EPA/600/A-96/070

96-TA30.05

EPA Method TO-15
VOCs in Air Collected in SUMMA™ Canisters and Analyzed by Gas Chromatography/Mass Spectrometry

William A. McClenny
U.S. EPA
79 Alexander Drive
Research Triangle Park, NC 27711

Karen D. Oliver
Jeffrey R. Adams
ManTech Environmental Technology, Inc.
2 Triangle Drive
Research Triangle Park, NC 27709

INTRODUCTION

Method TO-15 is an addition to the EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air[1] and consists of guidance for the sampling and analysis of volatile organic compounds (VOCs) in air. The method has undergone an initial review by the EPA and has been placed on the AMTIC bulletin board maintained by EPA's Office of Air Quality Planning and Standards (OAQPS) for further comments before final review and formal acceptance as a new method. The method is a companion method to the previously published TO-14 method entitled, "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA™ Polished Canister Sampling and Gas Chromatographic (GC) Analysis". TO-15 differs from TO-14 in the following ways: (1) the water management system consists of the use of a small sample volume or a multisorbent/dry purge technique or both to dry the air sample; (2) the more extensive set of compounds given in Title III of the Clean Air Act Amendments (CAAA) of 1990 constitutes the target list; (3) GC/MS techniques are recommended as the only means to identify and quantify target compounds; (4) method performance criteria are specified for acceptance of data, thereby allowing the use of alternate but equivalent sampling and analytical instrumentation; and (5) enhanced provisions for quality control are included.

WATER MANAGEMENT BY THE MULTISORBENT/DRY PURGE METHOD

In the approach to water management taken in EPA Method TO-14, a permeable membrane dryer is recommended. The membrane was determined to effectively dry air samples while leaving the TO-14 target list intact[2]. However, the method is inadequate for the target list in Title III of the CAAA because some of the compounds (generally water soluble compounds) are altered or lost during passage through the membrane. Method TO-15 addresses this issue by offering alternatives for water management. These alternatives are either the simple expedient of using a small sample volume, the use of a multisorbent packing of solid adsorbents for drying, or a combination of the two. With the multisorbent/dry purge technique, the air sample passes through the packing and the VOCs are collected by adsorption while, either during sampling or during a post-sampling neutral gas purge, a significant portion of the water vapor breaks through[3,4]. In practice, the combination of adsorbents chosen must retain the most volatile target compounds, a consideration that leads to a limitation of the sample volume, while collecting sufficient sample volume to meet the requirements for quantitation. For example, for compound target lists such as the Title III list which include volatile organic compounds such as methyl chloride, ethyl chloride, vinyl chloride, methyl bromide, and vinyl bromide, a strong adsorbent such as the carbon molecular sieve Carbosieve SIII is generally required. Carbosieve SIII retains enough water vapor for typical sample volumes of 0.2 to 1.0 liter to require a dry purge subsequent to sampling. As an example of water retention, consider Figure 1 in which the water retention for four different multisorbent packings are shown. The water vapor as detected with an atomic emission detector increases linearly with volume and then breaks through.

Accumulation of the target VOCs continues after breakthrough while the retained quantity of water vapor remains approximately constant.

Depending on the tolerance of the analytical system for water vapor, a dry purge with helium may be used. During the dry purge of a trap consisting of Tenax, Ambersorb and Charcoal (see reference 4), the residual water vapor is noted to decrease almost exponentially with volume of purge gas as noted in Figure 2.

Several other water management techniques of comparable efficacy have been adapted by commercial companies. These include variations of a combination cold-trapping technique and a purge and trap method. Initial trapping of VOCs along with water, carbon dioxide, etc. occurs followed by increasing the temperature of the trapped components to near ambient and preferential removal and retrapping of VOCs released from sample water. Reference 5 gives the basis for this approach.

LIST OF TARGET COMPOUNDS

Subsets of the 97 VOCs listed in Title III are the target compounds for TO-15. However, not all of these have been successfully measured and documented using the TO-15 method. Compounds listed in TO-14 and the SOW for the Superfund Contract Laboratory Program as well as some additional compounds listed in two recent papers[6,7] have been monitored with the Method TO-15. However, this set of compounds does not provide full coverage of the Title III target list and is a limitation of the method at the present time. Part of the measurement uncertainty for those compounds not covered is their storage stability in canisters and part is the uncertainty in the results of the concentration/water management procedure.

Reliable calibration techniques for a majority of the 97 compounds has been established. Those Title III compounds that are not being routinely monitored, i.e. compounds not listed in TO-14 or covered in References 6 and 7, are subject to best-effort procedures for generation of calibration gases and reliable calibration techniques must still be demonstrated in those cases. For the majority of compounds, standards in the ppbv to ppmv levels can be obtained from commercial companies or from NIST. These standards can be diluted and humidified to the desired calibration levels. In addition to this approach, TO-15 lists three means for the analyst to generate calibration standards of VOCs either for direct calibration or for calibration after dilution: (1) the static dilution bottle technique; (2) the preparation in high pressure cylinders; and (3) the preparation by a water purge and trap method. These methods are covered in Section 3.4 of the TO-15 method.

GC/MS ANALYSIS

GC/MS analysis is chosen in order to assure a high degree of certainty in compound

identification. Specific detectors such as the flame ionization detector are often used in addition to benchtop mass spectrometers to provide more sensitive detection. Since GC/MS analysis with benchtop systems are often pressed into service for analysis, the response variations due to water vapor in these systems must be considered. The adequate drying of the sample before analysis has been determined to be of great importance in achieving good results.

METHOD PERFORMANCE CRITERIA

Section 4 of the Method TO-15 lists performance specifications that are recommended before analyses are accepted. These performance criteria include:

- Method Detection Limit: Generally 0.5 ppbv
- Replicate Precision: 25%
- Audit Accuracy: ± 30%

The method performance criteria are included in TO-15 in response to requests to make the method general enough to allow the use of technology that provides equal or better results. Such technical options are obviously viable and should be accepted if equivalence in performance is shown.

QUALITY CONTROL

The TO-15 method retains the use of canister cleaning and certification guidelines used in TO-14. In addition, TO-15 establishes a number of commonly-used quality assurance procedures in place of the periodic calibrations suggested in TO-14. These procedures are identical to those used in the SOW for the Superfund Contract Laboratory Program and include the use of internal standards and technical acceptance criteria based on measurement of relative response factors and relative retention times for both internal standards and target compounds.

CONCLUSIONS

The TO-15 method has been written in order to recommend a sampling and analytical approach to monitoring VOCs on the list of compounds in Title III of the CAAA of 1990. This list includes compounds with a wide range of chemical properties including water solubility; these compounds require special attention to water management during sample conditioning and preconcentration. TO-15 has several limitations including, in some cases, the successful testing of the target compounds and the demonstrated ability to generate known concentrations of the target compounds. Future testing of the method in these cases is expected to provide further validation.

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency (EPA) under Contract 68-D0-0106 to ManTech Environmental Technology, Inc. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REFERENCES

1. W. T. Winberry, Jr., N.T. Murphy and R. M. Riggin, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA 600-4-84-041, U.S.Environmental Protection Agency, Research Triangle Park, NC., 1988, pp 10-13.

2. K.D. Oliver, J.D. Pleil, and W.A. McClenny, "Sample Integrity of Trace Level Volatile Organic Compounds in Ambient Air Stored in SUMMA™ Polished Canisters." Atmos. Environ. 14: 1105 (1986).

3. T.J. Kelly, et al. "Method Development and Field Measurements for Polar Volatile Organic Compounds in Ambient Air, " Environ. Sci. Technol. 27: 1146 (1993).

4. W.A. McClenny, et al. "Analysis of VOCs in Ambient Air using Multisorbent Packings for VOC Accumulation and Sample Drying," J.Air Waste Management Assoc., 45: 792 (1995).

5. J.F. Pankow, "Technique for Removing Water from Moist Headspace and Purge Gases Containing Volatile Organic Compounds; Application in the Purge with Whole-Column Cryotrapping (PWCC) Method," Environ. Sci. Technol. 25: 123 (1991).

6. K.D. Oliver, et al. "Technique for Monitoring Ozone Precursor Hydrocarbons in Air at Photochemical Assessment Monitoring Stations: Sorbent Preconcentration, Closed-Cycle Cooler Cryofocusing, and GC-FID Analysis," Accepted for publication, Atmos. Environ. (1996).

7. K.D. Oliver, et al. "Technique for Monitoring Toxic VOCs in Air: Sorbent Preconcentration, Closed-Cycle Cooler Cryofocusing, and GC-MS Analysis," Accepted for publication, Environ. Sci. Technol. (1996).

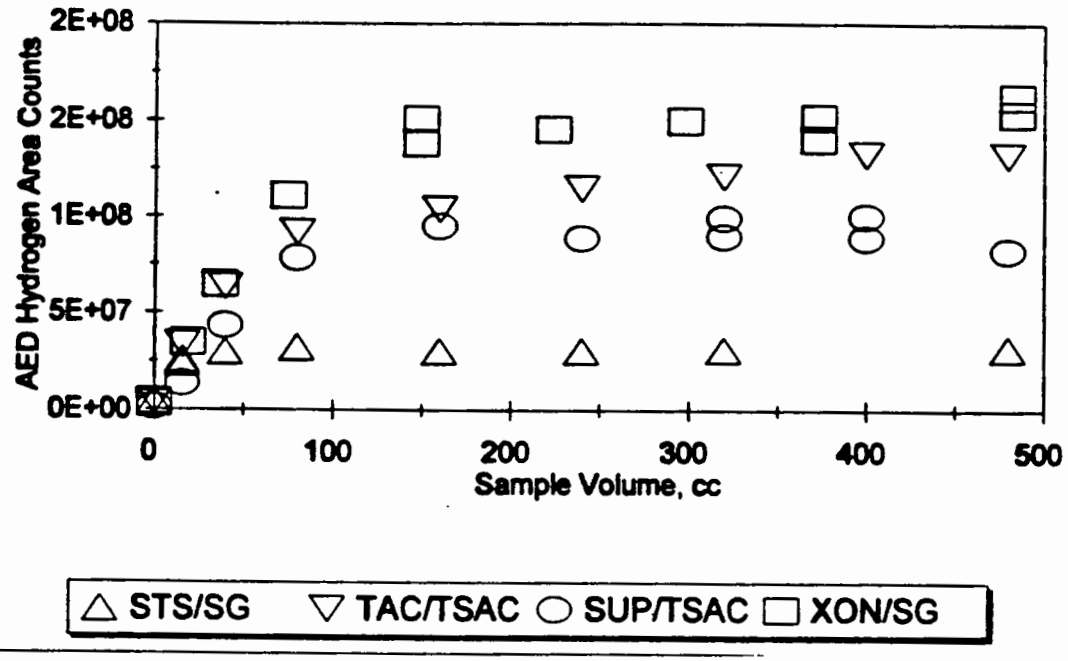

Figure 1. Retention of Water on Various Sorbent Combinations: STS/SG, TAC/TSAC, SUP/TSAC, and XON/SG refer to combinations of primary and focusing traps used in autoGCs or sample packings, e.g. STS/SG refers to a Carbotrap/Carboxen 1000 primary trap and a silica gel focusing trap. See References 4 and 6 for others.

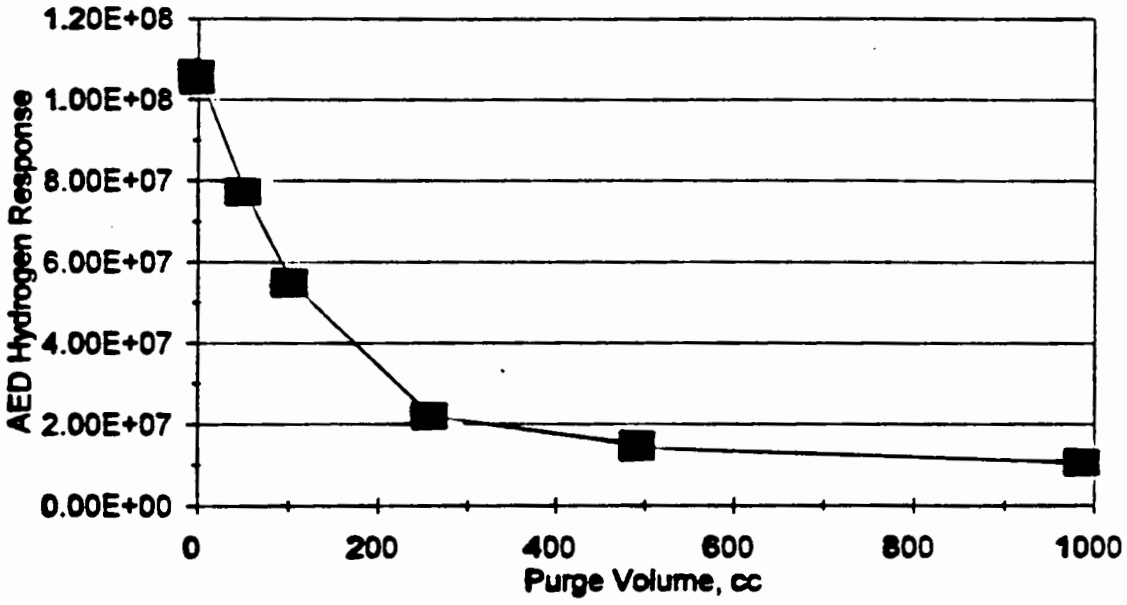

Figure 2. Removal of Water by Dry Purging a TAC (Tenax, Ambersorb, Charcoal) Trap with Helium.

TECHNICAL REPORT DATA

1. REPORT NO.	2.	3.RECIP!
EPA/600/A-96/070		

4. TITLE AND SUBTITLE	5.REPORT DATE
EPA Method TO-15 VOCs in Air Collected in SUMMA™ Canisters and Anlayzed by Gas Chromotography/Mass Spectrometry	6.PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W.A. McClenny; USEPA & J.R. Adams and K.D. Oliver; Mantech	8.PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Mantech Environmental Research Triangle Park, NC	10.PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-D0-0106
12. SPONSORING AGENCY NAME AND ADDRESS US Environmental Protection Agency Research Triangle Park, NC 27711	13.TYPE OF REPORT AND PERIOD COVERED publication of proceedings 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

Method TO-15 is an addition to the EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air and consists of guidance for the sampling and analysis of volatile organic compounds (VOCs) in air. The method has undergone an initial review by the EPA and has been placed on the AMTIC bulletin board maintained by EPA's Office of Air Quality Planning and Standards (OAQPS) for further comments before final review and formal acceptance as a new method. The method is a companion method to the previously published TO-14 method entitled, "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA™ Polished Canister Sampling and Gas Chromatographic (GC) Analysis". TO-15 differs from TO-14 in the following ways: (1) the water management system consists of the use of a small sample volume or a multisorbent/dry purge technique or both to dry the air sample; (2) the more extensive set of compounds given in Title III of the Clean Air Act Amendments (CAAA) of 1990 constitutes the target list; (3) GC/MS techniques are recommended as the only means to identify and quantify target compounds; (4) method performance criteria are specified for acceptance of data, thereby allowing the use of alternate but equivalent sampling and analytical instrumentation; and (5) enhanced provisions for quality control are included.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b.IDENTIFIERS/ OPEN ENDED TERMS	c.COSATI

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21.NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	
	20. SECURITY CLASS *(This Page)*	22. PRICE
	UNCLASSIFIED	