CHROM. 10,283

COLLECTION AND ANALYSIS OF TRACE ORGANIC EMISSIONS FROM NATURAL SOURCES*

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SUMMARY

A study was undertaken to develop practical techniques for measurement of hydrocarbons and oxygenated volatiles in rural areas. A limited number of rural and urban samples were taken to demonstrate the general applicability of the method. Sampling locations were selected in a large forest at a distance of about 35 miles from a heavily populated area. It turned out that this distance was not sufficient to escape the urban influence and compounds typical of urban activities were found at dilute concentrations.

The sampling method is based on adsorption of the trace organics on suitable adsorbents with subsequent thermal elution. Besides Tenax GC and Carbopack BHT the use of a new carbonaceous adsorbent, Ambersorb XE-340 (Rohm and Haas, Philadelphia, Pa., U.S.A.), was investigated. In preliminary experiments, this material had shown very good adsorption properties for low molecular weight compounds. The analysis of the volatile compounds was performed by gas chromatography–mass spectrometry with both metal and glass capillary columns.

It was found that olefins, terpenes and other thermally labile compounds adsorbed on such materials were not altered even when stored over long periods of time. In general, the amount of volatiles found in rural air were 10–500 times lower than the corresponding levels in urban atmospheres, the lowest levels being found during the winter season. Semiquantitative data were obtained for some major compounds from rural areas. The level of organics strongly depends on season and meteorological conditions. Characteristic substances indigenous to plant life have been identified. Besides terpenes, a number of lower alcohols and esters have been found. Preliminary data are presented for a limited number of samples. Further studies are necessary to characterize and quantitate completely natural organic emissions.

INTRODUCTION

        Most recent efforts to analyze organic volatiles have been directed towards determination of man-made emissions. In general, three groups of organic substances in air can be distinguished. Gases, volatiles, defined as substances which are usually in the liquid state (having approximately the boiling point distribution of gasoline), and solids. For each of these groups, different analytical techniques must be applied. In nature, gases and volatiles are produced by a variety of sources, including plant life. Methane is predominant in air and is present at a concentration of approximately 1.4 ppm[1]. Non-methane organics produced from either man-made activities or natural sources generally decrease in concentration with increasing molecular weight.
        There are several mechanisms for the removal of organic compounds from air, including photochemical reactions. Organic substances vary greatly in their photochemical reactivity and potential for the formation of smog or haze[2-6]. Olefins and similar substances are the most reactive species. It is therefore important to determine accurately the relative contributions of the major emission sources towards the total hydrocarbon burden. Plants, especially trees, have long been suspected of being emitters of large quantities of reactive species, notably terpenes[7-9]. Quantity and identity of such natural hydrocarbons, however, has been the subject of controversy. Reasons for the lack of reliable data must be attributed to difficulties encountered in both sampling and analysis, since one deals with relatively reactive substances at the ppb levels and below. Attempts have been made to classify hydrocarbons in air according to their potential to react with $(NO)_x$ in forming secondary products such as aerosols[2,3,5]. Instrumental approaches have been suggested to separate the "reactive" from the "non-reactive" hydrocarbons[10].
        A wealth of data on trace volatiles in urban air and industrial atmospheres has been generated within the last few years and significant improvements in sampling technology have been implemented. The literature on sample concentration techniques has been covered in detail in a number of recent publications[11-14]. Procedures such as grab sampling with bags or metal containers, which is conceptually the simplest approach, do not provide sufficient quantities for analysis by present instrumentation. Preconcentration steps are necessary. Cryogenic procedures are very effective, especially for low boiling compounds. There are however some drawbacks, such as possible side effects due to condensed water (essentially one has to deal with very dilute aqueous solutions) and inconveniences in sampling and sample regeneration. Various carbonaceous materials of high surface area have been suggested in combination with solvent extraction.
        Irreversible sorption and problems with inhomogeneous surface make their application controversial.
        Organic polymers have recently become popular for the concentration of trace organics from dilute media (air and water) as well as for headspace analysis in general. A number of commercially available adsorbents have been systematically studied for the purpose of serving as vehicles for concentration from very dilute media[15,16]. Among these polymers, Tenax GC has become widely accepted in air and water analysis[11-14,17-30]. Dynamic enrichment on such polymers suffers principally from two shortcomings: (1) incomplete or substance-specific adsorption of low molecular weight and polar compounds and (2) generation of artifacts during thermal elution.

The first effect is an inherent limitation of the method; the latter, however, can largely be eliminated by proper clean-up and conditioning procedures. The greatest assets of the ambient adsorption–thermal elution principle are its extreme simplicity and speed.

It should be noted at this time that the most favorable method for sampling depends on the analytical procedure to be used. High-resolution capillary columns are a necessity because of the observed sample complexity and low concentration levels involved in such samples. A suitable procedure must therefore be found to transfer the sample concentrate into the low volume column. Instrumental requirements have been discussed in detail by Grob and Grob[31]. Glass capillary column technology has developed to a high level of sophistication. Unfortunately only a few of the laboratories in which trace environmental analysis is performed actually make use of such high-resolution systems at this time.

EXPERIMENTAL

Sampling

The principal approach to air sampling has been described previously[17]. Sample tubes were made of glass, 110 × 8 mm O.D. Before filling with adsorbent, three small indentations were made on the upper end of the adsorbent tube with a micro-torch, to hold the glass wool plugs in place. This measure proved useful since sudden application of vacuum under field sampling conditions sometimes dislocated some of the adsorbent leading to channeling effects. The glass tubes were deactivated by gas phase silylation[32]. Tenax GC, 60–80 mesh (Applied Science Labs., State College, Pa., U.S.A.), Carbopack BHT, 60–80 mesh (Supelco, Bellefonte, Pa., U.S.A.) and a 60–80 mesh fraction of crushed Ambersorb XE-340 (Rohm and Haas, Philadelphia, Pa., U.S.A.) were tightly packed into these tubes. Occasionally, some batches of Tenax were subjected to Soxhlet extraction with methanol, ethyl acetate and pentane (purchased from local sources and redistilled in our laboratories). Initial conditioning took place over 24-h periods at 360° for Tenax GC and Carbopack BHT. Ambersorb XE-340 was heated to 450°. A slightly yellow appearance of the Tenax material had no adverse effects.

For field sampling, tanks of approximately 35 l volume were used. The tanks were equipped with metering valves and evacuated prior to field sampling. The sample tubes were attached to the vacuum tanks singly or in series using shrinkable PTFE sleeve connectors. The valve was adjusted to flow-rates between 100 ml/min and 300 ml/min. Sample volumes were between 3 l and 30 l. At the end of the sampling period, the tubes were placed in PTFE-capped vials and stored in the refrigerator until the time of analysis.

The retention behavior of some model substances was studied using stainless steel columns, packed with adsorbent. The standards were injected at three different column temperatures. The specific retention volume (V_g) was extrapolated to 25° according to the formula $\log V_g = a/T + b$ using an HP-97 programmable calculator[*].

Analysis

For gas chromatographic analysis, several gas chromatographs were used

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[*] The computer program was provided by Dr. R. E. Kaiser, I.F.C., Bad Dürkheim, G.F.R.

including a Perkin-Elmer 900 with parallel flame ionization (FID) and electron capture detectors (ECD), a Perkin-Elmer 3920 with dual FID and a Hewlett-Packard 5830 with single FID. All instruments were modified to accept the sample tubes and operate without loss of efficiency with capillary columns. Both metal[17] and glass capillary columns[13] were used with operational conditions as described previously.

Gas chromatography–mass spectrometry (GC–MS) was performed on an LKB 9000 instrument[30], equipped with a single stage jet separator and a Model 2700 gas chromatograph, combined with a CH5 mass spectrometer[19] (Varian MAT, Bremen, G.F.R.). The latter was interfaced to a gas chromatograph via a heated platinum capillary and was equipped with a high speed pumping system. Data were handled manually for the LKB 9000 GC–MS combination. The Varian MAT CH5 was interfaced to a spectro system 100 MS computer. Identification was done by comparison with a small MS library kept in our laboratories and by reference to published spectra[33].

Chromatographic conformation was only done in a few cases since an extensive set of retention data on principal air pollutants is available in our laboratories.

RESULTS AND DISCUSSION

The degree to which organic volatiles in air participate in photochemical reactions in the atmosphere depends on a number of factors, including the chemical structure of the compound. It has long been suspected that smog episodes generated under adverse conditions in large urban areas have a counterpart in nature. Data have been collected on the formation of haze above large forest areas, such as the Great Smokey Mountain National Park, which derives its name from this phenomenon. Plants in general and trees in particular, do emit organic volatiles as a part of their respiratory cycle. Total amounts and nature of natural emission depends on factors such as type and density of vegetation, season, temperature, etc. The samples were taken at several locations in the Talladega National Forest (Alabama). The closest urban activities were 20–35 miles away, depending on sampling location. Vegetation in this forest is generally mixed; however, coniferous trees dominate.

Fig. 1 demonstrates a typical pattern. The samples were taken in the late fall of 1976 at a location approximately balanced with respect to hardwood and evergreen trees. Despite a thick underbrush, the area is relatively open and allows a fast exchange of air. The wind was blowing from a direction such that any emission generated from the close industrial or urban activity would be carried away. Table I confirms the identity of common components in both samples. In general, the basic urban pattern which is found in rural areas has been diluted by up to approximately two orders of magnitude. However, other compounds which are derived from natural sources appear in rural air. This observation has been substantiated by Bergert and Betz[34].

Table II summarizes some quantitative data for a few recognizable key components from urban and ruran samples. It should be noted that the absolute levels are strongly dependent on weather conditions.

Samples were taken from the summer of 1976 to the spring of 1977. The sample integrity is assured upon storage as demonstrated by the following set of circumstances. Two sets of samples taken during October and early December 1976
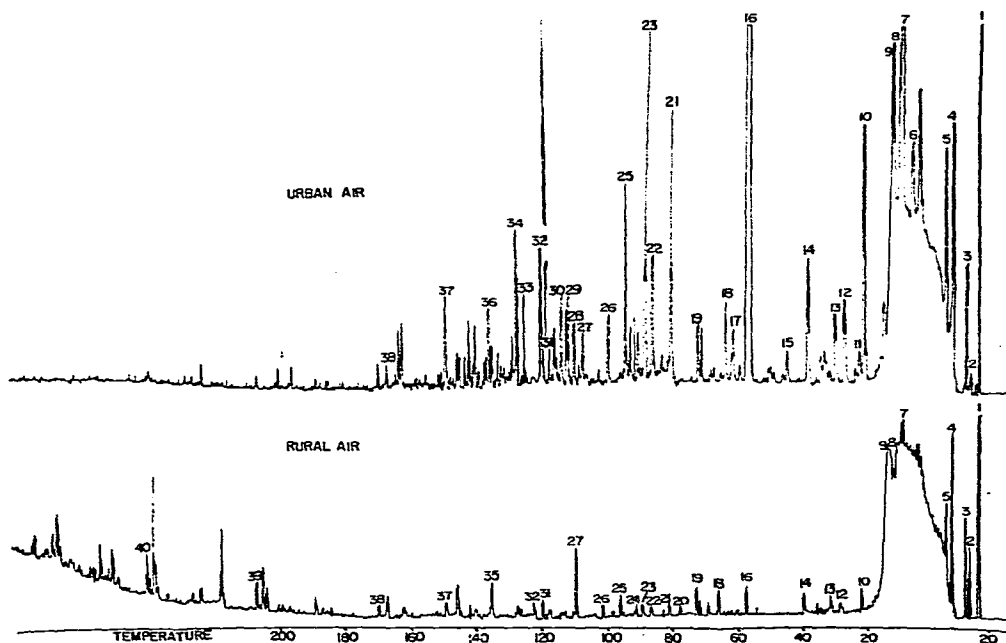
Fig. 1. Total ion current chromatograms (LKB 9000) of urban air (Tuscaloosa, Ala., U.S.A.) and rural air (Talladega National Forest, Ala., U.S.A.). Samples were collected in December 1976. Adsorbent, Tenax GC; sample size, 25 l; glass capillary column, 40 m × 0.35 mm I.D. coated with OV 101; carrier gas (helium) flow-rate, 3 ml/min; temperature program, 20° for 12 min, 20°–200° at 3°/min. For identification of the peaks, see Table I.

TABLE I

VOLATILES IDENTIFIED IN URBAN AIR AND RURAL AIR

No.	Compound	No.	Compound
1	Air*	21	C_8H_{16}
2	C_5H_{10}	22	Ethylbenzene
3	Acetaldehyde	23	m,p-Xylene
4	C_5H_{12}	24	Isoamyl acetate
5	Diethyl ether	25	Styrene
6	2-Methylpentane	26	Dimethylheptane
7	n-Hexane	27	α-Pinene
8	Chloroform	28	$C_{10}H_{20}$
9	Ethyl acetate	29	C_3-Alkylbenzene
10	Benzene	30	C_3-Alkylbenzene
11	Cyclohexane	31	β-Pinene
12	C_6H_{12}	32	$C_{10}H_{22}$
13	Trichloroethylene	33	1,3-Dichlorobenzene
14	n-Heptane	34	C_4-Alkylbenzene
15	2,4-Dimethylhexane	35	Limonene
16	Toluene	36	C_4-Alkylbenzene
17	2,5-Dimethylhexane	37	$C_{11}H_{24}$
18	Diethylcyclohexane	38	$C_{13}H_{26}$
19	n-Octane	39	$C_{14}H_{28}$
20	n-Butyl acetate	40	Benzophenone

* Introduced into the mass spectrometer by the sample introduction method.

TABLE II

CONCENTRATION (ppb*) OF SOME REPRESENTATIVE COMPOUNDS IN URBAN AND RURAL AREAS

Data from 6 sets of samples taken during February 1977. Adsorbent, Carbopack BHT; for conditions, see text. tr = detectable trace, also determined by ECD.

Compound	Tuscaloosa			Talladega National Forest		
	High	Low	Average	High	Low	Average
Benzene	60	16	25	1.3	0.2	0.4
Toluene	85	24	38	1.3	0.2	0.4
Chloroform	3	0.1	0.8	0.2	tr	0.1
Trichloroethylene	6	1	2	0.6	tr	0.2
n-Heptane	17	4	11	0.5	tr	0.2
C_8H_{16} (isomer)	17	3	9	0.6	0.1	0.2
n-Nonane	9	3	5	0.4	0.1	0.1

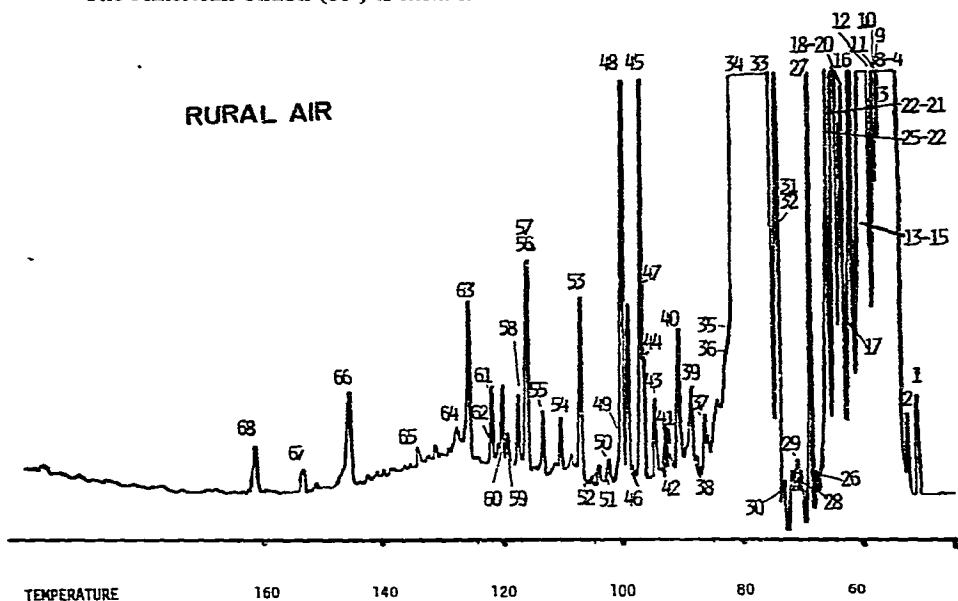* The American billion (10^9) is meant.

Fig. 2. Total ion current chromatogram (Varian MAT, CH5) of rural air (Talladega National Forest, Ala., U.S.A.). Sample was collected October 1976. Adsorbent, Carbopack B; sample size, 25 l; Ni-column, 100 m × 0.5 mm I.D. coated on Emulphor ON-870; carrier gas (helium) flow-rate, 4 ml/min; temperature program, 60° for 16 min, 60°–175° at 2°/min. For identification of the peaks, see Table III.

were sent overseas for MS analysis. The October sample inadvertently went by surface mail and arrived approximately at the same time as the second sample which was delivered within three days after it was taken. Both samples were quite reproducible, which indicates that no major changes in the volatile emissions occurred between October and December.

These particular samples were taken in an area which is primarily covered by hardwood and located some 20 miles from the nearest habitation. The weather was

TABLE III

VOLATILES IDENTIFIED IN RURAL AIR

No.	Compound	No.	Compound
1	Air*	35	$C_{10}H_{22}$
2	C_5H_{12}	36	$C_{10}H_{22}$
3	Ethylamine	37	Butyl acetate
4	Acetaldehyde	38	C_8H_{16}
5	n-Pentane	39	α-Pinene
6	Monofluorotrichloromethane	40	n-Decane
7	Diethyl ether	41	$C_{10}H_{20}$
8	C_6H_{14}	42	$C_{10}H_{20}$
9	Methylcyclopentane	43	1-Butanol
10	C_7H_{16}	44	Isoamyl acetate
11	n-Heptane	45	Ethylbenzene
12	Cyclohexane	46	$C_{10}H_{20}$
13	C_7H_{14}	47	1,4-Dimethylbenzene
14	Acetone	48	1,3-Dimethylbenzene
15	Methyl acetate	49	$C_{10}H_{20}$
16	C_7H_{14}	50	β-Pinene
17	n-Octane	51	$C_{10}H_{20}$
18	Ethyl acetate	52	$C_{10}H_{20}$
19	Methanol	53	1,2-Dimethylbenzene
20	C_8H_{16}	54	Undecane
21	C_8H_{16}	55	n-Propylbenzene
22	Trichloroethane	56	Styrene
23	2-Propanol	57	C_3-Alkylbenzene
24	Ethanol	58	Limonene
25	C_8H_{16}	59	Isobutylbenzene
26	C_8H_{16}	60	C_3-Alkylbenzene
27	Benzene	61	C_3-Alkylbenzene
28	Ethylfuran	62	C_4-Alkylbenzene
29	C_9H_{18}	63	C_4-Alkylbenzene
30	C_9H_{18}	64	C_3-Alkylbenzene
31	Chloroform	65	Methylstyrene
32	Trichloroethylene	66	Dichlorobenzene
33	Toluene	67	Benzaldehyde
34	Tetrachloroethylene	68	Octanol

* Introduced into the mass spectrometer by sample introduction method.

cool and sunny on both days with only a slight wind. Figs. 1 and 2 summarize the results of these experiments. Again, it is apparent that traces of organic compounds typical of urban activity are persistent (Table III). A variety of the oxygenated compounds are also present in both samples.

Another set of samples was taken at the same location during May 1977. The results in general agree with the data obtained during late fall 1976. Cyclohexanone and methyl octanoate which were not found in the December sample, could be identified. Furthermore, the concentration of some oxygenated compounds is much higher in the May sample, notably butanone, 2-pentanone, isoamyl acetate and n-butanol. The source of these oxygenated compounds is not known at this time.

The samples taken during the cold season showed a considerable decrease in terpenoids. At this time only a small amount of quantitative data have been col-

lected. The principal goal of this project has been the establishment of reliable concentration procedures and the qualitative interpretation of the nature of organic compounds emitted from vegetation.

One of the obvious shortcomings of the dynamic enrichment procedures on an adsorbent is the significant loss of low molecular weight components. As pointed out earlier, a good sampling technique should provide a reasonable retention of organic volatiles and relative freedom from artifacts during the adsorption–storage–thermal elution cycle. A large variety of moderate to large surface area adsorbents is available, however only a very few meet the specifications. The major problem appears to be the generation of spurious peaks during thermal elution. Although such effects cannot be avoided completely, especially with organic polymers, outgassing can be greatly reduced by extraction with proper solvents. In our opinion, styrene divinylbenzene-based polymers are unsuitable as adsorbents for high temperature thermal elution regardless of pretreatment. Materials such as Carbopack and Tenax GC however, perform well under such conditions. The retention behavior of some model substances on Tenax GC is demonstrated in Table IV. The substances were sampled at temperatures between 100 and 200°. Before extrapolation to 25°, the linearity of the values was examined by statistical control data. Under the specified field sampling conditions the approximate lower range of application for Tenax GC at which quantitative collection occurs is in the C_7 region.

We have tested numerous materials to extend the range of adsorption for more volatile components. Such a material could be part of a system, which consists of several tubes in series, with each tube adsorbing compounds of a certain molecular weight range. Thermal elution should then be possible under relatively mild conditions. The typical carbon type adsorbents and carbon molecular sieves unfortunately have a very narrow range of application and are far too reactive. Ambersorb XE-340,

TABLE IV

SPECIFIC RETENTION VOLUME OF STANDARDS ON TENAX GC

Column: 5 ft. × 1/8 in. stainless steel, 0.95 g Tenax GC; sampling temps.: between 100° and 200°; injection: 0.01–0.1 μl.

Substance	V_g at 25° (l/g)
Dichloromethane	0.9
Chloroform	5.1
Carbon tetrachloride	25.1
Benzene	26.0
Toluene	128.0
Ethylbenzene	560.0
n-Propylbenzene	1560.0
1-Butene	0.6
1-Pentene	3.0
1-Hexene	17.4
1-Heptene	116.0
1-Octene	370.0
1-Nonene	2300.0
Acetone	3.2
Methyl ethyl ketone	13.6
Ethyl acetate	30.1
Ethyl propionate	117.0

which has properties intermediate to the polymeric and carbonaceous adsorbents, now appears promising.

Preliminary results were obtained from injections of n-alkanes. Table V illustrates, that the retention capacity of the adsorbent is adequate in the C_4 region. This adsorbent in combination with Tenax GC could trap a wide range of volatile substances. However, further evaluation is necessary. We are presently investigating recovery rates and temperatures of standard compounds on XE-340.

TABLE V

SPECIFIC RETENTION VOLUME OF n-ALKANES ON AMBERSORB XE-340

Column: 5 ft. × 1/8 in. stainless steel, 2.6 g Ambersorb XE-340; sampling temps.: between 100° and 300°; injection: 0.01–0.1 μl.

Substance	V_g at 25° (l/g)
Ethane	0.8
n-Propane	8.5
n-Butane	81.0
n-Pentane	880.0
n-Hexane	7600.0
n-Heptane	74000.0

CONCLUSION

Samples from rural areas contain small amounts of hydrocarbons and halocarbons which are also found in urban areas. It appears that compounds which are associated with plant life such as terpenoids greatly vary in concentration, depending primarily on season and meteorological conditions. It also appears that the type of vegetation in the immediate vicinity of the sampling location plays a strong role in the nature and distribution of the volatiles. Several oxygenated classes of compounds (alcohols, ketones and esters) have been identified in rural air samples.

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