Supplement to EPA Compendium Method TO-15—Reduction of Method Detection Limits to Meet Vapor Intrusion Monitoring Needs

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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 parts per billion by volume (ppbv), as cited in Method TO-15, to much lower concentrations. Revisions were made to the wording of Method TO-15 where the original language proved limiting to the goal of extending Method TO-15 to low parts per trillion by volume (pptv) levels or where minor omissions 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 pptv 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.

INTRODUCTION

TO-15 is a performance-based method prepared by the United States Environmental Protection Agency (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.[1] 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 bench-top quadrupole mass spectrometers. These performance criteria specify 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.

TO-15 has the following performance specifications: a MDL, defined as 3.143 times the standard deviation for seven replicates, of 0.5 parts per billion by volume (ppbv); replicate precision, defined as $[(A - B) \times 200] / (A + B)$, of $\pm$ 25%; and accuracy, defined as [(Measured – True) × 100] / True, of $\pm$ 30%. The goal of the supplement is to extend the MDL to concentration levels needed to achieve the 10^{-6} risk levels (see Table 1). Further details concerning 10^{-6} risk levels are available at www.epa.gov/iris.

Table 1. 10^{-6} Risk levels for NATA compounds.

Compound	Risk Level (pptv)	Compound	Risk Level (pptv)
Vinyl chloride	90	*trans*-1,3-Dichloropropene	44
1,1-Dichloroethene	50	1,1,2-Trichloroethane	11
Dichloromethane	576	1,2-Dibromoethane	1
Trichloromethane	8	Tetrachloroethene	NE
1,2-Dichloroethane	10	1,1,2,2-Tetrachloroethane	3
Benzene	41	Hexachlorobutadiene	5
Carbon tetrachloride	11	Acrylonitrile	5
1,2-Dichloropropane	NE	1,3-Butadiene	1
Trichloroethene	NE	Ethylene oxide	NE
cis-1,3-Dichloropropene	44		

NE = not established

We prepared 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 demonstrate how well such samples are likely to be analyzed, it does not mean 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.[2] The analytical guidelines developed by the Colorado Department of Public Health and Environment (CDPHE) for use by its contract laboratories, for example, provide a useful and practical approach for current monitoring applications. The agreement among the four laboratories 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.

TEST METHODS

To verify that TO-15 can be modified to meet the requirements for monitoring at 10^{-6} risk levels, the factors needed to improve detection limits must be identified and the performance of methods must be tested.

Improving Method Detection Limits

Canister Cleanliness

Canister cleanliness is the first key to improving detection limits. TO-15 specifies 0.2 ppbv as a canister-cleanliness standard, developed when MDL goals were more relaxed. Blank values must be less than MDLs. Our experience has been that to achieve a realistic measure of MDLs, humidified scientific-grade (HSA) air must be used for the evaluation. We also strongly recommend that an oil-free vacuum pump be used for evacuation of the canisters, as backstreaming of vacuum pump oil vapors can contaminate the canisters. Use of a humidified airstream as part of the cleaning cycle has been shown to greatly improve the attainable MDLs. Finally, it is critical that canister cleanliness be verified by periodic testing.

Standards

Two issues are raised for the calibration and quality control samples to be used. The first is that the standards should be traceable to those prepared by the National Institute of Standards and Technology (NIST). It is preferable to have a NIST standard of the compounds of interest, but this is difficult to obtain for all compounds. Calibration for a subset of the compounds of interest for which NIST standards are available, coupled with certification of NIST-traceable gravimetric standards for the balance of the compounds, is acceptable when NIST standards are not available. No matter which method is chosen, monitoring of standard concentration over the life of a cylinder is needed. We have our standards periodically analyzed by another researcher who uses a NIST-traceable propane standard for gas chromatography (GC) with flame ionization detection (FID) analysis.

The second issue is that the calibration standard must be appropriate to the expected analytical range. For our "normal" TO-14 or Photochemical Assessment Monitoring Station (PAMS) analyses, we usually employ a 10-ppbv working standard prepared by dynamic dilution of a 2 parts per million by volume (ppmv) cylinder standard. This is clearly too high to be able to accurately calibrate at the tens of parts per trillion range required for this study. We procured a 10-ppbv 1,1-DCE standard, which allowed for preparation of standards as low as 2.5 pptv using our dynamic dilution technique.

Storage Stability

Demonstrated storage stability of 30 days is needed to allow for transit time and for unanticipated delays. A goal of no change greater than 20% over the 30-day period is desired.

GC-MS Conditions

Two methods were considered for evaluation. Our laboratory used sorbent preconcentration followed by GC-ion trap detection.[2,3] CDPHE proposed selected ion monitoring mass spectrometry (MS) as a candidate method to achieve the required detection limits.[4] This does not preclude other methods that meet the performance criteria.

Performance Testing

Choice of Laboratories

We requested from CDPHE the names and contact information for contract laboratories with whom they did business. We contacted three of these to obtain information regarding services they offered, prices, and turnaround time. We ordered each laboratory's modified TO-15 analysis with full data report and one TO-14 analysis.

Experimental Design

The following test samples were generated:

- Samples to test canister cleanliness (3 cans/lab)
- 1,1-DCE at 20–40 pptv in a humid ambient air matrix (3 cans/lab) to test the method slightly above the detection limit
- 1,1-DCE at 50–80 pptv in the presence of a mixture of 14 chlorinated VOCs in a humid ambient air matrix (2 cans/lab) to test at a slightly higher level in the presence of other chlorinated VOCs
- 1,1-DCE at low ppbv levels in the presence of ppbv levels of 60 hydrocarbons in a synthetic air matrix using Method TO-14 (1 can/lab) to test each contract laboratory's ability to analyze the TO-14 target list

RESULTS AND DISCUSSION

Canister Cleanliness

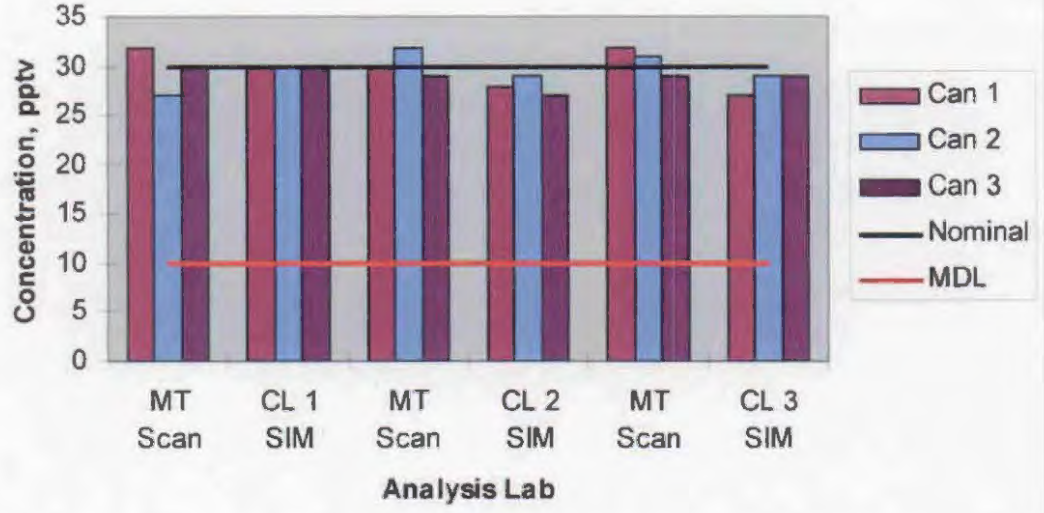
Clean, evacuated canisters were received from the contract laboratories. We filled the canisters with HSA and analyzed them after they were allowed to sit for 24 hours. The HSA-filled canisters were then returned to the contract laboratories for analysis. All results for modified TO-15 analytes were below detection limits for our laboratory. The same held true for the contract laboratories except laboratory 1 found four compounds slightly above their reporting limits and laboratory 3 found two compounds above their detection limits but below the practical quantitation limits. Toluene, which was not on the

target list, was consistently above the MDL specified by each laboratory, including one canister at 714 pptv that would have failed the original TO-15 criteria.

Analysis of Synthetic Samples

Nine canisters loaded with a nominal 30 pptv 1,1-DCE standard diluted with ambient air were analyzed in our laboratory and, of these, three canisters were submitted to each contract laboratory for analysis. The results are shown graphically in Figure 1. As can be seen, the agreement between the nominal concentration and the results from our laboratory and the three contract laboratories (CL 1, CL 2, and CL 3) is well within the criteria for precision and accuracy.

Figure 1: Comparison of Results of Analysis for 1,1-DCE of Ambient Air Spiked with a 30-pptv 1,1-DCE Standard by ManTech and Three Contract Laboratories



Six canisters of a nominal 60-pptv 1,1-DCE standard in ambient air spiked with a chlorinated VOC mixture were prepared and analyzed. Of these, two canisters were sent to each of the three contract laboratories. The results from these analyses are presented in Figure 2. Again, the agreement among all the results and the nominal concentration is within the specified precision and accuracy limits.

We also wanted to evaluate the method when the normal TO-14 analysis was performed by the contract laboratories. We prepared a combined standard that consisted of 60 hydrocarbons from the PAMS/terpene standard mixture plus 1,1-DCE, all at a nominal concentration of 5 ppbv. Results, as shown in Figure 3, were reasonable except for the results from laboratory 3, which were more than double those of the other laboratories.

This was also reflected in the results for other compounds for laboratory 3, but not to the same extent.

Figure 2: Comparison of Results of Analysis for 1,1-DCE of Ambient Air Spiked with a Chlorinated Gas Mixture Containing 60 pptv 1,1-DCE by ManTech and Three Contract Laboratories

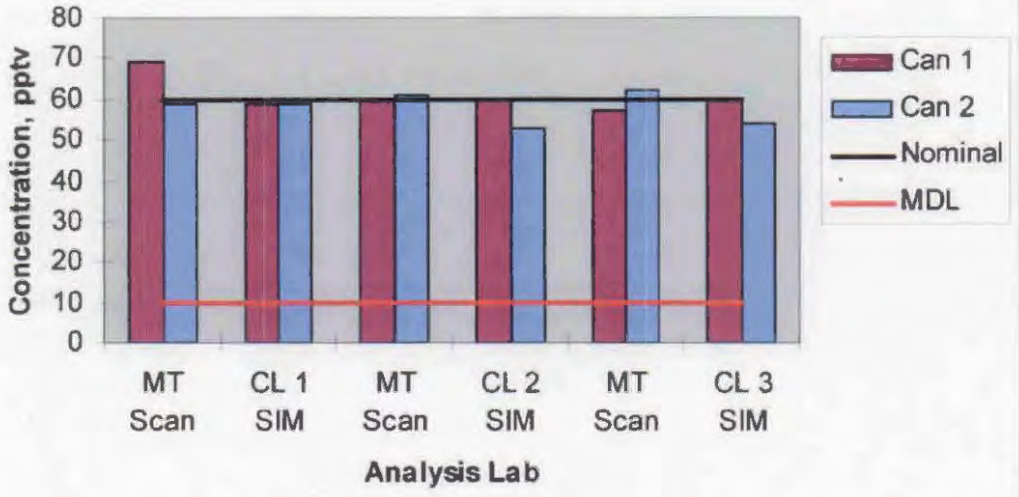
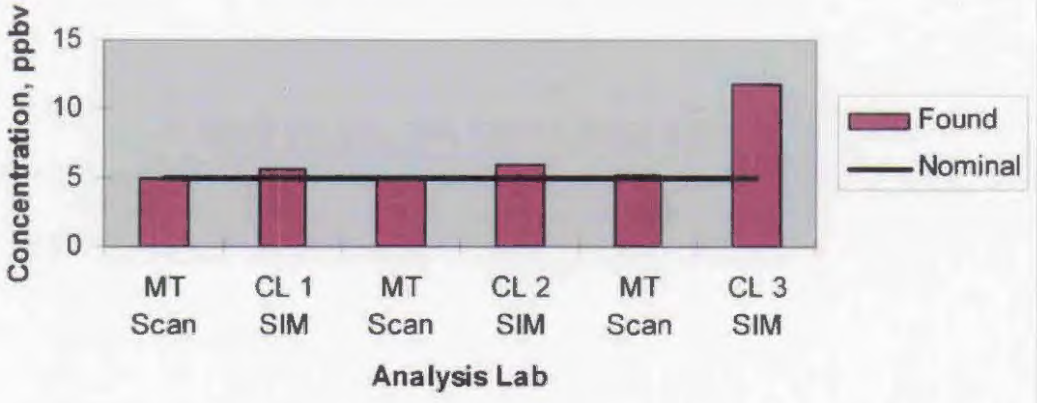


Figure 3: Comparison of Results of Analysis for 1,1-DCE of PAMS/Terpene Standard Spiked with a 5-pptv 1,1-DCE Standard by ManTech and Three Contract Laboratories



CONCLUSIONS

- The TO-15 Supplement[2] 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 data quality objectives (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%.

- The supplement includes revisions and additions by section to the original Method TO-15. 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., and the other is a concise restatement of the guidance developed by CDPHE for the analysis of high-risk compounds associated with the problem of vapor intrusion into buildings.

- Samples of 30 and 60 pptv of l,l-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.

RECOMMENDATIONS

- 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.

- Laboratories that wish 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.

- 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 NIST-traceable standards from commercial suppliers, or fundamentally derived standards.

- 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.

- To confirm consistent sampling technique, a number of replicate samples should be collected and analyzed.

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KEY WORDS

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method detection limit
parts per trillion
TO-15
vapor intrusion
VOC
volatile organic compound

DISCLAIMER

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