



Project Summary

Laboratory Evaluation of Non-Methane Organic Carbon Determination in Ambient Air by Cryogenic Preconcentration and Flame Ionization Detection

R. K. M. Jayanty and A. Blackard

Results of this study demonstrate the feasibility of a technique for analyzing samples of ambient air for gaseous nonmethane organic compounds (NMOC) using a cryogenic trap to both preconcentrate and separate NMOC from methane (CH_4). The NMOC is subsequently measured by warming the trap to release the NMOC and channeling the concentrated sample of NMOC into a modified commercial flame ionization detector. The system response per carbon atom is linear and uniform for a large group of hydrocarbons analyzed singly or in mixtures. Analyses of aromatic hydrocarbons indicate a reduced per-carbon response that varies with each compound but is linear with concentration. Precision is within ± 5 percent for standard gas calibrations and generally within ± 10 percent for ambient samples. Accuracy for ambient air samples has been determined to be ± 15 percent by comparison with compound-specific GC analysis. Experimental results also show no significant effect from humidity over a wide range of concentrations (75 to 5,000 ppbC). The analytical method is simple, rapid, and cost effective, and the NMOC measurements can be used to establish a basis for control of hydro-

carbon emissions in order to meet oxidant criteria levels.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Ambient nonmethane hydrocarbons and nitrogen oxides (NO_x) are primary precursors of ozone (O_3) and other oxidants, which are key constituents of photochemical smog. Current strategies for controlling photochemical oxidants depend on abatement of nonmethane organic carbon (NMOC) as the primary means of control. A variety of photochemical models have been developed to describe the quantitative relationships between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of ozone.¹ An important application of such models is to determine the degree of control of organic compounds that is necessary in a particular area to achieve compliance with applicable ambient air quality standards for

ozone.^{1, 2} Simple empirical models such as the Empirical Kinetic Modeling Approach (EKMA) require total NMOC concentration data, specifically the average total NMOC concentrations for 6 a.m. to 9 a.m. daily.²

For many EKMA applications, NMOC measurements are required at urban, center-city-type sites.² The moderately high NMOC concentrations typically found at such urban sites can be measured adequately by commercially available continuous (or semicontinuous) NMOC analyzers. However, if transport of precursors into an area is to be considered, then NMOC measurements upwind of the area also are necessary.² Upwind NMOC concentrations are likely to be very low (less than a few tenths of 1 ppm) and, therefore, may not be measured adequately by conventional NMOC analyzers. GC measurements of individual NMOC species can be used by summing the various components to obtain a total NMOC. But for EKMA, the species data are not needed, and species analysis cost is high.

The method described herein can be used instead to obtain the requisite, upwind NMOC measurements by direct measurements. Also, bag or canister samples from urban sites can be brought to the upwind site for subsequent analysis. The higher concentrations at the urban sites tend to minimize the effect of losses or contamination of the bag or canister samples, while the low, upwind concentrations are measured directly. Thus, all measurements can be made with a single analytical system.

Analytical System

The analytical system consists of a trapping system to preconcentrate the sample and a total organic carbon (TOC) analyzer. The sample trapping system serves two primary purposes: (1) it separates methane and air from the

NMOC sample, and (2) it concentrates the NMOC, which enhances the method's sensitivity. Figure 1 shows a schematic of the system. The design of the cryogenically cooled, open tubular sample trap and the use of either liquid argon or liquid oxygen as a cryogen are critical points for this technique.

A detailed description of the operating procedures used for this system is presented in the project report. Briefly, a precisely measured volume of sample air is drawn through the analysis system by monitoring the pressure rise in an evacuated reservoir. As this air sample is drawn through the cryogenically cooled, open tubular trap, the NMOC are concentrated on the trap's inner surface either by adsorption or condensation.

After the desired volume of ambient sample air has passed through the trap, a helium carrier gas is directed through the trap and into the TOC analyzer. When the trap is purged of residual methane and oxygen and when the baseline becomes steady (usually taking 2 to 5 minutes), the Dewar of cryogen is removed from the trap, and the trap is heated to release the NMOC as a single peak (or a few peaks) as seen by the TOC analyzer.

A variety of sample collecting techniques may be used, including clean evacuated canisters, Tedlar® bags, or Teflon® bags. Ambient air or calibration standards may also be sampled directly from a sample manifold.

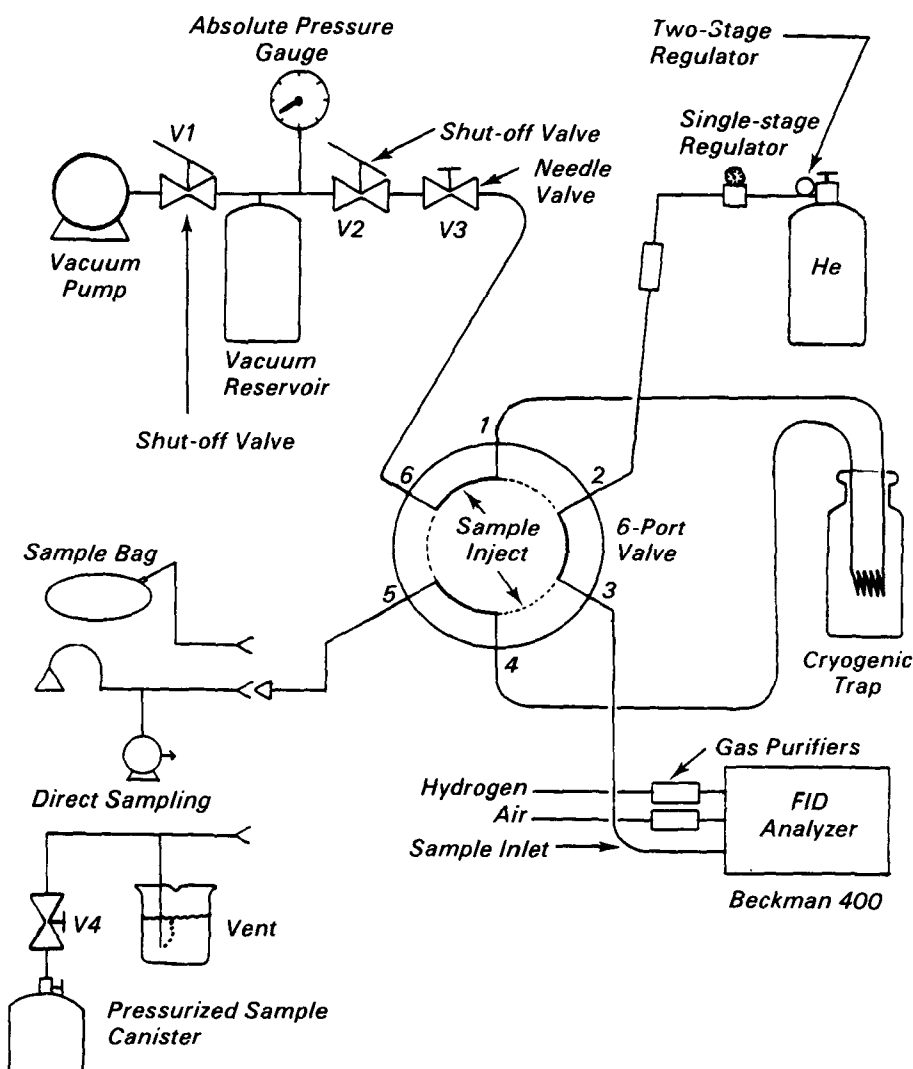


Figure 1. Schematic of analysis system showing three sampling modes.

Office of Air Quality Planning and Standards Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors EPA-450/2-77-021a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977 120 pp

² Office of Air Quality Planning and Standards Guidance for Collection of Ambient Air Nonmethane Organic Compound (NMOC) Data for Use in 1982 Ozone SIP Development, and Network Design and Siting Criteria for the NMOC and NO_x Monitors. EPA-450/4-80-011, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1980. 27pp

Results and Discussion

Two prototype NMOC analysis systems were evaluated. The first prototype was delivered to the Research Triangle Institute (RTI) by the U.S. Environmental Protection Agency (EPA) after construction and some preliminary evaluation by J. M. McBride and Dr. W. A. McClenny of EPA; the second was constructed by RTI in an effort to produce a portable unit and to incorporate some minor changes to improve cryogenic trapping.

The system response to known mixtures of hydrocarbons in air is summarized in Figure 2. FID response peaks are integrated and plotted for various loadings, in nanograms carbon. Analysis of 9.56 ppmV methane in air gave no response. All paraffinic and olefinic hydrocarbons show approximately equal and linear response per carbon atom. The per-carbon responses for toluene, benzene, and ethylbenzene are approximately 19 percent lower and the responses for xylenes are 50 percent lower than those for the paraffinic and olefinic hydrocarbons. To identify the cause of reduced system response to aromatics, several experiments were performed. In the first, two traps (100 cm long) were placed in series. When p-xylene was sampled, no p-xylene was collected in the second trap, implying a 100-percent trapping efficiency in the first trap. To determine the flame response for p-xylene, an experiment was performed by direct injection of p-xylene and propane (for reference) into the flame. The results for two different concentrations (704 and 1,030 ppbC) showed the response of p-xylene to be 30 percent lower than the propane response in both cases. The 30-percent lower response of p-xylene is apparently due to nonuniform FID response. The remaining 20 percent difference between p-xylene and the propane responses is unknown but could be due to losses in sampling lines. The same is probably true for low response of benzene, ethylbenzene, and toluene. Further work is needed to substantiate these speculations.

Several operational parameters were varied to determine system sensitivity. The humidity of the sample air varied from ~15,000 to 30,000 ppm at approximately 23°C and caused negligible response variation (± 5 percent) in trial runs using propane in air, provided that the trap and lines were not contaminated. When contamination was present, unusually broad peaks and long tailing were observed. The effect of vari-

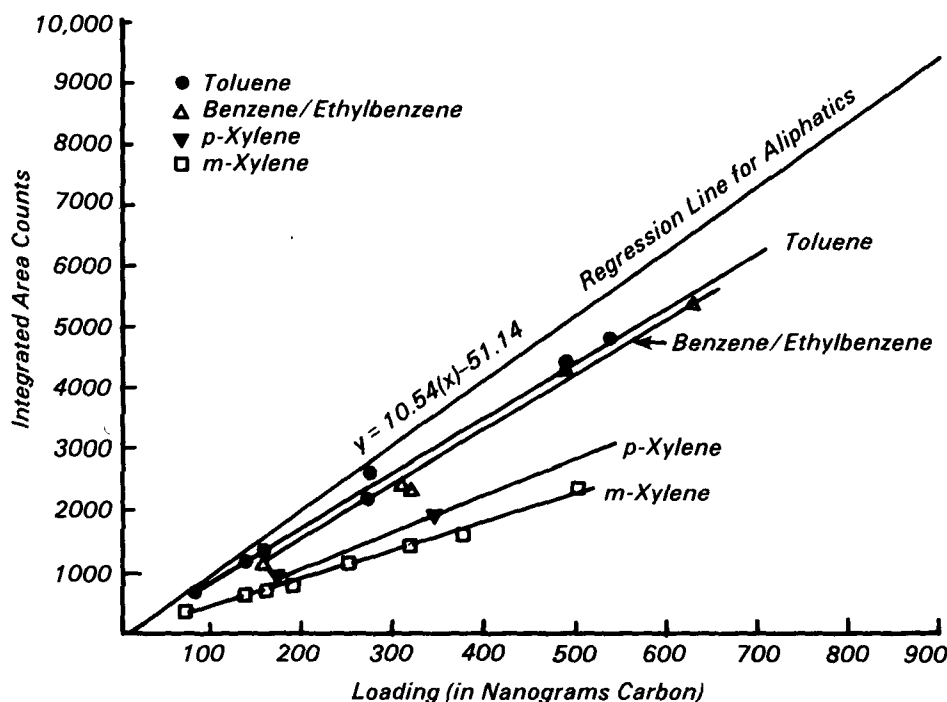


Figure 2. Aromatic hydrocarbon responses for the RTI prototype system.

ation in sample volume from 100 to 500 mL using both propane and a hydrocarbon mix was also studied. Linear response was obtained for volumes in the range of 250 mL to 500 mL. For lower volumes of 100 mL and 125 mL, the response was lower by 27 and 14 percent, respectively, probably due to the finite volume of the system between the six-port valve and the cryogenic trap.

A series of ambient air samples collected in stainless steel canisters was analyzed using the second NMOC analytical system and GC analysis of individual compounds. The analytical results are compared in Table 1. The 12 comparative analyses showed the NMOC method to average 17.6 percent higher than GC analyses, with 8 of 12 analyses falling within ± 15 percent. When a standard mixture of C₂-C₁₀ aliphatic and aromatic compounds in air was analyzed, excellent agreement was obtained (± 8 percent). Precision has been within ± 5 percent for standard gas calibrations and generally within ± 10 percent for ambient samples.

Conclusions

A simple, rapid, and cost-effective procedure for measuring ambient NMOC was established and evaluated.

The precision and linearity of the measurement technique and the lack of significant interference from H₂O and CH₄ are especially encouraging. A major accomplishment was the selection of trap and flow parameters that permit valve and gas stream switching while maintaining a stable FID response and quantitatively trapping non-methane hydrocarbons. The technique is promising for applications where ambient hydrocarbons are sampled remotely in containers and then returned to a central location for analysis.

Recommendations

Further testing seems necessary to obtain improved comparisons with compound-specific GC analyses of ambient samples and to improve the method's efficiency with aromatic compounds.

Table 1. Comparison of NMOC Concentration in Ambient Samples Collected in Stainless Steel Canisters and Analyzed by NMOC Method and Gas Chromatography

Sample No.	Date	GC Analysis (as NMOC) (ppbC)	NMOC Analysis (ppbC)	RSD* NMOC (%)	NMOC-GC (ppbC)	Percent Error†
1	1/9/81	846	929	11	+ 83	+ 9.8
2	1/12/81	380	500	12	+120	+31.6
3	1/13/81	945	984	2	+ 39	+ 4.1
4	1/14/81	120	175	6	+ 55	+45.8
5	1/14/81	129	188	10	+ 59	+45.7
		120	---			+56.7
6	1/16/81	390	437	3	+ 68	+12.0
7	1/16/81	769	982	6	+213	+27.7
8	1/20/81	533	469	1	- 64	-12.0
9	1/20/81	328	365	2	+ 37	+11.2
10	1/20/81	223	252	9	+ 29	+13.0
11	1/20/81	549	469	12	- 80	-14.6
12	1/27/81	443	422	11	- 21	- 4.7
					Mean + 45	Mean +17.4

*Relative Standard Deviation of NMOC Results (RSD) = $\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$.

†Percent Error = $\frac{\text{NMOC result} - \text{GC result}}{\text{GC result}} \times 100$.

R. K. M. Jayanty and A. Blackard are with the Research Triangle Institute, Research Triangle Park, NC 27709.

Frank F. McElroy and William A. McClenny are the EPA Project Officers (see below).

The complete report, entitled "Laboratory Evaluation of Non-Methane Organic Carbon Determination in Ambient Air by Cryogenic Preconcentration and Flame Ionization Detection," (Order No. PB 82-224 965; Cost: \$10.50, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

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Telephone: 703-487-4650

The EPA Project Officers can be contacted at:

Environmental Monitoring Systems Laboratory

U.S. Environmental Protection Agency

Research Triangle Park, NC 27711

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