

CANISTER-BASED SAMPLING AND SUBSEQUENT GC/MS ANALYSIS FOR MEASUREMENT OF TRACE-LEVEL VOLATILE ORGANOHALOGEN COMPOUNDS

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The determination of trace-levels of volatile organic compounds has been implemented in the U.S. in response to concerns about health effects from prolonged low-level exposures and effects on atmospheric chemistry. The method relies upon collection of whole-air samples in specially treated stainless steel containers with subsequent laboratory analysis utilizing cryogenic preconcentration, capillary column gas chromatography, and mass spectrometry. Targeted compounds (including Freons, halogenated aliphatics, and halogenated aromatics) can be unambiguously measured at detection limits of 100 parts per trillion by volume.

INTRODUCTION

The U.S. Environmental Protection Agency has developed whole-air collection with stainless steel sampling canisters as an alternative to solid sorbent collection methods for the volatile organic compounds (VOCs). The canisters used are typically 6-liters in volume and are manufactured with an interior surface treatment (SUMMA polishing) that deactivates possible adsorption or reaction sites. They are evacuated in the laboratory and then used in the field to collect whole-air under a variety of flow conditions, depending upon the needs of the project. Sampling protocols can include "grab" sampling where the evacuated canister is opened and rapidly filled (5 to 10 sec.), "passive" sampling where a restrictive flow orifice is used to fill the canister to ambient pressure over a longer time period (up to 2 hours) and "active" sampling where a combination of pumping and accurate flow control fills the canister from the original vacuum up to a positive pressure of 1 to 2 atmospheres (typically over a 24-hour period). Analysis is performed in the laboratory where an aliquot of the collected air sample is cryogenically preconcentrated, thermally desorbed onto a chromatographic column and then detected with a mass spectrometer tuned only to the ions of the targeted analytes. The analytical method is fully automated, including the data reduction to a calibrated report for 40 analytes. Details of the basic methodology are available in EPA's Compendium of Methods for the Determination of Toxic Organic Compounds, Method TO-14 (1). This paper presents a brief description of the canister-based sampling/analytical method and gives some representative results for U.S. tropospheric concentrations of halogenated organics.

EXPERIMENTAL

Sampling canisters with a passivated interior finish (SUMMA polish) are available from a number of U.S. companies; the units used for the bulk of this work were purchased from SIS, Inc., (Moscow, Idaho), Biospheric, Inc. (Hillsboro, Oregon), and Andersen Samplers, Inc. (Atlanta, Georgia). Prior to field work they are cleaned by evacuation to less than 35 μm at 95 C and then pressure checked 24 hours later to assure they are leak free. A subset of each canister batch is filled with humidified zero grade air and then analyzed as a quality control step against contamination. Typically, 10% to 20% of the prepared canisters are tested prior to field sampling.

With the exception of preliminary screening work or certain projects requiring short term resolution of concentrations to characterize local sources of VOCs, U.S. monitoring of VOCs is performed with 24-hour integrated samples. This requires the use of active sampling systems that utilize air pumps and accurate flow control; a typical arrangement incorporates a weather-proofed case, a programmable timing system for unattended on/off operation, a sample pressurization pump and a mass flow controller. A 24-hour integrated sample is collected at a flow rate of 11 ml/min into a 6-liter canister from a vacuum to about 22 psig (2.5 atm.). Sampling systems have been built by EPA for specific projects; similar units are now commercially available from the canister manufacturers (listed above) and from other companies such as Xontech, Inc. (Van Nuys, California) and Nutech, Inc. (Durham, North Carolina).

Samples are analyzed by high resolution gas chromatography using a non-polar stationary phase column; typical columns are OV-1 with 0,32 mm i.d. by 50 meter length and SPB-1 with 0,32 mm i.d. by 60 meter length. Up to 500 ml of the sample is preconcentrated in a high purity Nickel tube trap loosely packed with glass wool (0,2 cm o.d. by 10 cm length) at -160 C. Upon completion of the concentration step, a 6-port sampling valve is used to route the column carrier gas through the trap which is then heated to +100 C to transfer the analytes onto the analytical column. The GC oven temperature is programmed to start at -50 C and then ramped to 200 C at 8 C/min. The mass spectrometer is programmed to selectively acquire data for specific ions in retention time windows matching the elution times of targeted analytes; typically 2 or 3 ions per compound are sought. The sample concentrator was designed at EPA and is now commercially available (Model 320-1, Nutech Corp., Durham, North Carolina). The analytical instrumentation is an HP-5880 Level 4 gas chromatograph and an HP-5970B MSD, both manufactured by Hewlett-Packard, (Avondale, Pennsylvania and Palo Alto, California, respectively). All three are interfaced via the GC computer to fully automate the analysis from sample preconcentration to printing the calibrated report. The nominal sensitivity for all target compounds is about 0.05 to 0.1 nanograms, or 0.1 parts per billion by volume (ppbv) concentration.

RESULTS AND DISCUSSION

The analytical methodology was implemented in a number of nationwide EPA studies and field tests. Certain data have been selected and averaged for presentation here to demonstrate the ambient concentrations of various halogenated organics in the U.S. The largest data base is for the Toxic Air Monitoring System (TAMS) program that utilized 24-hour sampling in the urban airshed of four U.S. cities: Boston, Massachusetts; Chicago, Illinois; Houston, Texas; and Seattle, Washington (2). In addition, research study data is available for work performed near industrial areas of Richmond, Virginia (3), and New Castle, Delaware (4). The TAMS data is summarized in Table 1 for 1988, and in Table 2 for 1989. Because of the nature of the TAMS study as a trends analysis vehicle, the reported organohalogenes are limited to 6 compounds for 1988 and 5 compounds for 1989. The data show that in the urban air the organohalogenes are generally below 1 ppbv in concentration, though methylchloroform averages are as high as 3 ppbv. Some additional compounds, particularly Freons and aromatic halocarbons, were measured in the research studies in Richmond and New Castle, as presented in Table 3. Once again, the average concentrations are generally below 1 ppbv even though there were known local industrial sources located less than 5 km from the sampling sites. Freons 12 and 11 are considered high (2 to 3 ppbv) in the Richmond area and, in the New Castle data, chlorobenzene and the dichlorobenzenes were found well above the usually encountered ambient levels.

This representative data indicates that there are ubiquitous concentrations of a variety of organohalogenes across the U.S. at trace-levels. The TO-14 methodology is capable of unambiguously measuring these compounds for providing data for health risk assessments and for atmospheric chemistry modeling.

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REFERENCES

1. EPA's Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Method TO-14: "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA Passivated Canister Sampling and Gas Chromatographic Analysis", EPA 600/4-89/017, U.S. EPA, Research Triangle Park, NC, 27711.
2. "Final Report on the Operations and Findings of the Toxic Air Monitoring System (TAMS)", Draft Report, Gary F. Evans, AREAL, U.S. EPA, Research Triangle Park, NC, 27711.
3. W.A. McClenny, K.D. Oliver, and J.D. Pleil, "A Field Strategy for Sorting Volatile Organics into Source Related Groups", Environ. Sci. Technol., Vol. 23, No. 11, November, 1989.
4. J.D. Pleil, W.A. McClenny, M.W. Holdren, A.J. Pollack and K.D. Oliver, "Sector Sampling for Volatile Organics Contributions to Ambient Air from Industrial Sources", Proceedings: 1990 EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, Raleigh, NC, May 1990.

TABLE 1: Average Organohalogen Concentrations (ppbv) for 1988 TAMS Study in 4 U.S. Cities

Compound	Boston	Chicago	Houston	Seattle
Methyl Chloride	0.63	0.67	0.83	0.54
Dichloromethane	0.78	0.62	1.50	1.80
Methylchloroform	1.60	1.07	2.99	2.03
Carbontetrachloride	0.11	0.11	0.16	0.11
Trichloroethylene	0.12	0.24	0.27	0.00
Tetrachloroethylene	0.34	0.28	0.24	0.05

TABLE 2: Average Organohalogen Concentrations (ppbv) for 1989 TAMS Study in 4 U.S. Cities

Compound	Boston	Chicago	Houston	Seattle
Methyl Chloride	0.57	0.58	0.77	0.64
Dichloromethane	0.48	0.75	1.68	1.05
Methylchloroform	0.81	0.90	1.01	0.95
Carbontetrachloride	0.12	0.12	0.16	0.12
Trichloroethylene	NA	NA	NA	NA
Tetrachloroethylene	0.29	0.25	0.12	0.10

TABLE 3: Average Organohalogen Concentrations (ppbv) for 1987 Study in Richmond, Virginia and 1989 Study in New Castle, Delaware, Both Near Industrial Sites

Compound	* Richmond	* New Castle
Freon 12	2.02	0.58
Methyl Chloride	NA	0.47
Freon 11	3.20	0.35
Dichloromethane	1.64	0.95
Freon 113	0.03	NA
Chloroform	0.19	0.00
Methylchloroform	0.38	0.55
Carbontetrachloride	0.18	0.16
Trichloroethylene	0.00	0.00
Tetrachloroethylene	0.06	0.00
Chlorobenzene	0.00	0.25
p-Dichlorobenzene	0.00	0.61
o-Dichlorobenzene	0.00	0.13
Trichlorobenzene	0.10	0.04

* These concentrations are averages of data from instrument development field tests; no rigorous in-field OA was performed.