC-22	208	013	454	RSD	PQL
	LAB												
1,1-Dichloroethene	32	27	30	30	32	29	32	31	29	5.7	18		

RSD = relative standard deviation  
 PQL = practical quantitation limit

**Table 4. Low-Level Method TO-15 SIM Analytical Results for Ambient Air Spiked with a Chlorinated Gas Mixture Containing 1,1-DCE (results in pptv)**

Compound	CANISTER		Percent Difference		RL		Percent Difference		RL		Percent Difference		PQL
	LAB	N-3	726		096	727		9682-B	9677-B				
1,1-Dichloroethene	1	1	1	1	2	2	2	3	3	3	3	3	3
		59	59	0.0	10	60	53	12.4	10	60	54	10.5	10

RL = reporting limit

PQL = practical quantitation limit

**Table 5. Low-Level Method TO-15 Scan Analytical Results for Ambient Air Spiked with a Chlorinated Gas Mixture Containing 1,1-DCE (results in pptv)**

Compound	CANISTER		Percent Difference				RSD		PQL
	LAB	N-3	726	096	727	9682-B	9677-B		
1,1-Dichloroethene	4	4	4	4	4	4	4	4	
		69	59	60	61	57	62	6.7	18

RSD = relative standard deviation

PQL = practical quantitation limit

**Appendix A**  
**Determination of Low-pptv Concentrations of 1,1-Dichloroethene in**  
**Ambient Air Collected in Specially Prepared Canisters and Analyzed by**  
**Gas Chromatography/Mass Spectrometry (GC/MS)**

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## Abstract

An optimized mass spectrometry (MS) scan method was developed in this laboratory for the detection of 1,1-dichloroethene (1,1-DCE) at low parts per trillion by volume (pptv) levels. A cylinder standard of 10 parts per billion (ppb) 1,1-DCE in nitrogen was purchased from a commercial vendor and is used for the preparation of canister standards of 1,1-DCE at concentrations as low as 2.5 pptv. A method detection limit (MDL) of 6 pptv was determined for 1,1-DCE using the optimized scan method, and linearity of detector response over a range of 10 to 200 pptv was demonstrated. Next, an experiment was designed to assess the capabilities of several contract laboratories that currently offer low-level Method TO-15 type analyses of 1,1-DCE and other volatile organic carbons (VOCs) to their clients. Despite differences in instrumentation, MS mode of operation (SIM or scan), MS tuning methods, and calibration standards and techniques used by the four laboratories, excellent agreement was achieved for the determination of 1,1-DCE at nominal concentrations of 30 and 60 pptv in canister samples of spiked ambient air. The excellent agreement for 1,1-DCE is indicated by relative standard deviations of replicate measurements of  $\leq 7\%$ , computed for experiments in which three to 18 measurements were available. Replicate precision results (calculated as percent difference) for those experiments in which two samples were analyzed by each individual contract laboratory were  $< 13\%$  for 1,1-DCE.

The excellent agreement in analytical results for the four laboratories that analyzed canister samples of ambient air containing 1,1-DCE at 30 and 60 pptv demonstrates that Method TO-15 has been successfully extended to low-pptv concentrations of analytes. MDLs of 0.5–6 pptv and reporting/quantitation limits of 10–20 pptv have been achieved. Additionally, since the four laboratories used different approaches for the low-level Method TO-15 analyses, the results support the premise of a performance-based methodology that focuses on MDLs, audit accuracy within 30%, and replicate precision within 25% as indicators of method acceptability.

## **Preface**

The EPA was asked by William P. Yellowtail, the Regional Administrator of Region 8, to review protocols from the Colorado Department of Public Health and Environment (CDPHE) for determining low-pptv concentrations of 1,1-dichloroethene (1,1-DCE) in ambient air in support of vapor intrusion monitoring. Tom Aalto of Region 8 coordinated the effort with EPA, and technical input on the CDPHE method was provided by Ken Niswonger and Edgar Ethington of CDPHE. The effort was funded under EPA's Regional Monitoring Initiative. In response to this request, NERL, EPA developed a work assignment to ManTech Environmental Technology, Inc., the current on-site contractor to the National Exposure Research Laboratory (NERL) at the EPA facility in Research Triangle Park, NC. The task consisted of: (1) developing a capability to support monitoring of 1,1-DCE at low-pptv concentrations at the EPA laboratory facilities; (2) documenting the existence of similar capabilities at representative contract laboratories; and (3) providing a TO-15 supplement that contains guidance for meeting the enhanced performance criteria.

## **Foreword**

This technical report presents the results of work performed by ManTech Environmental Technology, Inc., under Contract 68-D-00-206 for the Human Exposure and Atmospheric Sciences Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency (EPA), Research Triangle Park, NC. This technical report has been reviewed by ManTech Environmental Technology, Inc., and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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## Acronyms and Abbreviations

%D	percent difference	m	meter
µm	micrometer	mm	millimeter
1,1-DCE	1,1-dichloroethene	MS	mass spectrometry
AGC	automatic gain control	m/z	mass to charge ratio
amu	atomic mass units	NIST	National Institute of Standards and Technology
autoGC-MS	automated gas chromatograph/mass spectrometer	PAMS	Photochemical Assessment Monitoring Stations
cc	cubic centimeter	ppbv	parts per billion by volume
CDPHE	Colorado Department of Public Health and Environment	pptv	parts per trillion by volume
CV	coefficient of variation	PQL	practical quantitation limit
ECD	electron capture detector	psig	pounds per square inch gauge
EPA	U.S. Environmental Protection Agency	RF	radio frequency
FID	flame ionization detection	RH	relative humidity
g	gram	RL	reporting limit
GC	gas chromatography	RSD	relative standard deviation
h	hour	sccm	standard cubic centimeters per minute
HSA	humidified scientific-grade air	SD	standard deviation
i.d.	inside diameter	SIM	selected ion monitoring
LMB	laboratory method blank	SRM	Standard Reference Material
MDL	method detection limit	VOCs	volatile organic compounds
		°C	degrees Celsius

## Chapter 1 Introduction

The U.S. Environmental Protection Agency (EPA) Method TO-15 is titled “Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)” and is a part of the EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. It is a performance-based method consisting of three performance criteria and guidance (including a suggested set of technical acceptance criteria) to verify analytical system control in order to meet the performance criteria.

In the current effort, Method TO-15 has been modified to reduce the method detection limits (MDLs) while maintaining the specifications for replicate precision and audit accuracy. Suggestions for technical approaches that will enhance analytical system performance so as to meet replicate precision

and audit accuracy at the lowered MDLs have been provided in the supplement. In addition, guidance on sampling using canister-based systems is provided. Finally, the achievement of the performance criteria at representative laboratories has been demonstrated.

This report documents the experimental evidence that is the basis for the supplement to Method TO-15 and is complementary to the supplement. The essential result of this report and the Method TO-15 Supplement is a modified Method TO-15 for determination of parts per trillion by volume (pptv) concentrations of 1,1-dichloroethene (1,1-DCE) (and by implication other VOCs) and the verification that laboratories using different technical acceptance criteria can meet a set of performance criteria consisting of pptv MDLs while retaining the replicate precision and audit accuracy requirements of Method TO-15.

## Chapter 2 Conclusions

An optimized MS scan method was developed in this laboratory for the detection of 1,1-DCE at low-pptv levels. A cylinder standard of 10 parts per billion (ppb) 1,1-DCE in nitrogen was purchased from a commercial vendor and is used for the preparation of canister standards of 1,1-DCE at concentrations as low as 2.5 pptv. An MDL of 6 pptv was determined for 1,1-DCE using the optimized scan method, and linearity of detector response over a range of 10 to 200 pptv was demonstrated. An informal storage stability study for low-pptv concentrations of 1,1-DCE in air samples collected and stored in canisters manufactured by several vendors was conducted.

An experiment was designed to assess the capabilities of several contract laboratories that currently offer low-level Method TO-15 type analyses of 1,1-DCE and other VOCs to their clients. Despite differences in instrumentation, MS mode of operation (selected ion monitoring [SIM] or scan), MS tuning methods, and calibration standards and techniques used by the four laboratories, excellent agreement was achieved for the determination of 1,1-DCE at nominal concentrations of 30 and 60 pptv in canister samples of spiked ambient air. The excellent agreement for 1,1-DCE is indicated by relative standard deviations (RSDs) of replicate measurements of  $\leq 7\%$ , computed for experiments in which three to 18 measurements were available. The RSDs of three replicate quantitative measurements of the additional VOCs (dichloromethane,

trichloromethane, 1,1,1-trichloroethane, benzene, and tetrachloroethene) measured by each individual contract laboratory were  $<12\%$ . Replicate precision results (calculated as percent difference) for those experiments in which two samples were analyzed by each individual contract laboratory were  $<13\%$  for 1,1-DCE and  $<15\%$  for 17 of 20 comparisons for the additional VOCs (chloroethene, dichloromethane, *cis*-1,2-dichloroethene, trichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, trichloroethene, and tetrachloroethene). The analytical results for 1,1-DCE from the contract laboratories showed better agreement for the low-level Method TO-15 type analyses than they did for the Method TO-14 analyses of canister samples containing 60 VOCs at nominal concentrations of 5 parts per billion by volume (ppbv).

The excellent agreement in analytical results for the four laboratories that analyzed canister samples of ambient air containing 1,1-DCE at 30 and 60 pptv demonstrates that Method TO-15 has been successfully extended to low-pptv concentrations of analytes. MDLs of 0.5–6 pptv and reporting/quantitation limits of 10–20 pptv have been achieved. Additionally, since the four laboratories used different approaches for the low-level Method TO-15 analyses, the results support the premise of a performance-based methodology that focuses on MDLs, audit accuracy within 30%, and replicate precision within 25% as indicators of method acceptability.



## Chapter 3 Recommendations

Recommendations for further sample integrity studies and the need for gaseous audit standards of VOCs at pptv concentrations are discussed below. In addition, practical advice is offered in several areas of importance for sampling and analysis of pptv concentrations of 1,1-DCE and other VOCs.

(1) Further sample integrity studies are needed in the following areas:

- *Storage stability studies.* A well-controlled storage stability study for samples of ambient air containing pptv concentrations of 1,1-DCE and additional VOCs that are collected and stored in canisters is needed. The experiments conducted for this report were informal “before and after” type experiments for a small number of samples. A more thorough experiment in which a statistically significant number of samples of ambient air containing pptv-level VOCs stored in canisters are analyzed on days 0, 2, 4, 7, 15, and 30 is needed. The experiment should be designed to include canisters from various vendors.
- *Investigation of initial losses.* A sample integrity study to investigate the possibility of initial losses of pptv concentrations of VOCs to the canister walls is needed. In the experiments discussed in this report, a small difference was observed in the real-time spiked ambient air measurements for 1,1-DCE that were made with the EPA autoGC/MS system using the optimized Method TO-15 scan method while the canister samples were being prepared as compared to the later measurements for the canister samples. For the samples of ambient air spiked with 1,1-DCE, the mean concentration of 1,1-DCE was 33 pptv for the real-time measurements versus 30 pptv for the canister measurements. For the samples of ambient air spiked with a mixture of chlorinated VOCs, the mean concentration of 1,1-DCE was 68 pptv for the real-time measurements versus 62 pptv for the canister measurements. Additional experiments are needed to investigate this difference between the real-time and canister measurements.

(2) A gaseous audit standard of pptv concentrations of 1,1-DCE and other VOCs is needed to determine whether a laboratory can meet the Method TO-15 performance criteria for audit accuracy. For this report, the results of analyses of spiked ambient air samples by four laboratories are used as a measure of audit accuracy. However, a National Institute of Standards and Technology (NIST)-certified audit standard is needed to evaluate those laboratories who analyze VOCs according to the Method TO-15 Supplement for analysis of low-pptv concentrations of 1,1-DCE.

(3) Practical advice for sampling and analysis of pptv concentrations of 1,1-DCE and other VOCs is offered here as a service to the reader:

- As expected, the preparation and analysis of air samples containing pptv levels of VOCs requires that the analytical and standards preparation systems be extremely clean. Laboratory personnel must take great care to ensure that the sample preparation system and/or analytical system is thoroughly purged with humidified air or nitrogen after higher concentrations of VOCs have been present in the systems and prior to preparation and/or analysis of low-pptv-level VOCs. Verification of cleanliness with a laboratory method blank (LMB) of humidified air or nitrogen is needed even if the samples that were prepared or analyzed previously contained VOCs at low-ppbv concentrations. Humidity is an essential factor in the cleanliness verification process because analysis of a dry sample does not always yield an accurate characterization of a system’s cleanliness.<sup>1,2</sup> An example of this is seen in this laboratory with the EPA autoGC/MS system in which analysis of a helium blank sample shows the system to be free of artifact peaks whereas analysis of a sample of humidified air results in the detection of artifact peaks such as benzene that are associated with the use of the multisorbent traps.

- Particular care must be given to canister cleanliness when samples containing pptv concentrations of 1,1-DCE and other VOCs are collected and analyzed. Once a laboratory has established an MDL and a practical quantitation limit (PQL) for an analyte such as 1,1-DCE, the sampling canisters should be subjected to a blank certification process to ensure that the analyte is not present in the canister at a concentration that is greater than the MDL for that analyte. The blank certification process should be conducted by filling a clean canister with humidified air or nitrogen and allowing the canister to “age” for a minimum of 24 hours prior to analysis. In the experiments conducted for this report, canisters in this laboratory that had previously been used for multicomponent VOC standards at concentrations as great as 40 ppbv were successfully cleaned and used for analysis of 1,1-DCE at concentrations as low as 5 pptv. Additionally, the results of the canister cleanliness tests that were conducted on canisters rented from the contract laboratories showed that the canisters generally were clean with respect to the target compounds. However, a non-target compound (toluene) was observed in one canister at 714 pptv, a concentration that is greater than that specified under Method TO-14 and TO-15 technical acceptance criteria. As an additional measure of quality control with respect to canister cleanliness, laboratory staff may wish to designate that specific canisters be reserved for use with samples containing ultra-trace-level concentrations of specific VOCs.
- While conducting the experiments discussed in this report, laboratory staff noted that a greater amount of time was required for thorough equilibration of the analytical sampling train when standards containing pptv concentrations of VOCs were analyzed as compared to the equilibration time required for standards containing ppbv concentrations of VOCs. Obviously, this observation is system specific and is dependent on both the length of tubing in the analytical system and the complexity of the individual analytical system. The issue of equilibration is mentioned here simply to generate awareness of a potential problem.

## Chapter 4

# Experimental Method and Results

Under contract to EPA, ManTech Environmental Technology, Inc., was given the task of evaluating the ability of several contract laboratories to determine 1,1-DCE at low-pptv concentrations in air samples. The results of this evaluation would be used to determine whether EPA Method TO-15 could be extended successfully to the analysis of low-pptv concentrations of 1,1-DCE. In response to this task, ManTech developed a work plan that called for (1) developing the capability of preparing pptv-level calibration standards for 1,1-DCE; (2) refining our current TO-15 GC/MS method for the detection of 1,1-DCE at pptv levels; (3) evaluating the cleanliness of our canisters and analytical system for monitoring pptv concentrations of 1,1-DCE; (4) determining the storage stability of 1,1-DCE at pptv levels in air samples collected and stored in canisters; and (5) evaluating the capabilities of contract laboratories that are already providing commercial analyses of selected chlorinated VOCs, including 1,1-DCE, at low-pptv levels for their clients.

### 4.1 Calibration Standard

Preparation of calibration standards of VOCs at concentrations of 0.5 to 100 ppbv has been accomplished in this laboratory by dynamic dilution of 2 to 10 parts per million concentrations of VOCs in high-pressure cylinders using scientific-grade air (National Specialty Gases, Durham, NC) and mass flow controllers.<sup>3</sup> In order to use this same technique for preparation of low-pptv concentrations of 1,1-DCE, a 10-ppb standard of 1,1-DCE in nitrogen in a high-pressure cylinder was purchased from Spectra Gases Inc. (Branchburg, NJ). An analysis value of 10 ppb was reported by Spectra Gases for 1,1-DCE. Dynamic dilution of the 10-ppb standard of 1,1-DCE allows for the preparation of calibration standards at concentrations as low as 2.5 pptv.

The cylinder concentration of 10 ppb for 1,1-DCE was verified by analysis in an independent laboratory within EPA. In that laboratory, a GC with flame ionization detection (FID) per carbon approach is employed and the instrument calibration is based on a NIST/Standard Reference Material (SRM) propane in air cylinder.<sup>4</sup> The concentration of the standard sampled directly from the cylinder in February 2002 was determined by the GC-FID method to be 10.10 ppbv  $\pm$ 0.98% coefficient of variation (CV). The cylinder was reanalyzed in June 2002, and the concentration of 1,1-DCE was determined to be 10.23 ppbv  $\pm$ 1.24% CV. In September 2002, a third

analysis of the 1,1-DCE standard was performed in the same GC-FID laboratory. For this analysis, the standard was provided in a canister that had been prepared by injecting 90  $\mu$ L of water into the evacuated canister and then pressurizing the canister with the gas standard directly from the cylinder. The GC-FID analytical result for the canister standard was 10.52 ppbv  $\pm$ 0.58% CV based on the NIST/SRM propane standard calibration.

For the experimental work discussed in this report, the nominal value of 10 ppb was used for the standard cylinder to calculate concentrations of 1,1-DCE canister standards prepared by dynamic dilution.

## 4.2 Method Development

### 4.2.1 Optimization of the MS Scan Method

An autoGC/MS system was operated in this laboratory to determine VOCs in whole air samples using a modified Method TO-15 approach.<sup>5</sup> The autoGC/MS system consisted of a XonTech 930 organic vapor concentrator, which uses two multisorbent traps and a XonTech 940 cryogenic concentrator (RM Environmental Systems, Inc., Van Nuys, CA), interfaced to a Varian 3800 GC and Saturn 2000 ion trap MS (Varian Inc., Walnut Creek, CA). The multisorbent traps contained 0.05 g of Tenax GR, 0.04 g of Carbotrap, and 0.51 g of Carbosieve S III. A total sample volume of 285 cc was collected; however, a 4:1 split at the head of the column reduced the sample volume that was routed to the detector from 285 to 57 cc. A 60 m by 0.32 mm by 1.0  $\mu$ m DB-1 capillary column (Agilent Technologies, Wilmington, DE) was used for separation of analytes. The GC oven temperature was programmed as follows: 35  $^{\circ}$ C for 5 min, a 6  $^{\circ}$ C/min ramp to 210  $^{\circ}$ C, and a 0.84-min hold at 210  $^{\circ}$ C, for a total analysis time of 35 min. The standard MS operating parameters are listed in Table 4-1. In the Saturn software, quantitation ions are used to compute the concentrations of the analytes after they are identified within a specific retention time window by fitting the spectra of the compound of interest to spectra in a user-generated calibration library. The quantitation ion for 1,1-DCE was 61.

In order to enhance the sensitivity of the method for 1,1-DCE, the standard analytical procedure described above was modified by adjusting the MS parameters as shown in Table 4-2.

**Table 4-1.** Saturn 2000 MS Operating Conditions<sup>6</sup>

Scan range, amu	26–300
Scan rate, s/scan	0.8 (3 $\mu$ scans per analytical scan)
Background mass, amu	25
Segment breaks <sup>a</sup>	70/78/150
Segment tune factors <sup>b</sup>	120/70/100/70 (segment time, %) 25.0/25.0/25.0/25.0 (segment radio frequency [RF], V)
Automatic gain control target	15000-20000
Emission current, $\mu$ A	15

<sup>a</sup>The segment breaks recommended by Varian for our mass range and compounds of interest divide the mass range into the following four segments: 26–70, 71–78, 79–150, and 151–300 m/z.

<sup>b</sup>The segment tune factor determines the actual ionization time for one segment; segment RF is an RF voltage that is used to hold ions in the trap during the ionization period.

**Table 4-2.** Adjustments Made to Saturn 2000 MS Operating Parameters

	Standard Method	1,1-DCE Method
Scan range, amu	26–300	47–110
Scan time, s/scan	0.8	0.4
Background mass, amu	25	45
Segment RF values	25.0	45.0
AGC prescan storage level	25.0	43.0

### 4.2.2 Method Detection Limits

The MDL for 1,1-DCE had been determined with our standard autoGC/MS analytical method in earlier experiments to be 180 pptv.<sup>3</sup> In more recent unpublished experiments, the MDL was determined to be 100 pptv. For the current task, MDLs for 1,1-DCE were determined using the autoGC/MS system and the optimized MS method. To determine the MDL, a canister standard of 1,1-DCE at 23 pptv in a humidified air matrix was analyzed seven times on each of the XonTech 930 multisorbent traps. The MDLs were calculated by using the following formula which is defined in the *Federal Register*:

$$\text{MDL} = t_{(n-1, 1-\alpha = 0.99)}S$$

where  $S$  is the standard deviation (SD) of replicate analysis and  $t$  is the Student's  $t$ -value appropriate to a 99% confidence level and a SD estimate with  $n - 1$  degrees of freedom ( $t = 3.143$ ). The MDLs were determined to be 7 and 5 pptv for traps 1 and 2, respectively. The results of the MDL experiment are listed in Table 4-3. As defined in Method TO-15, section 10.7.5, the quantitation limits ( $3 \times \text{MDL}$ ) for this method are 21 and 15 pptv for traps 1 and 2, respectively. For the discussion that follows, a mean MDL of 6 pptv and a mean quantitation limit of 18 pptv will be used.

**Table 4-3.** Results of MDL Experiment—23 pptv 1,1-Dichloroethene Standard

	Trap 1	Trap 2
	23	23
	27	23
	28	22
	26	22
	24	22
	23	19
	23	20
Mean (n=7)	25	22
SD	2.1	1.5
MDL (pptv)	7	5

### 4.2.3 Linearity of Response

Linearity of response on our autoGC/MS system using our standard MS method has been documented for 1,1-DCE over a range of 0.5 to 40 ppbv. For this work, canister standards of 1,1-DCE at nominal concentrations of 10, 25, 100, and 200 pptv were prepared and analyzed using the autoGC/MS system. A linear system response to the standards in the range of 10 to 200 pptv was demonstrated. Graphs of the trap 1 and trap 2 data with linear regression results are shown in Figures 4-1 and 4-2.

### 4.3 Cleanliness Issues

To verify the cleanliness of our analytical system and canisters, multiple analyses of various samples were performed using the optimized method for 1,1-DCE. Analyses of helium blank samples collected by placing the preconcentrator in helium blank mode, analyses of humidified scientific-grade air (HSA) in canisters, and analyses of a nominal 10-ppbv Photochemical Assessment Monitoring Stations (PAMS)/terpenes canister standard all resulted in either nondetection of 1,1-DCE or detection of 1,1-DCE below the quantitation limit of 18 pptv. Additionally, ambient air samples were analyzed from the manifold in the mobile laboratory using the modified method for enhanced detection of 1,1-DCE. Concentrations of 1,1-DCE ranged from not detected to approximately 20 pptv (which is just above the quantitation limit) in these samples.

In the middle of the study, the trap 2 results for pptv concentrations of 1,1-DCE began to exhibit a positive bias. In an effort to correct the problem of divergence of trap response, a new set of multisorbent traps was installed on the Model 930 concentrator. Similar results were observed for the new set of traps, and we are unable to explain the bias in the trap 2 results. For this reason, we have chosen to report only the trap 1 analytical results for the low-pptv concentrations of 1,1-DCE that were determined using the optimized MS method.

#### 4.4 Informal Storage Stability Studies

An informal storage stability study was conducted for canister samples of HSA containing 10, 25, 100, and 200 pptv of 1,1-DCE. The concentration of 1,1-DCE in 10 canisters from

various vendors compared well from the beginning of the two-month study until the end, but the 1,1-DCE concentration in three canisters from one vendor had decreased substantially by the end of the study.

Figure 4-1. Linearity Plot for 1,1-Dichloroethene, Trap 1

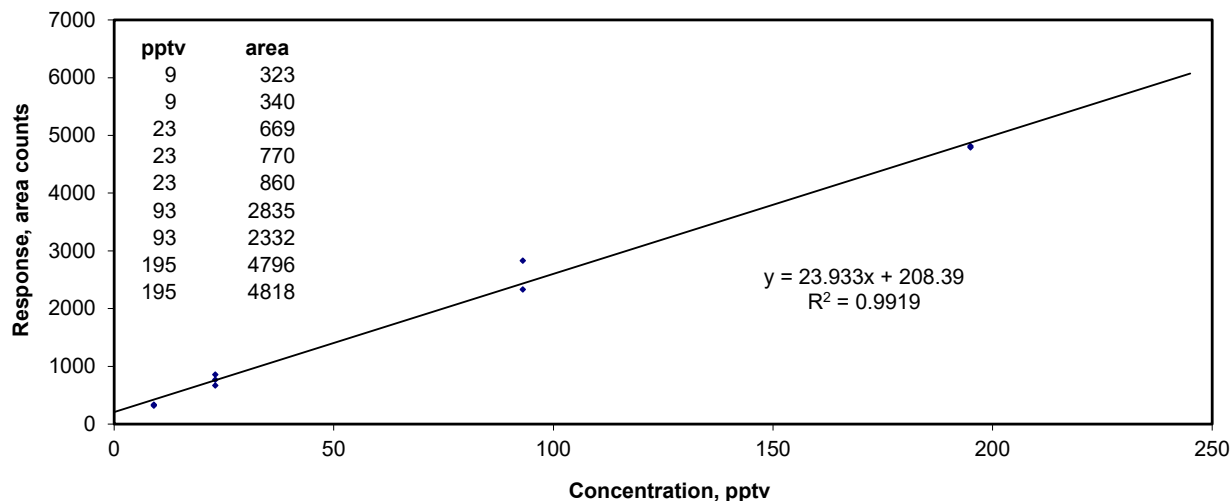
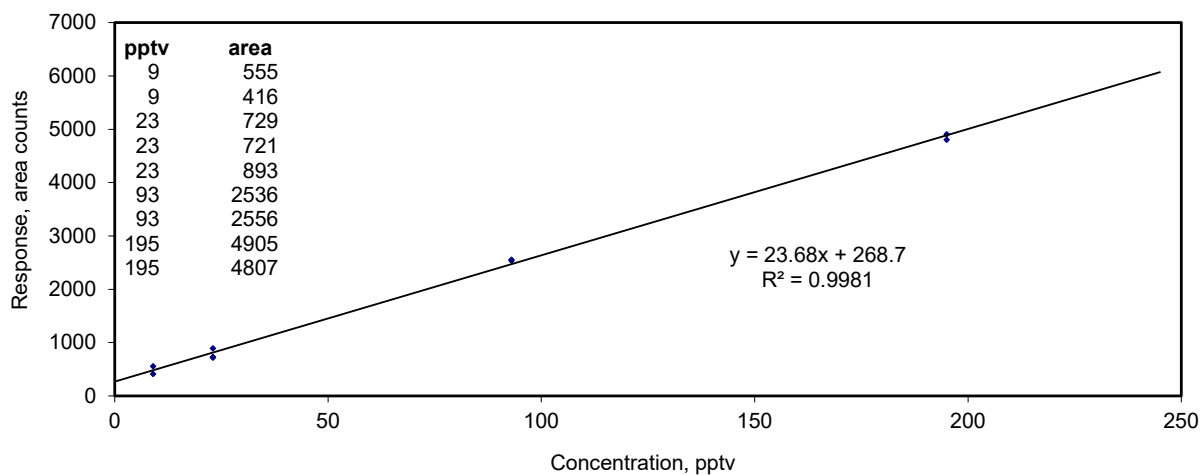


Figure 4-2. Linearity plot for 1,1-Dichloroethene, Trap 2



## Chapter 5

# Contract Laboratory Experiment

### 5.1 Experimental Design

An experiment was designed to assess the capabilities of three contract laboratories that provide Method TO-15 type analyses for pptv concentrations of 1,1-DCE in air samples, but *without their knowledge*. The rationale for conducting the experiment in this manner was to ensure that the samples and analytical results would be treated the same as any other samples that the laboratories might receive. The experiment would then result in “real-world” data suitable for use in determining the performance criteria that are necessary to produce valid measurements for low-pptv concentrations of target VOCs. A second criterion for the experiment was that it be conducted with the expenditure of a reasonable amount of money for sample analyses. With these two criteria in mind, an experimental plan was developed that required the preparation of four sets of samples to validate the performance of the laboratories with respect to (1) the cleanliness of their canisters, (2) their ability to determine 1,1-DCE at 20–40 pptv in a humid ambient air matrix, (3) their ability to determine 1,1-DCE at 50–80 pptv in the presence of a mixture of 14 chlorinated VOCs in a humid ambient air matrix, and (4) their ability to determine 1,1-DCE at low-ppbv levels in the presence of ppbv levels of 60 hydrocarbons in a synthetic air matrix.

### 5.2 Experimental Method

In preparation for the experiment, the three contract laboratories were contacted, and purchase orders were prepared for rental of three canisters from each laboratory as well as for the analysis of nine canister samples by each laboratory.

In our laboratory, calibration standards for the autoGC/MS system were prepared in canisters and included a 10-ppbv PAMS/terpenes standard, a 10-ppbv 1,1-DCE standard, a 500-pptv TO-14 standard, and a 100-pptv 1,1-DCE standard. Additionally, 18 canisters were cleaned for use in the experiment. The canister filling pump apparatus, which consisted of a Metal Bellows Corporation (Sharon, MA) Model MB-151 pump, a 500 sccm Tylan mass flow controller (Millipore Corporation, Bedford, MA), .25-inch stainless steel tube fittings, and .25-inch FEP

tubing, was purged thoroughly with HSA from the dynamic dilution manifold in preparation for the experiments. Canisters of HSA were prepared and analyzed to verify the cleanliness of the manifold and canister filling pump system.

By using a glass manifold in our mobile laboratory that is set up to continually pull in ambient outdoor air,<sup>7</sup> we were able to spike the ambient air by using high-pressure cylinders of either 1,1-DCE or a mixture of 14 chlorinated VOCs that contained 1,1-DCE. The flow rates of the spike gases from the cylinders were controlled with mass flow controllers. The spiked ambient air in the manifold was monitored using the autoGC/MS system to determine the appropriate mass flow controller settings that were needed to achieve the target 1,1-DCE concentrations for the experiment.

### 5.3 Canister Sample Preparation

The canister sample preparation schedule was carefully planned to prevent the possibility of carryover of VOCs in the analytical systems and the canister filling pump system from one experiment to the following experiments. This was accomplished by pressurizing the sets of canisters with air samples containing the lowest concentrations of VOCs at the start of the sample preparation portion of the experiment and by pressurizing the set of canisters with the greatest concentration of VOCS at the end of the sample preparation portion of the experiment. The canister sample preparation procedures for each of the four samples are described below.

#### 5.3.1 Test of Canister Cleanliness

Initially, the nine canisters rented from the three contract laboratories were pressurized simultaneously with HSA from the dynamic dilution manifold. The humidity and temperature of the air in the manifold were 35% RH and 25.3 °C during the filling cycle. The canisters were pressurized to 23 psig over a 6-h period. The GC-FID system with an electron capture detector (ECD) was used to monitor the dynamic dilution manifold as the canisters were being filled.

### **5.3.2 Test of Ability to Determine 1,1-DCE at 20–40 pptv in a Humid Ambient Air Matrix**

The filling pump apparatus was moved to the mobile laboratory, and nine canisters were pressurized simultaneously with ambient air spiked with 1,1-DCE from the manifold in the mobile laboratory. The humidity and temperature of the air in the manifold were 60% RH and 25.3°C during the filling cycle. The canisters were pressurized to 17 psig over a 5-h period. The autoGC/MS system was used to analyze the air in the manifold on an hourly basis as the canisters were being pressurized from the manifold. The concentrations of 1,1-DCE in the trap 1 samples collected during the 6-h period bracketing the fill cycle were 32, 30, and 38 pptv, with a mean concentration of 33 pptv.

### **5.3.3 Test of Ability to Determine 1,1-DCE at 50–80 pptv in the Presence of a Mixture of 14 Chlorinated VOCs in a Humid Ambient Air Matrix**

Next, six canisters were pressurized simultaneously with ambient air spiked with a mixture of chlorinated compounds, one of which was 1,1-DCE, from the manifold in the mobile laboratory. The following are the 14 chlorinated compounds in the spike gas mixture:

- Chloroethene
- 1,1-Dichloroethene
- 1,1,2-Trichloro-1,2,2-trifluoroethane
- Trichloromethane
- 1,2-Dichloroethane
- 1,1,1-Trichloroethane
- Carbon tetrachloride
- Trichloroethene
- *cis*-1,3-Dichloropropene
- *trans*-1,3-Dichloropropene
- 1,2-Dibromoethane
- Tetrachloroethene
- Chlorobenzene
- Benzyl chloride

The humidity and temperature of the air in the manifold were 70% RH and 25.0°C during the canister filling cycle. The six canisters were pressurized to 16 psig over a 3.5-h period. The autoGC/MS system was used to analyze the air in the manifold on an hourly basis as the canisters were being pressurized from the manifold. The concentrations of 1,1-DCE in the trap 1 samples collected during the time period bracketing the fill cycle were 71 and 66 pptv, with a mean concentration of 68 pptv.

### **5.3.4 Test of Ability to Determine 1,1-DCE at Low-ppbv Levels in the Presence of ppbv Levels of 60 Hydrocarbons in a Synthetic Air Matrix Using a Method TO-14 Analysis**

Finally, the filling pump apparatus was returned to the laboratory, and three canisters were pressurized from the dynamic dilution manifold with 10 ppbv of a 60-component PAMS/terpenes mixture. The humidity and temperature of the air in the manifold were 35% RH and 25.5 °C during the canister filling cycle. The three canisters were pressurized to ~1 psig over a 50-min period. Afterwards, these three canisters were vented to 0 psig and then pressurized to 15 psig with the 10-ppb cylinder standard of 1,1-DCE in order to generate a final nominal concentration of 5 ppbv per compound for both the PAMS/terpenes 60-component mixture and 1,1-DCE. The GC-FID/ECD system was used to monitor the contents of the dynamic dilution manifold while the canisters were being pressurized with the PAMS/terpenes mixture.

## **5.4 Canister Sample Analyses**

Following canister sample preparation, all 27 canister samples were analyzed on the autoGC/MS system on both of the multi-sorbent traps, for a total of 54 analyses. The 15 spiked ambient air canister samples were analyzed using the DCE method, which is the MS scan method that was optimized for detection of 1,1-DCE and is discussed in section 4.2.1. The nine HSA canister samples were analyzed using both the DCE method and the TO-15 method, which is the standard MS scan method used in this laboratory and is also discussed in section 4.2.1. The use of the two analytical methods for the HSA samples allowed the determination of 1,1-DCE at low-pptv levels as well as a determination of canister cleanliness for additional VOCs. HSA in a canister from our laboratory was also analyzed as a laboratory method blank, and the background values of analytes found in the blank analyses were subtracted from the analytical results for the HSA samples that were analyzed in this laboratory. The three samples containing ppbv levels of the PAMS/terpenes mixture and 1,1-DCE were analyzed using the standard TO-15 scan method.

After all of the samples were analyzed, the canisters were assigned code names and dates. The canisters were then shipped by overnight carrier to the three laboratories. A summary description of the canister samples that includes canister number, sample contents, sample preparation and analysis dates, MS method, canister pressure both before and after analysis, sample and date codes, laboratory code, and laboratory analysis date is presented in Table 5-1. The time between the analysis of a canister sample in our laboratory and the analysis of the same canister sample in a contract laboratory ranged from 5 to 25 days.

**Table 5-1. Contract Laboratory Experiment Sample Canisters**

Canister	Sample	Date Filled	Date Analyzed	Method Trap 1	Method Trap 2	Analysis (psig)	Final (psig)	Sample Code	Date Code	Contract Lab Code #	Contract Lab Analysis Date
A-701	Ambient Air + 1,1-Dichloroethene	9/17/02	9/18/02	DCE	DCE	17.0	14.5	House A-2	9-17	1	10-2-02
785	Ambient Air + 1,1-Dichloroethene	9/17/02	9/18/02	DCE	DCE	17.0	15.0	House A-5	9-20	1	10-2-02
GA-B	Ambient Air + 1,1-Dichloroethene	9/17/02	9/18/02	DCE	DCE	17.0	15.0	House A-7	9-24	1	10-2-02
120	Ambient Air + 1,1-Dichloroethene	9/17/02	9/18/02	DCE	DCE	17.0	15.0	House B-2	9-17	2	9-30-02
01578	Ambient Air + 1,1-Dichloroethene	9/17/02	9/18/02	DCE	DCE	16.5	15.0	House B-5	9-20	2	9-30-02
MTC-22	Ambient Air + 1,1-Dichloroethene	9/17/02	9/19/02	DCE	DCE	17.0	15.0	House B-7	9-24	2	9-30-02
208	Ambient Air + 1,1-Dichloroethene	9/17/02	9/19/02	DCE	DCE	17.0	15.0	House C-2	9-17	3	10-9-02
013	Ambient Air + 1,1-Dichloroethene	9/17/02	9/19/02	DCE	DCE	17.0	15.0	House C-5	9-20	3	10-9-02
454	Ambient Air + 1,1-Dichloroethene	9/17/02	9/19/02	DCE	DCE	17.0	15.0	House C-7	9-24	3	10-14-02
N-3	Ambient Air + Chlorinated Cmpds	9/17/02	9/23/02	DCE	DCE	16.0	14.0	House A-1	9-16	1	10-2-02
726	Ambient Air + Chlorinated Cmpds	9/17/02	9/23/02	DCE	DCE	16.0	14.0	House A-4	9-19	1	10-2-02
096	Ambient Air + Chlorinated Cmpds	9/17/02	9/23/02	DCE	DCE	16.0	14.0	House B-1	9-16	2	9-30-02
727	Ambient Air + Chlorinated Cmpds	9/17/02	9/23/02	DCE	DCE	16.0	14.0	House B-4	9-19	2	9-30-02
9682 B	Ambient Air + Chlorinated Cmpds	9/17/02	9/23/02	DCE	DCE	16.0	14.0	House C-1	9-16	3	10-9-02
9677 B	Ambient Air + Chlorinated Cmpds	9/17/02	9/23/02	DCE	DCE	16.0	14.0	House C-4	9-19	3	10-9-02
5226	Humidified Scientific Air (HSA)	9/16/02	9/24/02	DCE	TO-15	22.0	17.5	House A-3	9-18	1	10-2-02
5962	Humidified Scientific Air (HSA)	9/16/02	9/24/02	DCE	TO-15	23.0	21.0	House A-6	9-23	1	10-2-02
1299	Humidified Scientific Air (HSA)	9/16/02	9/24/02	DCE	TO-15	22.5	20.5	House A-8	9-25	1	10-2-02
063240	Humidified Scientific Air (HSA)	9/16/02	9/24/02	DCE	TO-15	22.0	20.0	House B-3	9-18	2	9-30-02
0102	Humidified Scientific Air (HSA)	9/16/02	9/24/02	DCE	TO-15	22.5	20.5	House B-6	9-23	2	9-30-02
02303	Humidified Scientific Air (HSA)	9/16/02	9/24/02	DCE	TO-15	18.0	16.0	House B-8	9-25	2	9-30-02
JMTC 034	Humidified Scientific Air (HSA)	9/16/02	9/25/02	DCE	TO-15	22.0	20.0	House C-3	9-18	3	10-9-02
JMTC 027	Humidified Scientific Air (HSA)	9/16/02	9/25/02	DCE	TO-15	23.0	21.0	House C-6	9-23	3	10-14-02
JMTC 035	Humidified Scientific Air (HSA)	9/16/02	9/25/02	DCE	TO-15	22.5	21.0	House C-8	9-25	3	10-14-02
801	PAMS + Terpenes + 1,1-DCE	9/18/02	9/25/02	TO-15	TO-15	15.0	12.5	Garage A	9-26	1	10-4-02
465	PAMS + Terpenes + 1,1-DCE	9/18/02	9/25/02	TO-15	TO-15	15.0	13.0	Garage B	9-26	2	9-30-02
321	PAMS + Terpenes + 1,1-DCE	9/18/02	9/25/02	TO-15	TO-15	15.0	10.0	Garage C	9-26	3	10-4-02

## 5.5 Analytical Results

The MDLs for 1,1-DCE reported by the contract laboratories for the low-level TO-15 SIM methods used here ranged from 0.5 to 3 pptv. Since the three contract laboratories supplied analytical results in different formats, we chose to present the results as integer values; therefore, some results were rounded to the nearest integer value. Statistical treatments of the data were performed on the integer values that are presented in the tables.

### 5.5.1 Test of Canister Cleanliness

Table 5-2 summarizes the results of the analyses of the HSA samples by all four laboratories. The results obtained using our standard TO-15 MS scan method for 35 VOCs are included along with the Method TO-15 SIM results for the 10–14 compounds reported by the contract laboratories. (The low-level TO-15 SIM compound list varies slightly among the three contract laboratories.) As in Table 5-1, the contract laboratories are designated as 1, 2, and 3; our laboratory is designated MT. Reporting limits (RLs), PQLs, and/or MDLs also are included where applicable in Table 5-2: Laboratories 1 and 2 provided RLs with their analytical results and laboratory 3 provided both

MDLs and PQLs, with the results that fell between the two values flagged as semi-quantitative.

Overall, the canisters from the contract laboratories were found to be clean. 1,1-DCE was not detected in any of the canisters by any of the four laboratories. For the TO-15 SIM results for additional VOCs, laboratory 1 reported dichloromethane, benzene, and trichloroethene above the RL in each of the three samples; laboratory 2 reported no analytes above the RL in any of the three samples; and laboratory 3 reported only chloroethane above the PQL in one of the three samples. Our TO-15 scan results showed toluene, *m,p*-xylene, and 1,2,4-trimethylbenzene in laboratory 1 canister samples; *m,p*-xylene and toluene in laboratory 2 canister samples; and toluene in two of the laboratory 3 canister samples. More specifically, in our analyses toluene was 714 pptv in one of the laboratory 2 canister samples and the remaining VOCs that were detected in the HSA canister samples were less than 165 pptv. The concentration of toluene that was detected in the laboratory 2 canister sample would not have passed the canister cleanliness acceptance criteria for a standard Method TO-14 or TO-15 type of analysis, both of which specify that target compounds be present at less than 0.2 ppbv; however, toluene was not on the low-level TO-15 SIM target list for any of the three contract laboratories.



**Table 5-2. Results for Humidified Scientific Air Samples Analyzed by Contract Laboratory Method TO-15 SIM and by a Scan Method (Results in pptv)**

#	SAMPLE NAME	METHOD	CANISTER	MDL	House	House	House	House	House	House	House	House	House	House	RL	House	House	House	House	House	House	PQL			
					A-3	A-3	A-6	A-6	A-8	A-8	B-3	B-3	B-6	B-6		B-8	B-8	C-3	C-3	C-6	C-6		C-8	C-8	
					TO-15	TO-15	TO-15	TO-15	TO-15	TO-15	TO-15	TO-15	TO-15	TO-15		TO-15	TO-15	TO-15	TO-15	TO-15	TO-15				
					Scan	SIM	Scan	SIM	Scan	SIM	Scan	SIM	Scan	SIM		Scan	SIM	Scan	SIM	Scan	SIM				
					5226	5226	5962	5962	1299	1299	RL	063240	063240	0102	0102	02303	02303	RL	JMTC-	JMTC-	JMTC-	JMTC-	JMTC-	JMTC-	
					034	034	027	027	035	035		034	034	027	027	035	035		034	034	027	027	035	035	
					MT	MT	1	MT	1	MT	1	MT	2	MT	2	MT	2	MT	3	MT	3	MT	3	MT	3
0	Bromodichloromethane			61	NA	NA	NA	NA	NA	NA	NA	NA	ND	NA	ND	NA	ND	NA	NA	NA	NA	NA	NA	NA	
1	1,2-Dichloro-1,1,2,2-tetrafluoroethane			106	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
2	Chloroethene			344	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	ND	ND	ND	ND	ND	
3	Bromomethane				ND		ND		ND		NA		ND		ND		NA		ND		ND		ND		
4	Chloroethane					NA		NA		NA		NA		NA		NA		11			6		12		
5	Trichlorofluoromethane			65	ND		ND		ND		ND		ND		ND		ND				ND		ND		
6	1,1-Dichloroethene			100	ND	ND	ND	ND	ND	ND	10	ND	ND	ND	ND	ND	ND	10	ND	ND	ND	ND	ND	ND	
7	Dichloromethane			722	ND	36	ND	36	ND	44	20	ND	ND	ND	ND	ND	ND	120	ND	NA	ND	NA	ND	NA	
8	1,1,2-Trichloro-1,2,2-trifluoroethane			38	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
9	1,1-Dichloroethane			41	ND	ND	ND	ND	ND	ND	10	ND	ND	ND	ND	ND	ND	20	ND	ND	ND	ND	ND	ND	
10a	cis-1,2-Dichloroethene			82	ND	ND	ND	ND	ND	ND	10	ND	ND	ND	ND	ND	ND	14	ND	ND	ND	ND	ND	ND	
10b	trans-1,2-Dichloroethene				NA	NA	NA	NA	NA	NA	NA	NA	ND	NA	ND	NA	ND	14	NA	ND	NA	NA	ND	NA	
11	Trichloromethane			44	ND	ND	ND	ND	ND	ND	10	ND	ND	ND	ND	ND	ND	14	ND	NA	ND	NA	ND	NA	
12	1,2-Dichloroethane			60	ND	ND	ND	ND	ND	ND	10	ND	ND	ND	ND	ND	ND	20	ND	ND	ND	ND	ND	ND	
13	1,1,1-Trichloroethane			48	ND	ND	ND	ND	ND	ND	10	ND	ND	ND	ND	ND	ND	110	ND	ND	ND	ND	ND	ND	
14	Benzene			55	ND	36	ND	24	ND	24	20	67	ND	ND	ND	ND	ND	62	ND	NA	ND	NA	ND	NA	
15	Carbon tetrachloride			33	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
16	1,2-Dichloropropane			93	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
17	Trichloroethene			29	ND	25	ND	20	ND	116	10	ND	ND	ND	ND	ND	ND	48	ND	ND	ND	ND	ND	ND	
18	cis-1,3-Dichloropropene			48	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
19	trans-1,3-Dichloropropene			86	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
20	1,1,2-Trichloroethane			41	ND	NA	ND	NA	ND	NA	NA	ND	ND	ND	ND	ND	ND	18	ND	NA	ND	NA	ND	NA	
21	Toluene			44	122		ND		106		10	714		145		ND		ND		48		56		ND	
22	1,2-Dibromoethane			47	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
23	Tetrachloroethene			101	ND	12	ND	ND	ND	ND	10	ND	ND	ND	ND	ND	ND	100	ND	31	ND	6	ND	4	
24	Chlorobenzene			83	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
25	Ethylbenzene			57	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
26	m,p-Xylene			62	66		ND		ND		10	138		ND		ND		ND		ND		ND		ND	
27	Styrene			93	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
28	1,1,2,2-Tetrachloroethane			69	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
29	o-Xylene			66	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
30	1,3,5-Trimethylbenzene			44	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
31	1,2,4-Trimethylbenzene			70	ND		162		ND		10	ND		ND		ND		ND		ND		ND		ND	
32	m-Dichlorobenzene			38	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
33	p-Dichlorobenzene			80	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
34	o-Dichlorobenzene			58	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
35	1,2,4-Trichlorobenzene			62	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	
36	Hexachlorobutadiene			79	ND		ND		ND		10	ND		ND		ND		ND		ND		ND		ND	

ND = not detected, or detected amount below either MDL or RL

NA = sample not analyzed for this compound

\*For sample # C-3: PQL = 10 pptv

### 5.5.2 Summary of Results for Samples Spiked with 1,1-DCE

Table 5-3 summarizes the analytical results for 1,1-DCE for all samples analyzed by all four laboratories. For the samples of ambient air spiked with 1,1-DCE, the analytical results for the optimized TO-15 scan method ranged from 27 to 32 pptv with a mean of 30 pptv of 1,1-DCE for the nine samples. For the low-level Method TO-15 SIM analyses, laboratory 1 results were 30 pptv for all three samples; laboratory 2 results ranged from 27 to 29 pptv; and laboratory 3 results ranged from 27 to 29 pptv. The mean of the contract laboratory results for 1,1-DCE for the nine canister samples was 29 pptv, and the mean of the results for 1,1-DCE from all four laboratories (a total of 18 measurements) was 29 pptv. A further statistical treatment of the data is presented in section 5.5.3.

For the samples of ambient air spiked with the chlorinated compound mixture, the analytical results for the optimized TO-15 scan method ranged from 57 to 69 pptv for all six samples with a mean of 62 pptv for 1,1-DCE. For the low-level Method TO-15 SIM analyses, laboratory 1 results were 59 and 60 pptv; laboratory 2 results were 53 and 60 pptv; and laboratory 3 results were 54 and 60 pptv. The mean of the contract laboratory results for 1,1-DCE for the six canister samples was 58 pptv, and the mean of the results for 1,1-DCE from all four laboratories (a total of 12 measurements) was 60 pptv. A further statistical treatment of the data is presented in section 5.5.4.

For the three PAMS/terpenes plus 1,1-DCE samples, the 1,1-DCE analytical results (trap 1 results only) for our standard TO-15 scan method were 5100 and 5200 pptv, and the contract laboratories' 1,1-DCE results were 5600, 6000, and 11700 pptv.

As stated earlier, 1,1-DCE was not detected in any of the HSA canister samples by any of the four laboratories.

### 5.5.3 Test of Ability to Determine 1,1-DCE at 20–40 pptv in a Humid Ambient Air Matrix

Table 5-4 presents the analytical results for 10–14 VOCs reported by the three contract laboratories for the canister samples of ambient air spiked with 1,1-DCE. As mentioned earlier, the low-level TO-15 SIM compound list varies slightly among the three contract laboratories. Data on VOCs other than 1,1-DCE are not available from our laboratory as our method development and calibration efforts at the low-pptv level were directed solely toward the determination of 1,1-DCE.

The RSD of the measurements was calculated as follows:

$$\text{RSD} = \text{SD}/\text{mean} \times 100$$

and is included in the table as a measure of replicate precision for the VOC results reported by each of the contract laboratories. (Note: Replicate precision is defined in section 5.10 of Method

TO-15 as precision determined from two canisters, whereas duplicate precision is defined in section 5.11 as precision determined from the analysis of two samples taken from the same canister.) The RSD for 1,1-DCE was 0.0, 3.6, and 4.2% for laboratories 1, 2, and 3, respectively. The RSDs for other compounds reported by the contract laboratories were less than 12% for all measurements that were above the RL/PQL.

RSDs were also calculated for the 1,1-DCE results that are summarized in Table 5-3. For the nine canister samples analyzed in our laboratory using the optimized 1,1-DCE scan method, the RSD was 5.7%. The RSD for the combined contract laboratory results for the nine canister samples analyzed using the low-level TO-15 SIM methods was 4.2%. The RSD of the results from all four laboratories (a total of 18 measurements) was 5.5%.

### 5.5.4 Test of Ability to Determine 1,1-DCE at 50–80 pptv in the Presence of a Mixture of 14 Chlorinated VOCs in a Humid Ambient Air Matrix

Table 5-5 presents the analytical results for 10–14 VOCs reported by the three contract laboratories for the canister samples of ambient air spiked with a mixture of chlorinated compounds. As mentioned earlier, the low-level TO-15 SIM compound list varies slightly among the three contract laboratories. Data on VOCs other than 1,1-DCE are not available from our laboratory as our method development and calibration efforts at the low-pptv level were directed solely toward the determination of 1,1-DCE.

As a measure of replicate precision, the percent difference (%D) was calculated according to the definition in section 11.3.1 of Method TO-15 as follows:

$$\%D = \frac{|x_1 - x_2|}{\bar{x}} \times 100$$

where  $x_1$  is the first measurement value,  $x_2$  is the second measurement value, and  $\bar{x}$  is the average of the two values. The %D for 1,1-DCE was 0.0, 12.4, and 10.4% for laboratories 1, 2, and 3, respectively. The %D in the measurements for the other compounds reported by the contract laboratories was less than 25% for all of the replicate measurements except one (45.6% for tetrachloroethene for laboratory 1), and 20 of 23 replicate measurements (including 1,1-DCE) had a %D of <15%.

RSDs were calculated for the 1,1-DCE results that are summarized in Table 5-3. For the six canister samples analyzed using the optimized 1,1-DCE scan method, the RSD was 6.7%. The RSD for the combined contract laboratory results for the six canister samples analyzed using the low-level TO-15 SIM methods was 5.5%. The RSD of the results from all four laboratories (a total of 12 measurements) was 6.8%.

### 5.5.5 Test of Ability to Determine 1,1-DCE at Low-ppbv Levels in the Presence of ppbv Levels of 60 Hydrocarbons in a Synthetic Air Matrix Using a Method TO-14 Analysis

Table 5-6 summarizes the MS scan results for the PAMS/terpenes plus 1,1-DCE samples for all four laboratories. Since a TO-14 type analysis was requested of the contract laboratories for these three canister samples, most of the 60 hydrocarbons in the mixture were not on the target lists. The 1,1-DCE results were 5.6, 6.0, and 11.7 ppbv for the contract laboratories. The

1,1-DCE results obtained in this laboratory using the standard Method TO-15 scan method ranged from 4.5–5.9 ppbv with a mean of 5.1 ppbv for the eight analyses. Of particular concern is the 11.7-ppbv concentration measured by laboratory 3 for 1,1-DCE, as that measurement is approximately twice the concentration determined by the other three laboratories. Additionally, for all three contract laboratories certain measurements for various compounds (benzene, 6.8 ppbv; toluene, 6.0 ppbv; 4-ethyltoluene, 9.3 ppbv; 1,3,5-trimethylbenzene, 6.3 ppbv; and 1,2,4-trimethylbenzene, 7.3 ppbv) were somewhat higher than those determined by the other laboratories.

**Table 5-3.** Analytical Results for 1,1-Dichloroethene

#	Canister	Sample	MT (Trap 1) (pptv)	Contract Lab (pptv)	Contract Lab #
1	A-701	Ambient Air + 1,1-Dichloroethene	32	30	1
2	785	Ambient Air + 1,1-Dichloroethene	27	30	1
3	GA-B	Ambient Air + 1,1-Dichloroethene	30	30	1
4	120	Ambient Air + 1,1-Dichloroethene	30	28	2
5	01578	Ambient Air + 1,1-Dichloroethene	32	29	2
6	MTC-22	Ambient Air + 1,1-Dichloroethene	29	27	2
7	208	Ambient Air + 1,1-Dichloroethene	32	27	3
8	013	Ambient Air + 1,1-Dichloroethene	31	29	3
9	454	Ambient Air + 1,1-Dichloroethene	29	29	3
10	N-3	Ambient Air + Chlorinated Cmpds	69	59	1
11	726	Ambient Air + Chlorinated Cmpds	59	59	1
12	096	Ambient Air + Chlorinated Cmpds	60	60	2
13	727	Ambient Air + Chlorinated Cmpds	61	53	2
14	9682 B	Ambient Air + Chlorinated Cmpds	57	60	3
15	9677 B	Ambient Air + Chlorinated Cmpds	62	54	3
16	5226	Humidified Scientific Air (HSA)	ND	ND	1
17	5962	Humidified Scientific Air (HSA)	ND	ND	1
18	1299	Humidified Scientific Air (HSA)	ND	ND	1
19	063240	Humidified Scientific Air (HSA)	ND	ND	2
20	0102	Humidified Scientific Air (HSA)	ND	ND	2
21	02303	Humidified Scientific Air (HSA)	ND	ND	2
22	JMTC 034	Humidified Scientific Air (HSA)	ND	ND	3
23	JMTC 027	Humidified Scientific Air (HSA)	ND	ND	3
24	JMTC 035	Humidified Scientific Air (HSA)	ND	ND	3
25	801	PAMS + Terpenes + 1,1-DCE	5200	5600	1
26	465	PAMS + Terpenes + 1,1-DCE	5100	6000	2
27	321	PAMS + Terpenes + 1,1-DCE	5200	11700	3

ND = not detected, or detected amount below either MDL or RL.

MT = ManTech.

**Table 5-4. Contract Laboratory Method TO-15 SIM Analytical Results for Ambient Air Spiked with 1,1-Dichloroethene (Results in pptv)**

SAMPLE NAME	House	House	House			House	House	House			House	House	House		
	A-2	A-5	A-7	RSD	RL	B-2	B-5	B-7	RSD	RL	C-2	C-5	C-7	RSD	RL
CANISTER	A-701	785	GA-B		1	120	01578	MTC-22		2	208	013	454		3
Compound	LAB	1	1		1	2	2	2		2	3	3	3		3
Bromodichloromethane	NA	NA	NA		NA	ND	ND	ND		11	NA	NA	NA		NA
Chloroethene	ND	ND	ND		10	ND	ND	ND		7.8	ND	ND	ND		10
Chloroethane	NA	NA	NA		NA	NA	NA	NA		NA	7^	7^	6^	8.7	10
1,1-Dichloroethene	30	30	30	0.0	10	28	29	27	3.6	10	27	29	29	4.2	10
Dichloromethane	184	175	183	2.7	20	120	120	120	0.0	120	NA	NA	NA		NA
1,1-Dichloroethane	ND	ND	ND		10	ND	ND	ND		20	ND	ND	ND		10
cis-1,2-Dichloroethene	10	11	ND		10	ND	ND	ND		14	ND	ND	ND		10
trans-1,2-Dichloroethene	NA	NA	NA		NA	ND	ND	ND		14	ND	ND	ND		10
Trichloromethane	ND	25	17		10	30	30	28	3.9	14	NA	NA	NA		NA
1,2-Dichloroethane	ND	ND	ND		10	ND	ND	ND		20	3^	3^	ND		10*
1,1,1-Trichloroethane	38	36	36	3.1	10	ND	ND	ND		110	27	28	25	5.7	10
Benzene	311	288	297	3.9	20	230	230	230	0.0	62	NA	NA	NA		NA
Trichloroethene	ND	ND	41		10	ND	ND	ND		48	2^	2^	ND		50
1,1,2-Trichloroethane	NA	NA	NA		NA	ND	ND	ND		18	NA	NA	NA		NA
Tetrachloroethene	27	32	34	11.6	10	ND	ND	ND		100	39^	32^	18^	36.0	50

ND = not detected, or detected amount below either MDL or RL.  
 NA = sample not analyzed for this compound.  
 ^Semi-quantitative sample result value (value between MDL and PQL).  
 \*For sample # C-7, PQL = 20 pptv.

**Table 5-5. Contract Laboratory Method TO-15 SIM Analytical Results for Ambient Air Spiked with a Chlorinated Gas Mixture (Results in pptv)**

SAMPLE NAME	House	House			House	House			House	House		
	A-1	A-4	%D	RL	B-1	B-4	%D	RL	C-1	C-4	%D	PQL
CANISTER	N-3	726		1	096	727		2	9682-B	9677-B		3
Compound	LAB	1		1	2	2		2	3	3		3
Bromodichloromethane	NA	NA		NA	ND	ND		11	NA	NA		NA
Chloroethene	60	66	9.5	10	64	62	3.2	7.8	59	65	9.7	10
Chloroethane	NA	NA		NA	NA	NA		NA	7^	8^	13.3	10
1,1-Dichloroethene	59	59	0.0	10	60	53	12.4	10	60	54	10.5	10
Dichloromethane	147	161	9.1	20	ND	ND		120	NA	NA		NA
1,1-Dichloroethane	ND	ND		10	ND	ND		20	ND	ND		10
cis-1,2-Dichloroethene	14	16	13.3	10	ND	ND		14	ND	ND		10
trans-1,2-Dichloroethene	NA	NA		NA	ND	ND		14	ND	ND		10
Trichloromethane	31	38	20.3	10	87	91	4.5	14	NA	NA		NA
1,2-Dichloroethane	87	89	2.3	10	70	73	4.2	20	64	61	4.8	10
1,1,1-Trichloroethane	113	117	3.5	10	ND	ND		110	91	87	4.5	10
Benzene	276	263	4.8	20	200	190	5.1	62	NA	NA		NA
Trichloroethene	90	78	14.3	10	58	59	1.7	48	52	48^	8.0	50
1,1,2-Trichloroethane	NA	NA		NA	ND	ND		18	NA	NA		NA
Tetrachloroethene	175	110	45.6	10	ND	ND		100	98	77	24.0	50

ND = not detected, or detected amount below either MDL or RL.  
 NA = sample not analyzed for this compound.  
 ^Semi-quantitative sample result value (value between MDL and PQL).

**Table 5-6.** Analytical Results for the PAMS/Terpenes + 1,1-Dichloroethene Mixture (Results in ppbv)

<b>SAMPLE NAME</b>	Garage A	Garage A	Garage A	Garage B	Garage B	Garage B	Garage C	Garage C	Garage C	Garage C	Garage C	
<b>CANISTER</b>	801	801	801	465	465	465	321	321	321	321	321	
<b>Compound</b>	<b>LAB</b>	MT	MT	1	MT	MT	2	MT	MT	MT	MT	3
1,1-Dichloroethene		5.2	4.8	5.6	5.1	4.9	6.0	5.2	4.5	5.9	5.1	11.7
Benzene		4.7	4.7	4.9	4.8	4.7	4.9	4.5	4.6	5.4	4.9	6.8
Toluene		4.3	4.4	4.6	4.4	4.4	4.6	4.4	4.3	4.8	4.7	6.0
Ethylbenzene		4.2	4.4	5.4	4.4	4.4	4.7	4.1	4.2	4.7	4.6	5.5
<i>m,p</i> -Xylene		8.9	9.0	11	9.3	9.0	15 (total)	9.2	8.9	10.1	9.6	12.1
Styrene		4.1	3.9	4.6	4.4	4.0	4.2	4.1	3.8	4.8	4.1	5.4
<i>o</i> -Xylene		4.4	4.5	5.6	4.7	4.5	see <i>m,p</i> -Xyl	4.5	4.4	5.1	4.9	5.6
4-Ethyltoluene ( <i>p</i> -)		4.0	3.9	NA	4.1	4.2	9.3	4.1	3.9	4.9	4.5	NA
1,3,5-Trimethylbenzene		4.7	4.4	6.3	5.2	4.3	4.7	5.0	4.3	5.3	4.6	5.3
1,2,4-Trimethylbenzene		4.6	4.6	7.3	5.4	4.4	4.8	5.1	4.4	5.6	4.6	5.9

NA = sample not analyzed for this compound

## Chapter 6 References

1. McClenny, W.A., Joachim D. Pleil, Thomas A. Lumpkin, Karen D. Oliver. 1987. Update on canister-based samplers for VOCs. Proceedings of the EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants, VIP-8, Air & Waste Management Association, Pittsburgh, PA, pp. 253–258.
2. Lonneman, W.A., 2002. Personal communication.
3. Oliver, Karen D. and Joachim D. Pleil. 1985. Automated cryogenic sampling and gas chromatographic analysis of ambient vapor-phase organic compounds: Procedures and comparison tests. TN-4120-85-02 under EPA Contract No. 68-02-4035, Northrop Services, Inc. - Environmental Sciences, P.O. Box 12313, Research Triangle Park, NC 27709.
4. Lonneman, W.A. 1998. Comparison of hydrocarbon composition in Los Angeles for the year 1968 and 1997. Proceedings of the EPA/A&WMA Symposium on Measurement of Toxic and Related Air Pollutants, VIP-85, Air & Waste Management Association, Pittsburgh, PA, pp. 356–365.
5. Oliver, Karen D., Jeffrey R. Adams, E. Hunter Daughtrey, Jr., William A. McClenny, Matthias J. Yoong, Michael A. Pardee, Elizabeth B. Almasi, Norman A. Kirshen. 1996. Technique for monitoring toxic VOCs in air: Sorbent preconcentration, closed-cycle cooler cryofocusing, and GC-MS analysis. *Environ. Sci. Technol.* 30:1939-1945.
6. Saturn GC/MS Reference Manual. 1995. P/N 03-914354-40:3. Walnut Creek, CA: Varian Associates, Inc.
7. McClenny, W.A., Karen D. Oliver, Henry H. Jacumin, Jr., E. Hunter Daughtrey, Jr. 2002. Ambient level volatile organic compound (VOC) monitoring using solid adsorbents—Recent US EPA studies. *J. Environ. Monit.* 4:695–705.

## **Appendix B**

### **Example Guidance Provided by the Colorado Department of Public Health and Environment (CDPHE) from “Guidance for Analysis of Indoor Air Samples—April 2000”**

The CDPHE guidance addresses the analysis of indoor air samples from specially treated canisters by providing a set of technical requirements that place the analytical system under control and allow low-pptv detection of VOCs. These requirements were used by at least one of the laboratories in the laboratory comparison study mentioned in the main text with successful results at monitoring levels of 30–60 pptv. Other sets of technical requirements were also used to achieve these results in the laboratory comparison study, including the technical requirements used by ManTech Environmental Technology, Inc. (the NERL on-site contractor).

#### **B.1 Tuning Requirements for GC/MS-SIM Instruments**

CDPHE requires the use of the tuning compound perfluorotributylamine (PFTBA) and tuning algorithms to meet the following conditions: (1) The operator must confirm that the 69/70, 219/220, and 502/503 m/e ion ratios occur at the proper ratios of 1% ( $\pm 50\%$ ), 5% ( $\pm 25\%$ ), and 10% ( $\pm 10\%$ ), respectively; (2) the peak width at half height for the 502, 219, and 69 PFTBA m/e ions must be 0.5 amu  $\pm$  0.2 amu; and (3) the operator must confirm the correct mass assignment of these m/e ions to a tolerance of 0.1 amu (e.g., 69.0 amu  $\pm$  0.1 amu). Also, the operator must verify that the tuning is stable at a minimum of once per operating day to ensure correct mass axis alignment and eliminate data accumulated with contaminated ion sources.

#### **B.2 Data Acquisition Requirements for GC/MS-SIM Instruments**

CDPHE requires that GC/MS instruments operated in the SIM mode to meet Compendium Methods to acquire data with 1 amu of resolution and meet the following conditions: (1) the operator must demonstrate compliance with the tuning requirements; (2) the operator must confirm that the software method used to collect calibrant and sample data be set to the high-resolution

option (1 amu); (3) the ion dwell times must be optimized to obtain a minimum of 10 scans per peak; and (4) the electron multiplier (EM) voltages must be set to meet the detection limits of the project (conveniently accomplished by setting EM voltages at +300 volts relative to the tune voltage).

#### **B.3 Ion Selection for GC/MS-SIM and GC/MS-Scan**

CDPHE has provided a table of characteristic ions for four target compounds. The ions in Table B-1 are used to determine target compound concentrations by GC/MS-Scan and GC/MS-SIM methods.

#### **B.4 Summary of Technical Requirements from CDPHE for Analysis of Indoor Air Samples**

CDPHE has provided a summary table of minimal acceptable requirements for analysis of indoor air samples, which is presented in Table B-2.

#### **B.5 Contact Information**

CDPHE has agreed to provide the following contact listings so that interested readers can contact them for further information:

Colorado Department of Public Health and Environment  
Hazardous Materials and Waste Management Division  
Technical Assistance  
4300 Cherry Creek Drive South  
Denver, CO 80246-1530

Telephone: (303) 692-2000  
Toll-free: (800) 886-7689  
Fax: (303) 759-5355  
Website: <http://www.cdphe.state.co.us/>

**Table B-1.** Characteristic Ions for Four Target Compounds

Contaminant	Compendium Characteristic Ions <sup>(1)</sup>	CDPHE Preferred GC/MS-Scan Equivalent Method Characteristic Ions <sup>(2)</sup>	GC/MS-SIM Suggested Ions
1,1-DCE	61 <sup>(3)</sup> , 96	96, 61, 63	96, 98 <sup>(5)</sup>
1,2-DCA	62, 64	62, 98	62, 98 <sup>(5)</sup> or 62, 64
CH <sub>2</sub> Cl <sub>2</sub>	49 <sup>(3)</sup> , 84 <sup>(4)</sup> , 86	84, 86, 49	84, 86
TCE	130, 95 <sup>(4)</sup>	95, 130, 132	130, 132

(1) EPA Air Compendium Methods T0-14, T0-14a, and T0-15. Primary (quantitation ion) listed first.  
(2) EPA method(s) 8260B (SW-846), 624 (Clean Water), and 524 (Drinking Water). Primary ion listed first.  
(3) Interference detected on the primary (quantitation) ion, evaluation of 3 projects. Data from two laboratories using GC/MS-Scan and GC/MS-SIM.  
(4) Interference detected on the secondary (confirming) ion, evaluation of 3 projects. Data from two laboratories using GC/MS-Scan and GC/MS-SIM.  
(5) The selection of the 98 ion reflects the prominence of this ion for this compound, and observed interferences.

**Table B-2.** Minimum Acceptable Requirement for Analysis of Indoor Air Samples

Activity	Specifications	Documentation Needed
<b>GC/MS-SIM Tuning</b>	Autotune or equivalent. Acceptable isotopic ratios (1, 5, 10%). Peak width at half height (0.5 amu ± 0.2). Correct mass assignment (± 0.1 amu).	Printout of tune report.
<b>GC/MS-SIM Data Acquisition</b>	Meet tune specifications. Optimize ion dwell time.  Set electron multiplier voltage to achieve required detection limits. Collect calibrant and sample analysis data with the high-resolution (1 amu).	Printout of instrument method. 10 scans/peak minimum. Printout of extracted ion chromatogram. Data quality objectives. Printout of instrument method. Raw sample data.
<b>Ion Selection</b>		<b>Reference</b>
<b>GC/MS-SIM</b>	Select primary ions from 8260B tabular data, or at least two ions, justified from library spectra, that meet data quality objectives. (Free from interferences)  Consecutively evaluate ion selection. Adjust as necessary.	Method 8260B, library spectra  Library spectra, raw sample data
<b>GC/MS-SCAN</b>	Select primary ions from 8260B tabular data, or at least two ions, justified from library spectra that meet data quality objectives. (Free from interferences)  Consecutively evaluate ion selection. Adjust as necessary.	Method 8260B, library spectra  Library spectra, raw sample data
<b>GC/MS-SIM Reporting Requirements</b>		
Confirmed positive detections: (REPORT: Concentration, qualify quantitative estimates with a "J")		
<ul style="list-style-type: none"> <li>- Ion relative retention time (RRT) tracks that of standards (<b><u>± 0.10 RRT</u></b>)</li> <li>- Characteristic ion abundance ratio tracks ratio of standards (± 25 %)</li> <li>- Characteristic ions maximize within ± one scan</li> </ul>		
Unconfirmed detections: (REPORT: Detected not confirmed, specify reason. Qualify quantitative estimates with a "J")		
<ul style="list-style-type: none"> <li>- Ion relative retention time tracks that of standards (<b><u>± 0.10 RRT</u></b>)</li> <li>- Characteristic ion abundance ratio <u>fails</u> to track ratio of standards (± 25 %)</li> <li>- Characteristic ions <u>do not</u> maximize within ± one scan</li> </ul>		