

CHROM. 10,246

GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AN URBAN ATMOSPHERE

B. V. IOFFE, V. A. ISIDOROV and I. G. ZENKEVICH

Chemistry Department, Leningrad State University, 199164 Leningrad (U.S.S.R.)

SUMMARY

Polysorbimide and carbochrome, new sorbents with high temperature stability, have been used to concentrate trace amounts of atmospheric pollutants, and 136 C₁-C₁₃ organic compounds, including 126 hydrocarbons, 6 oxygen derivatives and 3 chlorides, were identified in air samples collected in the streets of Leningrad.

One of the major features of the composition of the organic constituents of the urban air sampled is the presence of a number of C_nH_{2n} hydrocarbons (mainly olefins), and also C_nH_{2n-2} and C_nH_{2n-4} unsaturated hydrocarbons (including α -pinene and camphene).

A comparison of the results with those of similar studies carried out on air samples from Zürich, Houston and Paris is of considerable interest in connection with the possible effect of geographical factors on the composition and lifetime of organic pollutants in the atmosphere.

INTRODUCTION

Among difficult analytical problems the solution of which has become possible only in the 1970s as a result of the very efficient combination of capillary gas chromatography and mass spectrometry (GC-MS), one of the most urgent and interesting is the problem of determining trace amounts of organic pollutants in the atmosphere. A detailed study of the composition of atmospheric pollutants is needed not only for the development of convenient techniques for everyday air-purity control, but also for establishing the general laws of ecological chemistry which determine the behaviour of various products of anthropogenic origin entering the environment and the role of the factors that control their composition and concentrations.

Several papers have been published on the GC-MS analysis of volatile organic pollutants in urban atmosphere, the most comprehensive results having been obtained for samples collected in Zürich¹, Houston² and Paris³. Table I gives some data on the number of constituents identified in those studies, the sorbents used for concentration and the geographical coordinates of the cities. The identification in atmospheric air of about 100 organic compounds at the concentration level of *ca.* 10⁻⁷% highlights an important stage in the study of the Earth's atmosphere and of the chemical pro-

TABLE I

GC-MS ANALYSIS FOR VOLATILE ORGANIC CONSTITUENTS IN URBAN ATMOSPHERES

City	Latitude	Longitude	Altitude (km)	Sample volume (l)	Sorbent	Number of constituents identified	Reference
Zürich	47°N	8°E	0.4	25,000	Activated charcoal	108	1
Houston	30°N	95°W	0.0	120-200	Tenax GC	98	2
Paris	49°N	2°E	0.0	200-2000	Graphitized carbon black	72	3
Leningrad	60°N	30°E	0.0	10	Carbochrome and polysorbimide	136	This work

cesses that take place in it. To reveal the general role of these atmospheric pollutants, one should accumulate information for various areas of the Earth differing in geographical and climatic conditions. This paper presents the results of the GC-MS identification of volatile organic pollutants in the air of Leningrad, which is located much further North than the three cities where similar measurements were carried out previously, and in different climatic conditions (*cf.* Table I).

The data on Leningrad air are of particular interest as this city is a centre of research on protection against atmospheric pollution and of the joint Soviet-American programme for air pollution modelling and development of air purification methods.

EXPERIMENTAL

Air sampling was performed at several points in the city by passing 10 l of air at a rate 0.2 l/min through sampling tubes mounted at a height of 1.5 m not closer than 2.5-3 m to the walls of buildings and oriented opposite to the wind direction at the sampling site. On finishing the sampling, the tubes were stoppered with PTFE plugs. As hydrophobic sorbents of high temperature stability we used polysorbimide-1⁴ and carbochrome K-5⁵, developed in the U.S.S.R. The latter is thermally graphitized carbon black modified with of polymethylsiloxane (110 m²/g with a grain size of 0.215-0.315 mm). Polysorbimide is obtained by polycondensation of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether (67.5 m²/g with a grain size of 0.25-0.315 mm). The glass tube containing 0.6 g of polysorbimide was 21 cm long (I.D. 4.3 mm). In experiments with carbochrome, we used tubes of the same length but with I.D. 6.5 mm, containing 0.5 g of sorbent between glass-wool plugs. Prior to work, the tubes were heated for 20 min in a flow of nitrogen at a rate 30 ml/min at 300° and 500°, respectively.

Thermal desorption of the organic compounds was carried out directly into a copper capillary column of 60,000 theoretical plates (50 m × 0.35 mm) with dinonyl phthalate. The entrance section of the column (2 m long) was formed into a spiral and placed in a Dewar flask, the coolant being ice-salt mixture (when using polysorbimide) or dry-ice (for carbochrome). The sampling tube was connected to the

gas system of the chromatograph by means of union nuts with heat-resistant silicone rubber packing between the injection port and the entrance section of the capillary tube so that the direction of carrier gas (helium) flow through the sorbent was opposite to that of the air flow during sampling. The other end of the capillary column was connected to the molecular separator of an LKB-2091 GC-MS system.

Desorption was carried out in a tubular oven at 280° for 20 min (with polysorbimide) or at 400° for 20 min (with carbochrome). The desorbing substances were swept out by the carrier gas and trapped in the cooled zone of the capillary column. When the desorption was finished, the input of the column was connected to the injection port, cooling was discontinued and the mixture was chromatographed in a temperature-programmed mode, the isothermal stage (50° for 10 min) being followed by a temperature increase up to 130° at the rate 5°/min. The duration of the chromatographic analysis was 60–70 min. Fig. 1 shows a typical chromatogram of the volatile organic pollutants in Leningrad air.

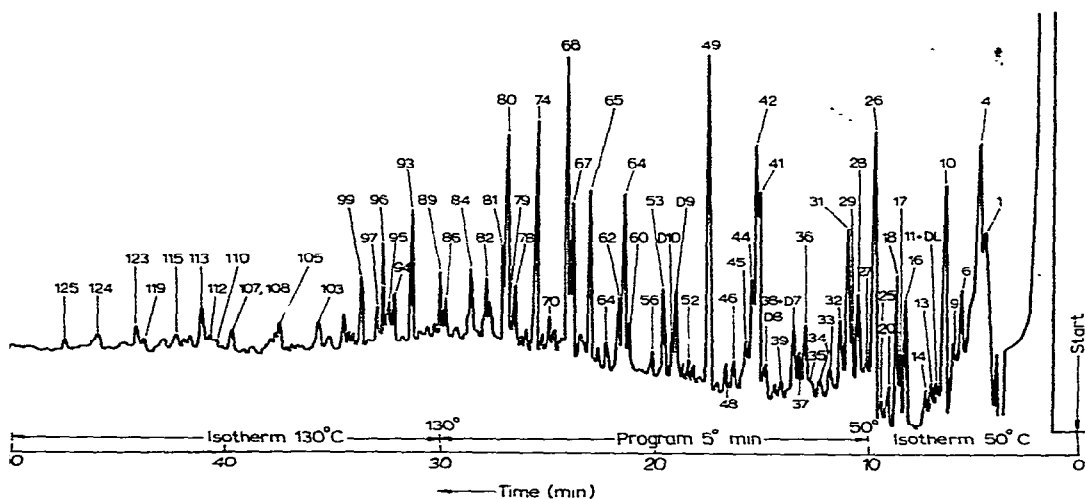


Fig. 1. Typical total ion current chromatogram of volatile organic pollutants of urban air. For identification of peaks, see Tables II and III.

The mass spectra were recorded under the following conditions: ionization voltage when recording the spectra, 70 eV; ionization voltage when recording chromatograms by total ion current, 20 or 12 eV; emission current, 25 μ A; accelerating voltage, 3.5 kV; resolution, 500; ion-source temperature, 180–200°; and separator temperature, 150–180°.

To correct for the background, the characteristic lines of dinonyl phthalate and of admixtures in the carrier gas ($m/e = 40, 44, 73, 133$ and 149) were subtracted. The other background lines sometimes overlapped with the mass spectral lines of the constituents, but their consideration without a computer in the temperature-programmed mode would be difficult and was not carried out. As a result, the weakest peaks in the chromatograms were not identified, and in some instances we had to restrict ourselves to determining the molecular formula. Individual and group identification

of the constituents was performed with the help of compilations of mass spectra^{6,7}. The C_nH_{2n} olefins differed from the isomeric naphthenes by the presence of strong $(C_nH_{2n+1})^+$ peaks in addition to the $(C_nH_{2n-1})^+$ peaks. Monoterpenes were recognized by their characteristic peaks at m/e 136 (M^+), 121, 93 (100%), 79 and 77. Individual identification was possible only for limonene, α -pinene and camphene. Many isomeric aromatic hydrocarbons that differ only in the positions of the side-chains exhibit very similar mass spectra, their identification being possible only when taking into account the retention parameters (order of elution).

RESULTS AND DISCUSSION

In each of the five air analyses carried out in the summer and autumn of 1976 we identified 60–80 constituents, with only partial duplication, the total number of organic pollutants detected being 136. Most of them (126) were hydrocarbons, which are listed in Table II. Twenty-two hydrocarbons were present in each of the samples collected at different points in the city and at different times, so that they can be considered to be permanent constituents of the air in Leningrad. Starting with n -octane and toluene, all the 17 alkane and aromatic hydrocarbons (of the benzene series) which were permanently present in the Leningrad air were also detected earlier in Zürich, Houston and Paris. Taking into account that the presence of some light hydrocarbons (e.g., benzene, hexane and heptane) in the Paris air pollutants³ is probably due to the drawbacks of the technique employed (column cooling was not used when desorbing the pollutants into it), the C_6 – C_{10} benzene hydrocarbons and C_6 – C_{12} n -alkanes can be considered to be permanent constituents of the volatile organic pollutants in the modern urban atmosphere, independent of their geographical location.

Of particular interest are the atmospheric constituents identified in our work for the first time. Of the permanent constituents of Leningrad air, only one hydrocarbon, trimethylcyclohexane, was not detected in the atmospheric air of the other three cities.

Of the non-permanent constituents that we found, the number of organic compounds among them identified for the first time is large. In this list, one should discount several hydrocarbons that we identified for the first time as individual compounds while they were classified in the earlier studies as groups of isomers (Nos. 37, 123 and 124), after which the number of Leningrad atmospheric constituents specified in Table II and not found in other cities becomes 60, *i.e.*, almost half of the total list. A comparison of the nature of these pollutants detected for the first time with that of the hydrocarbons in the second half of the list indicates the existence of clear regularities rather than their being a random set of compounds. The group composition of the list of hydrocarbons detected only in Leningrad differs considerably from those found in the other cities with different geographical and climatic conditions (Table III). Among the hydrocarbons detected by us for the first time, there are only four alkanes (C_5 – C_7 , all branched-chain) and only one aromatic hydrocarbon (cumene), which is apparently the least resistant to oxidation of all benzene homologues detected in the urban atmosphere. The number of these hydrocarbons constitutes less than 10% of the total, whereas in the list of hydrocarbons that occur in different cities the alkanes and aromatic hydrocarbons constitute almost 90%.

Hydrocarbons of the C_nH_{2n} series make up the main fraction (almost two-thirds) of the hydrocarbons specific to Leningrad air. Some of them have been identified as olefins and some as naphthene hydrocarbons. We have not yet succeeded in identifying a large number of the C_nH_{2n} constituents, but many of them are undoubtedly olefins. Also of interest is the presence of a large number of highly unsaturated hydrocarbons of the C_nH_{2n-2} and C_nH_{2n-4} series, which were almost absent from the air of the other cities. In general, unsaturated hydrocarbons constitute more than 90% of the hydrocarbons detected by us for the first time.

These qualitatively different features of the chemical nature of organic pollutants specific to Leningrad air cannot be attributed to any particular sources of atmospheric pollution. We conclude that there are continuously acting objective factors that substantially affect the chemical composition of the organic constituents of the atmosphere, apparently associated with geographical and climatic conditions. The presence in Leningrad air of a large number of highly reactive unsaturated hydrocarbons is due not to their emission there being larger than in the other cities, but rather to their longer lifetime at comparatively high latitudes and the retardation of chemical transformations (primarily oxidation). Indeed, Leningrad lies much further North than the other cities (see Table I). In more southern cities (*e.g.*, Houston is located at 30° N), unsaturated compounds should become oxidized faster, subsequently being removed from the atmosphere. One of the major factors favouring their oxidation may be the UV radiation level, which depends primarily on latitude, as well as on the altitude above sea level.

The establishment of features similar to those discussed above is of considerable interest for the ecology and should undoubtedly become the subject of further detailed studies.

Prior to investigating organic atmospheric constituents other than hydrocarbons, one should consider the presence in the atmosphere of hydrocarbons of non-naphtha origin, *i.e.*, $C_{10}H_{16}$ terpenes. Terpenes belong undoubtedly neither to the major nor to the permanent organic constituents of the atmosphere. Of the hydrocarbons of this class, limonene has previously been found in urban atmospheres (in Zürich¹ and Houston²). We identified it also in Leningrad in three cases out of five. In addition to limonene, however, we detected α -pinene twice and six other $C_{10}H_{16}$ hydrocarbons, including camphene, in one experiment. This air sample was collected at the end of October in an area on the lee side of a timber port. The major source of the terpene hydrocarbons in this instance was apparently not vegetation but rather a local accumulation of timber and fallen leaves. Possibly limonene, which is found in the urban air more frequently than other terpenes, represents, at least partially, a secondary product of transformation of less stable isomers, and it is due to its relative stability that it remains in the atmosphere for a longer time.

The volatile derivatives of hydrocarbons recognized in Leningrad air are much less numerous than the hydrocarbons proper, only 10 such derivatives being identified (Table IV), *i.e.*, about 7% of the total number of constituents identified. None of these compounds are permanent atmospheric constituents, but acetone, dioxan and tetrachloroethylene were detected more frequently. Tetrachloroethylene is the only one of these compounds that was also present in the atmospheric pollutants in Zürich and Houston. The main source emitting this solvent into the urban atmosphere is evidently dry-cleaning establishments. In such a large city as Leningrad about 2000

TABLE II
C₃-C₁₃ HYDROCARBONS DETECTED IN LENINGRAD AIR (JULY-OCTOBER 1976)

No.	Hydrocarbon	Identification method**	No.	Hydrocarbon	Identification method**
1	C ₄ H ₁₀ *	IV	64	C ₉ H ₁₈ *	IV
2	2-Methylbutane*	II ₅	65	<i>Ethylbenzene</i>	I, II ₃
3	C ₃ H ₈ *	IV	66	Terpene, C ₁₀ H ₁₆ *	III
4	<i>n</i> -Pentane	I	67	<i>m</i> -Xylene	I, II ₃ + GC
5	<i>n</i> -Pentene*	III ₅	68	<i>p</i> -Xylene	I, II ₃ + GC
6	2-Methylpentane*	I	69	α -Pinene*	I
7	C ₃ H ₆ *	IV	70	Isodecane	III
8	C ₆ H ₁₂ *	IV	71	<i>Isodecane</i>	III
9	3-Methylpentane*	I	72	Isodecane	III
10	<i>n</i> -Hexane***	I	73	Camphene*	III
11	<i>n</i> -Hexene*	III	74	<i>o</i> -Xylene	I, II ₃ + GC
12	2,4-Dimethylpentane	I	75	Terpene, C ₁₀ H ₁₆ *	III
13	C ₆ H ₁₂ *	IV	76	C ₁₀ H ₂₀ *	IV
14	Methylcyclopentane	I	77	Cumene*	II ₃ + GC
15	3,3-Dimethylpentane*	I	78	<i>Styrene</i>	II ₅
16	C ₇ H ₁₄ *	IV	79	C ₁₀ H ₂₀ *	IV
17	2-Methylhexane	I	80	<i>n</i> -Decane*	I
18	Isoheptane	III	81	<i>n</i> -Decene*	III
19	Cyclohexane*	I	82	C ₁₀ H ₂₀ *	IV
20	3-Methylhexane	I	83	Isoundecane	III
21	Dimethylcyclopentane*	III	84	<i>n</i> -Propylbenzene	II ₃
22	C ₇ H ₁₄ *	IV	85	C ₁₀ H ₁₄	III ₃
23	C ₇ H ₁₄ *	IV	86	<i>1,3- or 1,4-methylethylbenzene</i>	III ₄
24	C ₈ H ₁₀ *	IV	87	Terpene, C ₁₀ H ₁₆ *	III
25	C ₆ H ₆ *	IV	88	<i>1,3,5-Trimethylbenzene</i>	II ₅ + GC
26	<i>n</i> -Heptane	I	89	<i>1,2-Methylethylbenzene</i>	II ₅ + GC
27	<i>n</i> -Heptene	III	90	C ₁₁ H ₂₂ *	IV
28	C ₇ H ₁₄	IV	91	Methylstyrene*	III ₅
29	C ₁₁ H ₂₂ *	IV	92	Limonene	I

36	2-Methylheptane	I	99	1,2,3-Trimethylbenzene	II ₅ + GC
37	4-Methylheptane	I	100	C ₁₁ H ₂₂ *	IV
38	3-Methylheptane	I	101	C ₁₁ H ₂₂ *	IV
39	C ₈ H ₁₆ *	IV	102	C ₁₀ H ₁₄	III ₄
40	C ₇ H ₁₂ *	IV	103	<i>n</i> -Butylbenzene	III ₄
41	Dimethylcyclohexane*	III + GC	104	Indane	II ₅
42	<i>n</i> -Octane	I	105	Methyl- <i>n</i> -propylbenzene	III ₄
43	<i>n</i> -Octene	III	106	C ₁₀ H ₁₄	III ₄
44	Dimethylcyclohexane*	III + GC	107	Indene	II ₅
45	C ₈ H ₁₆ *	IV	108	Dimethylethylbenzene	III ₄
46	Dimethylcyclohexane*	III + GC	109	Dimethylstyrene*	III ₄
47	Isononane	III	110	Dimethylethylbenzene	III ₄
48	Isononane	III	111	Isododecane	III
49	Toluene	I, II ₁	112	C ₁₂ H ₂₄ *	IV
50	C ₉ H ₁₆ *	IV	113	<i>n</i> -Dodecane	I
51	Ethylcyclohexane*	I + GC	114	<i>n</i> -Dodecene*	III
52	Trimethylcyclohexane	III + GC	115	Diethylbenzene	III ₅
53	C ₉ H ₁₈ *	IV	116	Tetramethylbenzene	III ₅
54	2-Methyloctane	I	117	Tetramethylbenzene	III ₅
55	3-Methyloctane	I	118	Isotridecane	III
56	C ₉ H ₁₈ *	IV	119	C ₁₂ H ₂₄ *	IV
57	Terpene, C ₁₀ H ₁₆ *	III	120	C ₁₃ H ₂₆ *	IV
58	C ₉ H ₁₈ *	IV	121	<i>n</i> -Tridecane	I
59	C ₉ H ₁₆ *	IV	122	C ₁₃ H ₂₆	IV
60	C ₉ H ₁₈ *	IV	123	<i>n</i> -Amylbenzene	I
61	<i>n</i> -Nonane	I	124	Methyl- <i>n</i> -butylbenzene	III ₅
62	<i>n</i> -Nonene	III	125	Tetramethylbenzene	III ₅
63	Terpene, C ₁₀ H ₁₆ *	III	126	Naphthalene	II ₄

* Detected only in Leningrad.

** I = individual identification by complete spectra by comparison with Atlas of mass spectral data⁶ or spectra of known reference samples; II = individual identification by the given number of the strongest peaks using the Eight Peak Index⁷; III + GC = as II, using retention parameters; III = classification with a group of isomers with known structural fragments; IV = determination of molecular formula by mass numbers of molecular and strong fragment ions.

*** Hydrocarbons detected in all experiments are printed in italics.

TABLE III

GROUP COMPOSITION OF THE LIGHT HYDROCARBONS DETECTED IN THE URBAN ATMOSPHERES

Class of hydrocarbons	Detected only in Leningrad		Detected not only in Leningrad	
	No.	%	No.	%
Alkanes, C_nH_{2n+2}	4	6.5	28	42.5
Aromatic hydrocarbons (benzene, indane, naphthalene series)	1	2	29	44
Hydrocarbons, C_nH_{2n}	40	67	6	9
Olefins	5	8	3	5
Naphthenes	9	15	1	1.5
Unsaturated, C_nH_{2n-2}	4	6.5	0	0
Unsaturated, C_nH_{2n-4}	9	15	1	1.5
Aromatic unsaturated, C_nH_{2n-8} (styrene series)	2	3	2	3
Total	60	100	66	100

tons of this solvent are consumed annually for this purpose, and it eventually enters the atmosphere. The remaining nine compounds in Table IV were not found in the atmospheres of the other three cities. On the other hand, our list does not contain 17 derivatives (including eight aromatic aldehydes and ketones) that were identified in those cities.

The composition of the non-hydrocarbon part of the organic constituents of the atmosphere therefore appears to be impermanent and diverse. It is probably partially associated with a much higher solubility of the oxygen derivatives in water, their easier sorption on dust particles and, hence, with shorter lifetimes and their considerable variations depending on the climatic conditions. Another reason for the differences between the pollutants identified in the four cities may lie in the different conditions and techniques used for air sampling and analysis.

The investigation of oxygen-, nitrogen-, sulphur- and halogen-containing

TABLE IV

HYDROCARBON DERIVATIVES IDENTIFIED IN LENINGRAD AIR

No.	Compound	Identification method*
1	Acetone	II ₂
2	Ethanol	II ₃
3	Carbon disulphide	II ₂
4	Methylfuran	III ₃
5	Ethyl acetate	I
6	Carbon tetrachloride	II ₄
7	Trichloroethylene	II ₅
8	Dioxan	I, II ₂
9	Tetrachloroethylene	II ₇
10	<i>n</i> -Butyl acetate	I, II ₆

* See Table I.

compounds is also one of the most important ecological problems and certainly deserves detailed study.

ACKNOWLEDGEMENT

This work was carried out in close contact with and with the assistance of the Main Geophysical Observatory of the U.S.S.R.

NOTE ADDED IN PROOF

Analyses of atmospheric air in the number of cities located in the broad interval of geographic latitudes and under various climate conditions were performed by us while this paper was in print. They manifested that the above-mentioned peculiarities of the composition of atmospheric organic pollutants in our experiments were apparently influenced by the use of more effective sorbents stronger than by geographic conditions.

REFERENCES

- 1 K. Grob and G. Grob, *J. Chromatogr.*, 62 (1971) 1.
- 2 W. Bertsch, R. C. Chang and A. Zlatkis, *J. Chromatogr. Sci.*, 12 (1974) 175.
- 3 A. Raymond and G. Guiochon, *Envir. Sci. Technol.*, 8 (1974) 143.
- 4 K. I. Sakodinsky, N. S. Klinskaya and L. I. Panina, in A. Zlatkis (Editor), *Advances in Chromatography 1973*, Chromatography Symposium, Houston, Texas, 1973, p. 109.
- 5 A. V. Kiselev and Y. I. Yashin, *Gas Adsorption Chromatography*, Plenum Press, New York, 1969.
- 6 E. Stenhagen, S. Abrahamsson and F. N. McLafferty (Editor), *Atlas of Mass Spectral Data*, Vol. 1, Interscience, New York, 1969.
- 7 *Eight Peak Index of Mass Spectra*, Mass Spectrometry Data Centre, Aldermaston, 1970.