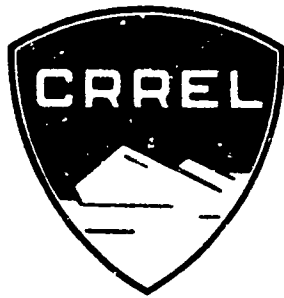


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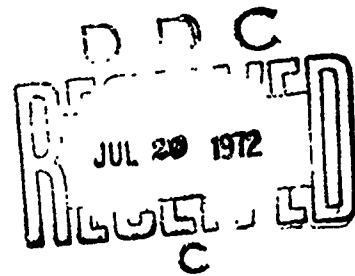
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A METHOD FOR CONCENTRATING AND DETERMINING TRACE ORGANIC COMPOUNDS IN THE ATMOSPHERE

D. C. Leggett, R. P. Murrmann,
T. J. Jenkins and R. Barriera

June 1972



CORPS OF ENGINEERS, U.S. ARMY
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY

HANOVER, NEW HAMPSHIRE

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PREFACE

This report was prepared by Mr. D.C. Leggett (Research Chemist), Dr. R.P. Murrmann (Research Chemist), Mr. T.F. Jenkins, Jr. (Research Chemist), and SP R. Barrera of the Research Division, U.S. Army Cold Regions Research and Engineering Laboratory (USA CRREL).

The work was supported by U.S. Army Mobility Equipment Research and Development Command, under DA Task A1J2200002.

This report was technically reviewed by Captain P. Hunt, Mr. J. Cragin, and SP M. Herron.

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CONTENTS

	Page
Introduction	1
Experimental	2
Materials and equipment	2
Preparation of collection tubes	2
Sample collection	3
Analytical procedures	4
Results and discussion	4
Summary	6
Literature cited	7
Abstract	9

ILLUSTRATION

Figure	
1. Schematic diagram of sample elution and injection system	3

TABLES

Table	
I. Chromatogram of 10-liter air sample, Grafton County, New Hampshire, 19 May 1971	5
II. Chromatogram of 10-liter air sample, Grafton County, New Hampshire, 9 June 1971	6
III. Electron capturing substances identified in atmospheric samples from rural Grafton County, New Hampshire, May and June 1971	7

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by

D.C. Leggett, R.P. Murrmann, T.F. Jenkins, and R. Barriera

INTRODUCTION

The development of trace gas sensors for detecting explosives and mines is of military significance. The development of these devices requires knowledge of the types of probable background contaminants that can interfere with the detection. Toward this end the authors have undertaken the development of methods for the analysis of trace organic compounds in the atmosphere, since this is the medium in which these detection devices are required to work.

Few data are available on the distribution of trace organic compounds in the unpolluted atmosphere, primarily because detection and measurement of these compounds at the levels found in unpolluted atmospheres requires sensitivity beyond the range of most commercially available instrumentation. For example, direct analysis of organic compounds by gas chromatography using flame ionization detectors is sensitive only to about 1 ppb.

Thus, the analysis of remote atmospheres for trace organic compounds required special inlet systems that enabled the compounds to be concentrated from several hundred milliliters of air before analysis.⁵ Even with prior concentration the levels observed were barely detectable. In fact, concentration techniques have generally been needed to measure hydrocarbons even in relatively polluted urban environments.^{1 2 7 11 15 20 21}

Typical concentration techniques have used cryogenic trapping of the trace organic compounds by a solid or liquid-coated chromatographic support.^{2 5 20 21} However, water vapor is also retained by this procedure. This poses a problem for chromatographic analysis and generally restricts the size of the air sample to a few hundred milliliters.

Procedures used in this laboratory for analyzing air samples in the presence of large amounts of water were described in earlier reports.^{14 22 24} The trace organic compounds in 3 liters of air were trapped cryogenically on glass beads and eluted later at elevated temperature onto a Porapak Q column. Water did not interfere in this process but resolution of the complex mixture of trace compounds found in the air samples was inadequate.

Removal of water by passing the air samples over desiccants before cryogenically trapping the trace compounds is a useful technique^{14 23} but is not applicable to some classes of compounds because of adsorptive losses.²⁵

Sample collection in remote environments is also a problem because it is often inconvenient to perform on-site analysis. The collection of samples in remote areas for later laboratory analysis

2 CONCENTRATING AND DETERMINING TRACE ORGANIC COMPOUNDS IN ATMOSPHERE

requires a source of refrigerant if concentration is to be done in the field, or some type of container if whole air samples are to be returned to the laboratory. In any case, care must be taken to preserve sample integrity during the time between collection of the sample and analysis.

Porous polymers such as the Porapak and Chromosorb 100 series apparently have not been used extensively as adsorbants for concentrating organic compounds from large volumes of air, despite their unique suitability. The analysis of halogenated hydrocarbons in a contaminated atmosphere by direct concentration on a Porapak Q column has been described.²⁴ More recently, Chromosorb 102 was used for concentrating volatile organic compounds from polluted atmospheric samples.⁶ However, no quantitative data were reported.

This report describes a method for acquiring and concentrating trace organic compounds in remote atmospheres. This method is illustrated by the determination of volatile organic compounds in a rural atmosphere at sub-ppb levels. By drawing an air sample through a tube containing Porapak Q-S, the organic compounds in large volumes of air are collected without using refrigerants. The small amounts of water retained by the adsorbant are completely removed by flushing the collection tube with dry helium before analysis of the sample, enabling the trace organic compounds to be determined by gas chromatography without interference from water. Finally, although this method is designed to determine trace gases in the atmosphere it will undoubtedly be useful for many other vapor analysis problems.

EXPERIMENTAL

Materials and equipment

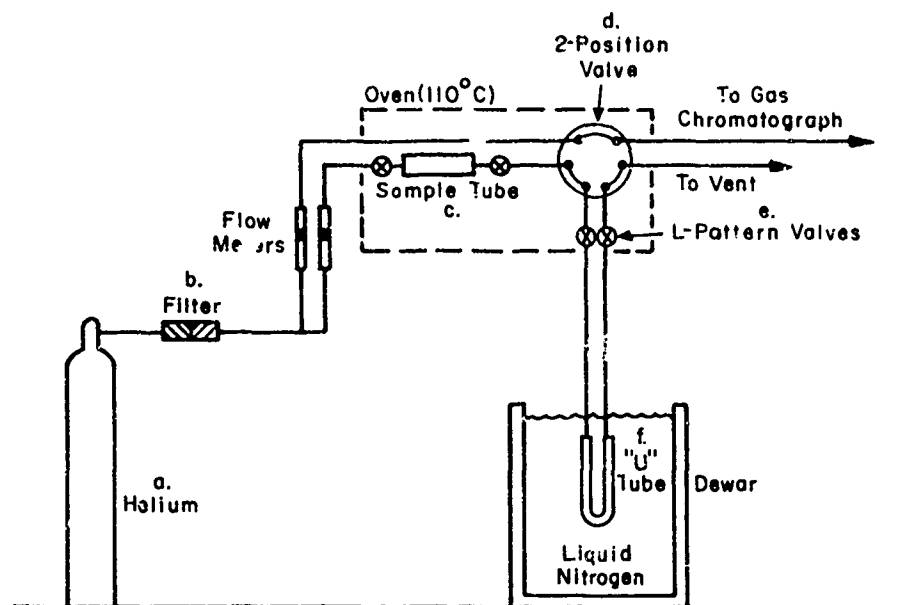
Sample collection tubes were made from 1/2-in.-OD 316 stainless steel tubing and valves that had been cleaned with acetone and chloroform. The tubes were filled with 2.0 g of Water Associates' 100- to 120-mesh Porapak Q-S adsorbant, and the valves were connected to the tubes with Swagelok nuts and Teflon ferrules. The packing was retained by silanized glass wool. The tube-valve assemblies were cleaned before and after they were filled with the adsorbant by baking them at 100 C with a helium flow of 50 ml/min until they were shown to be clean by a blank run on a chromatograph with a flame ionization detector operated at 8×10^{-11} amp/full scale. Forty-eight hours was generally sufficient baking time.

The Perkin-Elmer 900 gas chromatograph used in this work was modified to accommodate a special inlet system shown schematically in Figure 1. The sample loop, an 8-in. by 1/8-in. stainless steel U-tube partially filled with 100- to 120-mesh Anakrom ABS coated with 15% DC-200 silicone oil, was connected to a two-way Carle microvalve. Precision Sampling L-pattern capillary valves were placed between the U-tube and the microvalve so that the loop could be isolated. The entire inlet system except for the sample loop was enclosed in an oven.

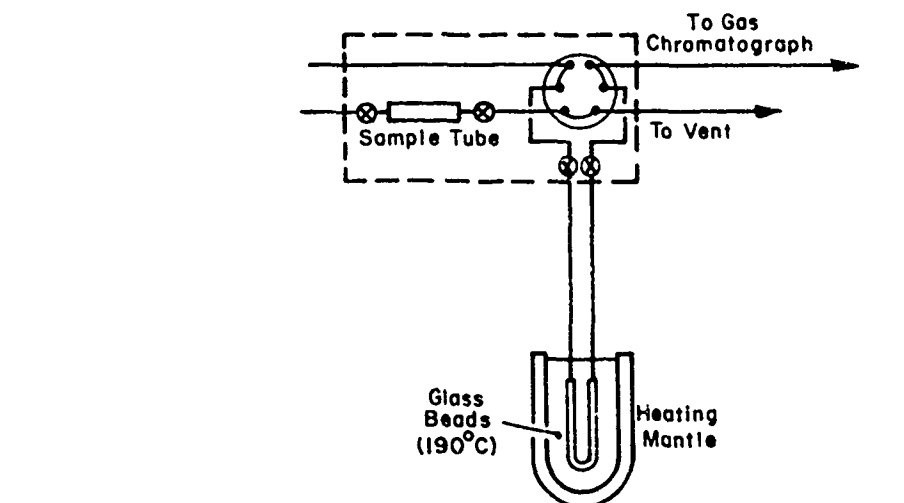
Preparation of collection tubes

The tubes used in this study were baked out immediately before being used and were analyzed immediately after the samples were collected. This precaution was taken to minimize the possibility of contamination seriously affecting the results at the extremely low levels of volatile compounds being measured.

Recent work has shown that with time the tubes become slightly contaminated even though no leaks around the tube fittings can be detected. This may be the result of degradation or diffusion processes occurring within the tubes that are not yet understood. Any leaks around the fittings produce significant contamination unless precautions are taken to protect the tubes from the atmosphere. Also, care must be taken to prevent the temperature of the tubes from rising much above 110 C during the analysis; otherwise, significant amounts of contaminants will be produced.



a. Sample elution.



b. Sample injection.

Figure 1. Schematic diagram of sample elution and injection system. a. Helium "zero" gas cylinder. b. Filter containing molecular sieve and silica gel. c. Sample collection tube containing Porapak Q-S adsorbant. d. 2-position microvolume valve (Carle). e. L-pattern microvalve. f. U-tube containing 15% DC 200 silicone oil on Anakrom ABS (100- to 120-mesh).

Sample collection

Samples were collected in the field by drawing air through the collection tubes with Welch Scientific Co. bicycle-type hand pumps having a displacement of about 400 ml. The pumps were calibrated before field use by water displacement. In the laboratory, samples were generally taken with a Gast portable electrical vacuum pump. The rate of the pump was calibrated with a soap-bubble flow meter.

4 CONCENTRATING AND DETERMINING TRACE ORGANIC COMPOUNDS IN ATMOSPHERE

Varying the rate of sample collection from 100 to 1000 ml/min did not significantly change the collection efficiency and gave the same results as the hand pump. Therefore, collection efficiency was considered to be complete up to the point at which a given compound began to elute (breakthrough volume). This volume varies according to the retention characteristic of the compound. In general, compounds of C₇ and larger were quantitatively adsorbed from a 10-liter air sample taken at 25°C. The breakthrough volume for compounds eluting earlier was determined by preparing a curve of observed concentration versus sample size while sampling the air in a large room, a relatively constant source.

Analytical procedures

After the sample was collected, the tubes were connected to a regulated source of helium and flushed in the direction in which they were collected for 30 min at a flow of 50 ml/min at ambient temperature (~25°C). This procedure removed residual water as well as early-eluting compounds including C₁-C₃ hydrocarbons. The sample was eluted into the sample loop by backflushing the tube with helium at a flow of 50 ml/min for 30 min. During the elution cycle the temperature of the oven was maintained at 110°C and the sample loop was cooled with liquid nitrogen. After the sample was eluted the loop was isolated and heated to 190°C; the two-way valve was rotated to the "inject" position and the microvalves were opened in sequence, sweeping the contents onto a chromatographic column.

The column chosen for this work was a 9-ft × 1/8-in. stainless steel tube filled with Waters Associates' Durapak, Carbowax 400 chemically bound to Porasil C. The column material was washed with acetone and dried in a vacuum at 80°C before the column was filled. The washing was important to obtain maximum resolution of sample components and minimal column bleed. However, this procedure somewhat changed the retention characteristics of the column. It is thought that some of the Carbowax was removed by this washing, exposing more adsorption sites on the solid. (Acetone elutes after toluene on this column.) The analytical conditions are given in Tables I and II.

The effluent from the column was either fed into a flame ionization detector or split between the flame and a pulsed electron capture detector. In the latter case the signals were recorded simultaneously on a Leeds and Northrup dual-channel millivolt recorder with a disk integrator. Peaks from the flame detector were integrated and converted to concentration using weighted response factors.¹³ The response of the flame detector was determined by periodic injections of 0.5 μl of n-heptane. Sample components were identified by comparing their retention times with those of known compounds. Electron capture peaks were not quantitated.

RESULTS AND DISCUSSION

Tables I and II show the results of representative analyses of 10-liter air samples from rural Grafton County, near Lyme, New Hampshire, taken in May and June 1971. Identifications are tentative since they were determined on only one column. Other liquid phases could have been used to confirm the presence of particular compounds, but the main purpose of this study was to evaluate a technique and not to rigorously identify individual compounds. However, most of the organic compounds tentatively identified have been reported in atmospheric analyses made by other investigators.^{2 5 11 12 16 17 20 21 23}

Most of these compounds are found in vehicle exhaust, which undoubtedly was a major source of atmospheric contaminants observed in this study. Other sources of atmospheric hydrocarbons include soils and vegetation^{4 17 18 19} and natural gas and gasoline vapors.^{1 16 20 21} Organic compounds containing oxygen are probably derived largely from natural sources such as vegetation in remote areas.⁵ In more polluted areas, vehicle emissions may contribute significant amounts of oxygenates.^{8 9 10} Volcanic emanations have been found to contain hydrocarbons and oxygenates as well as halogenated compounds, presumably derived from pyrolysis of organic matter at the source.²²

Table I. Chromatogram of 10-liter air sample,* Grafton County, New Hampshire, 19 May 1971.

Compound	Retention time (min)	Concentration (ppb)
isobutane	6.3	0.10
unknown	6.6	
n-butane	6.7	0.53
1-butene and isobutene	7.2	0.12
2-butene, trans	7.4	0.15
1, 3-butadiene	7.9	0.08
butyne and dimethylpropane	8.3	0.01
2-methylbutane	9.1	0.42
n-pentane	9.5	0.29
2-methyl-1-butene	9.7	0.01
1-pentene	9.9	0.01
2-pentene, trans	10.1	0.03
2-pentene, cis	10.4	0.03
2-methyl-1,3-butadiene	10.6	0.01
2,2-dimethylbutane	11.2	0.02
2-methylpentane	11.7	0.30
3-methylpentane and methylcyclopentane	11.8	0.21
n-hexane	12.0	0.25
unknown	12.4	
acetaldehyde	13.1	†
unknown	13.4	
2,2-dimethylpentane	13.7	0.01
benzene	13.9	0.53
trichloroethylene	14.1	†
n-heptane	14.7	0.02
unknown	15.0	
unknown	15.2	
unknown	15.7	
unknown	16.1	
unknown	16.3	
toluene	16.8	0.54
unknown	17.3	
acetone	18.1	2.5
ethylbenzene	20.6	0.10
m and p-xylene	21.3	0.24
o-xylene	22.3	0.34
unknown	23.6	

*Column: 9-ft \times $\frac{1}{8}$ -in. Carbowax 400 Durapak; temperature programmed from -15°C to 130°C at $10^{\circ}/\text{m}$; carrier gas: helium at 20 ml/min; detector: flame ionization.

†Not determined because of high background interference.

Electron capturing compounds, again identified by their retention times on the Carbowax column, are listed in Table III. Except for carbon disulfide, these compounds are halogenated hydrocarbons, all of which are commonly used industrial chemicals; this probably accounts for their presence in the atmosphere.^{22, 23} These compounds would not have been observed if flame ionization detection alone had been used, because the chromatographic peaks were obscured by the flame response to hydrocarbons eluting at the same time as these compounds or were below the detection limits of the flame (about 1 part in 10^{11} or less in this work). The advantage of using the electron capture detector is

6 CONCENTRATING AND DETERMINING TRACE ORGANIC COMPOUNDS IN ATMOSPHERE

Table II. Chromatogram of 10-liter air sample,* Grafton County, New Hampshire, 9 June 1971.

Compound	Retention time (min)	Concentration (ppb)
isobutane	6.6	0.01
n-butane	6.9	0.11
2-butene, trans	7.6	0.09
2-methylbutane and Freon 11	9.3	0.35†
n-pentane	9.6	0.18
2-methyl-1-butene	9.8	0.003
1-pentene	10.0	0.02
2-pentene, trans	10.2	0.08
2-methyl-2-butene	10.3	0.0005
2-pentene, cis	10.5	0.04
2-methyl-1,3-butadiene	10.7	0.19
2,2-dimethylbutane	11.3	0.02
2-methylpentane and Freon 113	11.8	0.12**
3-methylpentane and methylcyclopentane	11.9	0.09
n-hexane	12.1	0.06
acetaldehyde and tetrachloromethane	12.9	††
benzene	14.0	0.13
trichloroethylene	14.2	††
n-heptane	14.9	0.11
tetrachloroethylene	15.3	***
unknown	15.4	
unknown	15.7	
unknown	15.8	
unknown	16.0	
unknown	16.4	
unknown	16.8	
toluene	16.9	0.09
unknown	17.4	
acetone	17.8	1.7
unknown	17.9	
unknown	19.3	
ethylbenzene	20.6	0.08
unknown	21.8	
unknown	23.2	

*Column: 9-ft x 1/8-in. Carbowax 400 Durapak; temperature programmed from -15°C to 130°C at 10°/m; carrier gas: helium at 20 ml/min; effluent from the column was split (4:1) between a flame and a pulsed electron capture detector with purge of 50 ml/min of argon - 5% methane added between column and detector.

†As 2-methylbutane.

**As 2-methylpentane.

††Not determined because of high background interference.

***Electron capture peak not determined.

that it affords a high degree of specificity; that is, it responds to small amounts of certain types of compounds such as halogenated hydrocarbons without interference from relatively large amounts of hydrocarbons and oxygenates (e.g., see ref. 23).

SUMMARY

A method was developed for the detection and estimation of volatile organic compounds in the atmosphere in the sub-ppb range. Trace substances were concentrated from large volumes of air by

Table III. Electron capturing substances identified in atmospheric samples from rural Grafton County, New Hampshire, May and June 1971.

dichlorodifluoromethane (Freon 12)
 carbon disulfide
 fluorotrichloromethane (Freon 11)
 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)
 tetrachloromethane
 trichloroethylene
 trichloromethane
 tetrachloroethylene

drawing the sample through a tube containing Porapak Q-S adsorbant. Residual water was removed from the sample by flushing the tube with dry helium before backflushing the trace compounds at elevated temperature into a cold trap. The trap was then heated and the contents were flushed into a gas chromatograph. A tube packed with 2 g of 100- to 120-mesh Porapak Q-S was sufficient to completely adsorb hydrocarbons of C_5 and larger from a 10-liter sample of air taken at 25°C.

This method was applied to the determination of trace compounds in rural atmospheric samples. Probable sources of these compounds included vehicle exhaust, biological processes, and industrial chemicals.

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