CHROM. 5561

GAS-LIQUID CHROMATOGRAPHIC-MASS SPECTROMETRIC INVESTIGATION OF C_6–C_{20} ORGANIC COMPOUNDS IN AN URBAN ATMOSPHERE

AN APPLICATION OF ULTRA TRACE ANALYSIS ON CAPILLARY COLUMNS

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(Received July 22nd, 1971)

SUMMARY

Qualitative and quantitative investigations were made on the C_6–C_{20} volatile organic substances in the air of Zürich. The technique of trace analysis on high resolution capillary columns was developed further. To trap the organics, a specially designed filter was used containing 25 mg of cigarette filter charcoal. Important information about the adsorption/desorption mechanism was obtained by using two or more filters in series. The extraction of the filters with carbon disulphide is described. A mass spectrometer (CH5 from Varian MAT, Bremen, G.F.R.) specially designed to meet the requirements of coupling with high resolution gas chromatography was used. The majority of the hundred and eight substances identified were aliphatic and aromatic hydrocarbons. Among substances representing other groups were found benzaldehyde and several of its alkyl derivatives which may be oxidation products of aromatic hydrocarbons. The principle of quantitative determination is discussed and is applied to the most volatile part (benzene through C_3-substituted benzenes) of the spectrum.

INTRODUCTION

Among the numerous reports on new methods and advanced knowledge concerning air pollutants, surprisingly little has been published regarding the broad spectrum of organic substances in the air. The review by Altshuller[1] includes several papers dealing with low molecular weight hydrocarbons. Pioneers in this field were Huyten *et al.*[2], and the most original report is probably that by Williams[3]. While higher molecular weight organic compounds in particulates have been studied by many workers, the broad range of volatile substances containing 6–20 carbon atoms has been practically disregarded. Rasmussen and Went[4] very effectively determined trace substances such as terpenes in unpolluted air. Their technique, however, did not allow the handling of complex mixtures such as urban atmospheres. In the recent report on modern aspects of air pollution monitoring by Stevens and O'Keeffe[5], the only organic compound mentioned is methane. A very original and sensitive method, but confined to C_1–C_5 hydrocarbons, has recently been described by SAWICKI[6].

As emphasized by ALTSHULLER, the high molecular weight organic compounds represent very complex mixtures of hundreds of compounds. While resolving such mixtures by means of capillary columns (genuine high-resolution columns, not the widespread very poor capillaries) no longer presents great problems, the trace character of the material intensifies the difficulties. The following three aspects of the task may be treated separately: high resolution trace analysis on capillary columns as a necessary prerequisite; appropriate sampling of volatile organics for qualitative and/or quantitative analysis, and gas chromatographic–mass spectrometric (GC–MS) design maintaining the full separation power of a high-resolution column and working in the nanogram range.

The progress of our work in all three fields caused us to check the suitability of our methods to the analysis of an odourless urban atmosphere.

HIGH-RESOLUTION TRACE ANALYSIS ON CAPILLARY COLUMNS

The key to the possibility of injecting very dilute solutions on to capillary columns is the avoidance of stream splitting. In earlier reports, we have described the principle (direct sampling while the column is kept at a suitable temperature below the temperature of analysis) and technique of non-splitting injection[7,8] as well as several applications of the method[9–11]. Meanwhile, we have been using the technique extensively with great success on a wide variety of dilute mixtures. Venting the solvent through a precolumn is now generally confined to very special cases. There are high-resolution capillaries in several laboratories of our University on to which, for more than a year, samples of up to 5 μl have been injected daily without splitting, and without causing damage to the column. Difficulties encountered in some laboratories with our method, such as those mentioned by NOVOTNY AND ZLATKIS[12], are not due to the method itself, but rather to difficulties with the technique or equipment. The technique as we use it now will be described in detail elsewhere[13].

A fundamental limiting aspect of our method is the fact that the most volatile components of the mixture may be obscured by the large amount of solvent or, at least, may not be resolved sufficiently from the solvent. In the case of atmospheric hydrocarbons, the most volatile component of great toxicological interest is benzene. As, for practical reasons, we used as solvent carbon disulphide, which has a similar boiling point and polarity to those of benzene, the situation did not seem promising at first.

It was interesting, therefore, to determine the lowest concentration of benzene in carbon disulphide that still allowed sufficient resolution of benzene. Fig. 1 shows two chromatograms obtained by non-splitting injection of 1 μl of benzene solution, $1:10^5$ and $1:10^6$ in carbon disulphide with toluene added for comparison. Even when sampling a $1:10^7$ solution, the benzene peak is not affected by the solvent peak. Nevertheless, this concentration is below the practical limit because the benzene peak becomes masked by trace impurities of the solvent, even when using the purest redistilled carbon disulphide. The critical concentration, therefore, is of the order of $3 \cdot 10^{-7}$ g of benzene per gram of carbon disulphide (0.3 p.p.m.). This means that the especially difficult case of benzene does not preclude genuine trace analysis. For toluene, the limit is 10^{-8} g/g, *i.e.* close to the detection limit of the FID (0.02 ng in 2 μl of solution).

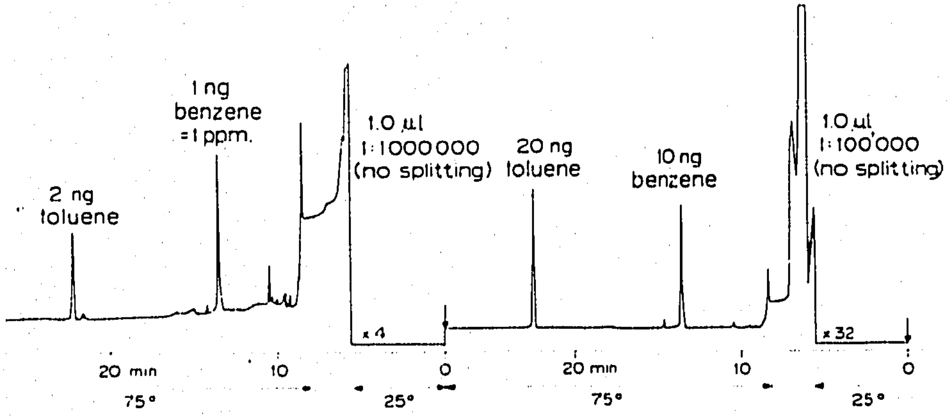

Fig. 1. Tests illustrating lowest dilution of benzene in carbon disulphide that allows sufficient resolution of benzene. Column: see text. Injection of 1.0 μl at room temperature; analysis at 75°.

It may be added that some preconditions have to be fulfilled to obtain these results. The most important one is column quality, with special emphasis on low adsorption activity. Further requirements concern details of the apparatus and its handling, which will be discussed elsewhere[13].

In the case of even lower concentrations, increased sample sizes must be used. According to our experience, even the very ingeniously designed means developed at the Technical University of Eindhoven[14,15] are not much help under these conditions because the capillary becomes blocked with condensed solvent.

SAMPLING OF VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE

For direct sampling of air the following considerations have to be made. As will be shown later, the majority of substances are present in the range of 0.1–10 p.p.b.*. If, for a single run, we wish to introduce not less than 0.1 ng of a substance, present in the air at a level of 0.1 p.p.b., our sample size becomes *ca.* 1 l. Introduction of this volume on to one of our ordinary capillary columns (flow *ca.* 4 ml of air per min, corresponding to 10 ml of He per min) would last *ca.* 4 h. This means that, except for a few major components, there is, at present, no opportunity to apply direct sampling.

In an earlier paper[11], we have extensively discussed the principles and means of trapping gaseous trace substances to suit our analytical conditions. Some results may be repeated here.

For qualitative analysis, a wide variety of adsorbents (charcoal, alumina, silica gel, coated celite, organic polymers) and techniques (desorption by heat or by solvent) may be used. For quantitative determination and for ultra trace conditions such as those involved with air, however, the corresponding selection becomes seriously restricted. In fact, only charcoal with liquid desorption can meet requirements such as controlled adsorption in the sub-p.p.b. range, low dependence on humidity, and full recovery without contamination by material originating from the adsorbent.

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* Throughout this article the American (10^9) billion is meant.

The size of a charcoal trap relative to the volume of the air sample is a fundamental point. Maximum recovery with minimum solvent volume calls for the smallest possible trap. This means that the trap has to be selected to be so small that, from a given air volume, the most volatile substances just begin to break through the filter. To ensure full adsorption of the substances of interest, a second filter is inserted behind the first one thus allowing a check of whether, or how much, organic material has passed the first filter. At most, only negligible traces of substances to be determined should be found on the second trap.

For a given air volume and a given flow rate, the filter size can be reduced when the particle size of the charcoal is reduced. Small filter particles, furthermore, facilitate desorption by a solvent. On the other hand, small particles produce a high flow resistance through the filter which becomes an obstacle for the liquid solvent, rather than for the air. Another important parameter is the length of the filter pad which, through the flow resistance, is correlated with its width.

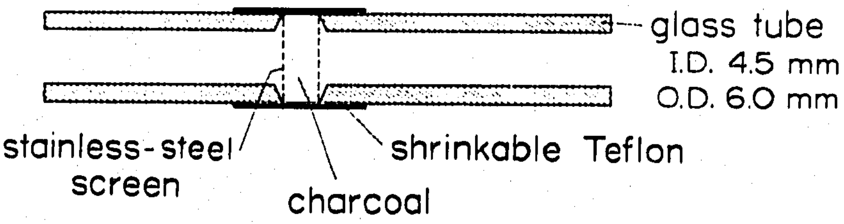


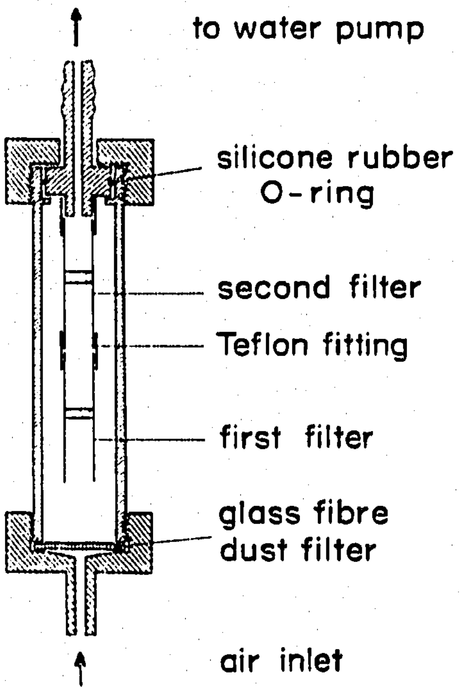
Fig. 2. Design of charcoal filter. For details, see text.

Fig. 2 shows a charcoal trap selected after a series of tests in which the above parameters had been varied systematically. The trap contains 25 mg of wood charcoal as used for cigarette filters with an average particle size of 0.08 mm. This filter retained constant characteristics through a long series of applications. Its design makes it easy to prepare a large number of filters with practically identical characteristics.

We designed a filter holder as shown in Fig. 3. To retain the aerosols, we used a disc of a glass-fibre filter which is specially manufactured for the retention of particulates in cigarette smoke (Phipps and Bird Inc., Richmond, Va., U.S.A.). The filtered air flows through two identical charcoal traps without coming into contact with materials other than metal, glass and Teflon. Shrinkable Teflon tubing, when shrunk to the correct width, shows just sufficient elasticity to assure tight fitting. The outlet end is connected to a water pump. By means of a needle valve, we set the air flow to 2.5 ml/min.

For the desorption we use a glass apparatus as shown in Fig. 4. The loaded filter, to which the internal standard has been added by means of a syringe, is fastened to the "cold finger" by a piece of Teflon tubing, the upper part of which is perforated. The flask is loaded with 0.3–0.5 ml of carbon disulphide and kept at 75°. The solvent vapour passes through the holes in the Teflon holder and, from the "cold finger", flows back through the charcoal. Extraction is complete after about 10 min; we use extraction periods of 30 min. We found the small quantity of solvent to be essential since subsequent concentration by any evaporation method causes severe losses even of less volatile components. Further details are given in the section QUANTITATIVE ANALYSIS.

Comparative tests with various solvents (pentane, methylene chloride, chloroform, ether) indicated a clear preference for carbon disulphide for the following reasons: most rapid desorption of almost every type of organic compound from charcoal; pure product with a low tendency for producing impurities such as peroxides; and low response factor in the FID. Similar reasons have previously been pointed out by JENNINGS AND NURSTEN[16].



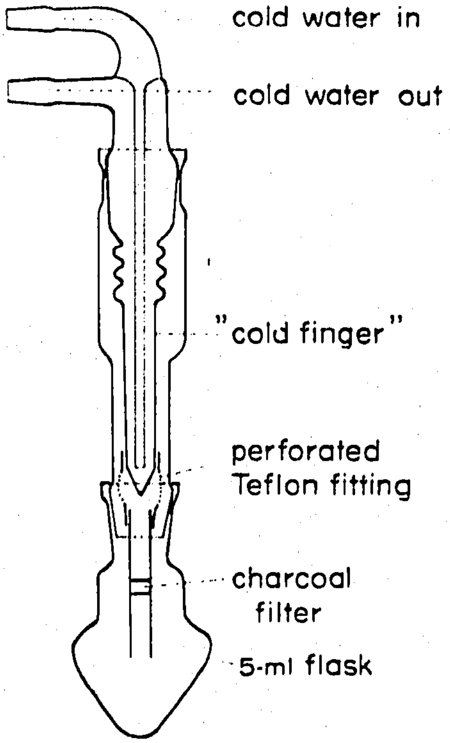


Fig. 3. Filter holder containing two charcoal filters in series. For sampling the holder is placed directly in the atmosphere.

Fig. 4. Glass apparatus allowing continuous extraction of charcoal filters using a very low volume of solvent.

A much greater weight ratio between trapped organic material and charcoal is obtained by the saturation method (frontal analysis) as described by NOVÁK *et al.*[17]. While this technique yields excellent results when a single major substance has to be determined, it fails in cases of complex mixtures with a wide volatility range. Displacement by specifically well adsorbed components prevents more volatile substances from reaching their predicted saturation equilibrium. Certain substances, even when present in the mixture in relatively high concentration, may totally disappear from the charcoal in the course of prolonged loading. For mixtures of this type the method is applicable for qualitative purposes only.

GAS CHROMATOGRAPHY–MASS SPECTROMETRY

To identify the components of a very complex mixture, coupling of GC with MS becomes indispensible. While the basic technique has been widespread for several years, the combination has, in our case, to meet specific demands, the most important of which are the following: the higher the GC resolution of the complex mixture, the more esssential it becomes that the separate substances are not mixed again before reaching the ion source, as happens with most interfaces; increase of chromatographic resolution is possible only with decrease of sample size, and sensitivity of the mass spectrometer and the avoidance of losses in the interface therefore become decisive; and the higher the chromatographic resolution, the shorter is the time span for a separate substance to pass the ion source (2–3 sec in our work). This calls for a high scanning speed (less than 1 sec per decade).

After studying the existing combinations, we found that none of them fulfilled these requirements. All types of interfaces for the purpose of reducing the gas flow to the ion source either reduce the chromatographic resolution or cause losses of substance. Other types of apparatus, *e.g.* the quadrupole instruments, have low sensitivity. The same is true of chemi-ionisation with methane as carrier gas, while several other aspects of this technique would make it the ideal one for our purpose[18]. The work reported here was carried out with a mass spectrometer model CH5 from Varian MAT, Bremen, G.F.R. The technical details involved have recently been described by SCHULZE AND KAISER[19].

With a constant input of 8 ml of He per min, this instrument maintains a vacuum of 10^{-5} torr at which its sensitivity is still far greater than that which is required. Our interface simply consists of a heated 25-cm long glass capillary of 0.2 mm I.D. with a constriction yielding 8 ml of air per min at a pressure drop of 1 atm. This capillary ends on one side 3 mm before the electron beam in the ion source, and on the other side in the column oven of a gas chromatograph suited for high-resolution work (Carlo Erba, Milan, Italy, Model GI). This end is directly coupled to the capillary column by shrinkable Teflon tubing. For work above 200°, we used a two- or threefold layer of Teflon, which withstands a constant temperature of 230°. Changing a column under these conditions is achieved in less than 30 min.

The model CH5 is equipped with a second ion source working at 20 eV in which the molecules passing the first source are detected. This second source produces the gas chromatogram which is not influenced when the main source, at 70 eV, is working.

Besides avoiding any loss of substance, this combination yields a chromatographic resolution that is always somewhat better than the best results obtained by pure GC (FID).

The GC columns used were a 120 m × 0.32 mm Ucon HB 5100 for the full spectrum (Fig. 5) and an 80 m × 0.33 mm Ucon LB 550 for the most volatile organic compounds. The separation numbers were 72 and 65, respectively. Both columns were run with a gas flow of *ca.* 8 ml of He per min. Besides separation efficiency, two other characteristics are essential for satisfactory results: a very low bleed rate to produce little background on the mass spectra when working at high sensitivity (see the chromatograms in Figs. 5 and 6, temperature programmed from room temperature to 190° and 120°, respectively); and a very low adsorption activity to avoid contamination of a resolved substance by adsorbed residues of foregoing ones.

The latter characteristics may be even more important than the separation efficiency itself. As we have reported recently[20], certain adsorption effects are due to unsuitable acidity of the column.

Some experience is needed to prepare columns meeting these requirements.

Coated glass capillaries similar to ours are now manufactured by H. Jaeggi, Laboratory for Gas Chromatography, 5642 Muehlau, Switzerland, and distributed by Dr. W. NESS, 8700 Kuesnacht, Switzerland.

QUALITATIVE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE

After a long series of attempts to obtain the complete spectrum from benzene to eicosane on the same chromatogram, we modified our aim because of the fact that the concentration of organic compounds decreases strongly with decreasing volatility which makes it difficult to trap on the same filter comparable amounts of the lower as well as of the higher molecular weight substances. As an example of a qualitative run, Fig. 5 shows an extreme run planned to give reasonable amounts of the heavier substances with corresponding, almost complete, loss of the light ones. A run as depicted by Fig. 6 may serve to fill the gap created this way.

Charcoal traps as described above were loaded with 25 m^3 of air within 8 days. During sampling, the filters were placed in the centre of our campus in the city of Zürich in a green area with a lawn and bushes, 300 m away from the nearest road. Pedestrians (smokers) did not pass within 80 m. No chimney or exhaust was located within 500 m. During the whole sampling period, the air was totally odourless. Weather and wind conditions varied. The average temperature (May) was *ca.* 14°. In the area around the campus, central heating units with oil burners were occasionally working. The campus itself is attached to a distant heating source.

We extracted the filters with carbon disulphide and analysed the solution as described above, without addition of an internal standard. All the major and some minor components were identified by their mass spectra. Identifications were confirmed by co-chromatography, provided pure reference substances were available. This was the case with all the substances indicated with their exact names in Table I.

A further search for substances of special interest was carried out in the following way. A 0.2-ml portion of the carbon disulphide solution was intensely vibrated for 15 min with 0.1 ml of sulphuric acid (7 ml conc. H_2SO_4 + 3 ml H_2O) according to method of HOFF AND VEIT[21]. This clean-up procedure eliminates or reduces all substances except alkanes and aryl alkanes. The disappearance or reduction of peaks reveals the presence of reactive compounds. Out of the 460 peaks observed in chromatogram A (Fig. 5), less than 20 were influenced by the sulphuric acid treatment while the others were exactly reproduced. The overwhelming majority of volatile organic substances in the atmosphere, therefore, are fuel constituents or pyrolytic transformation products (some aromatics) derived from fuel.

Comparison of chromatograms A and B (Fig. 5) strongly underlines our statement that in our case, charcoal never reaches a stable and defined adsorption equilibrium in prolonged contact with the atmosphere. Instead, the major components of this atmosphere, toluene and the xylenes (A, Fig. 6), have almost totally disappeared from the filter exposed for 8 days (A, Fig. 5). Even on the second filter (B, Fig. 5) only traces of these substances are found. The reason for these drastic losses is displacement of volatile substances from the adsorbent surface by less volatile ones. The absence of substances heavier than methylindane on the second filter shows, on the other hand, that in the less volatile part of the spectrum, total adsorption out of 25 m^3 occurs on as little as 25 mg of charcoal.

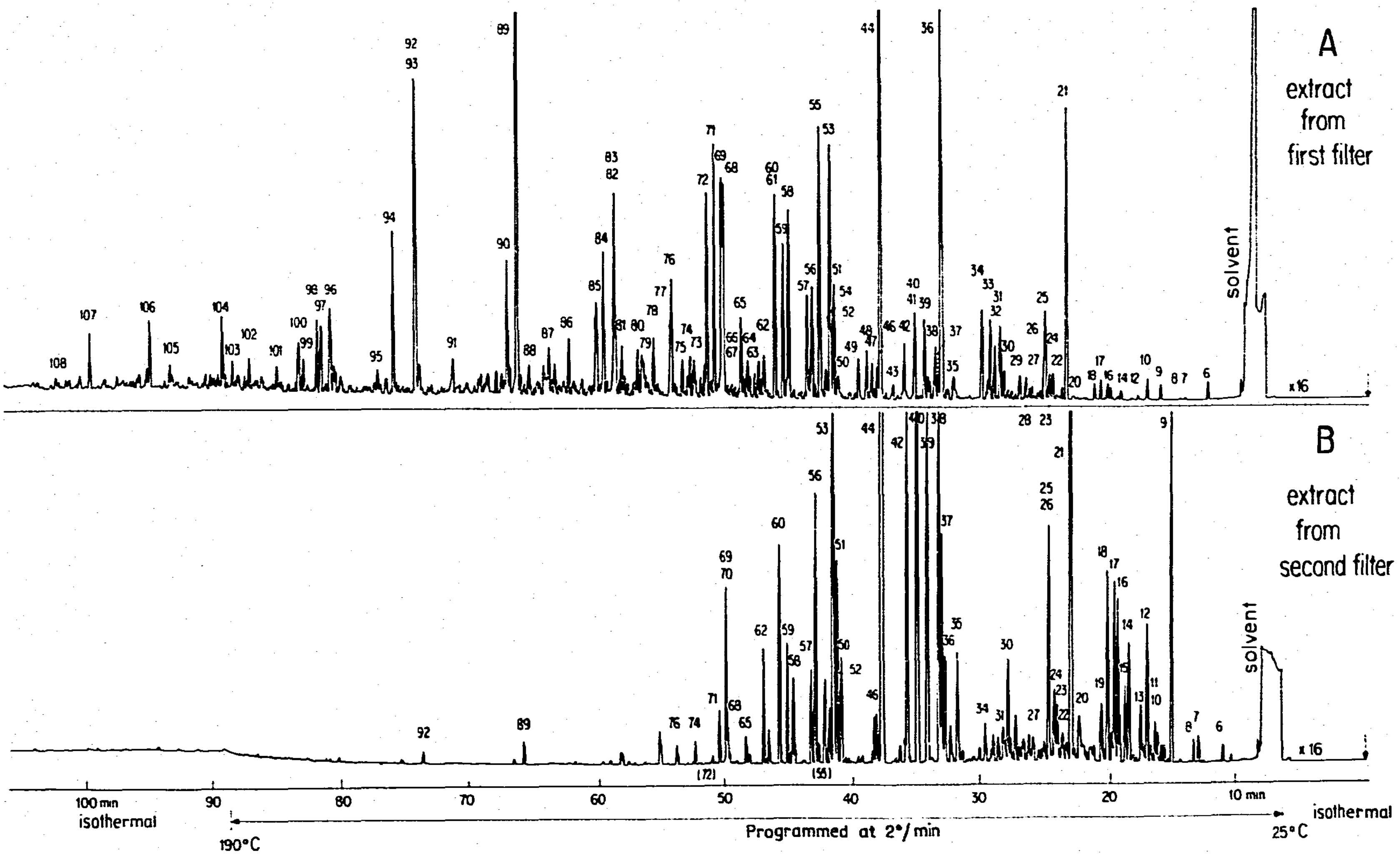


Fig. 5. Qualitative analysis of organic compounds in the atmosphere. Large sample volume (25 m³) to allow detection of heavier substances, with corresponding loss of lighter ones. Numbers refer to substances listed in Table 1. For column and chromatographic conditions, see text.

TABLE I

SUBSTANCES IDENTIFIED

Numbers correspond to those in Figs. 5 and 6.

No.	*Compound*	*No.*	*Compound*
1	2-Methylhexane	55	*n*-Dodecane
2	*n*-Heptane	56	Ethyldimethylbenzene
3	Isooctane	57	Propylmethylbenzene
4	Benzene	58	Ethyldimethylbenzene
5	2-Methylheptane	59	Isopropylmethylbenzene
6	*n*-Octane	60	Ethyldimethylbenzene
7	Isononane	61	Isopropylmethylbenzene
8	Isononane	62	Dichlorobenzene[a]
9	*n*-Nonane	63	Isotridecane
10	Toluene	64	Isotridecane
11	Isodecane	65	Ethyldimethylbenzene
12	Tetrachloroethylene[a]	66	C_4-substituted benzene
13	Isodecane	67	C_5-substituted benzene
14	Isodecane	68	1,2,4,5-Tetramethylbenzene
15	Isodecane	69	Benzaldehyde[a]
16	Isodecane	70	Benzofuran[a]
17	Isodecane	71	1,2,3,5-Tetramethylbenzene
18	Isodecane	72	*n*-Tridecane
19	Isodecane	73	C_5-substituted benzene
20	Isodecene[a]	74	Methylindane
21	*n*-Decane	75	C_5-substituted benzene
22	Ethylbenzene	76	1,2,3,4-Tetramethylbenzene
23	1,4-Dimethylbenzene	77	Methylindane
24	Isoundecane	78	Isotetradecane
25	Isoundecane	79	Isotetradecane
26	1,3-Dimethylbenzene	80	C_5-substituted benzene
27	1,2-Dimethylbenzene	81	4-Methylbenzaldehyde[a]
28	Isoundecane	82	3-Methylbenzaldehyde[a]
29	Isoundecane	83	Isotetradecane
30	Isoundecane	84	*n*-Tetradecane
31	Isoundecane	85	Acetophenone[a]
32	Isoundecane	86	Alcohol, $C_{10}H_{20}O$[a]
33	Isoundecane	87	Alcohol, $C_{10}H_{18}O$[a]
34	Isoundecane	88	2-Methylbenzaldehyde[a]
35	*n*-Propylbenzene	89	Naphthalene
36	*n*-Undecane	90	*n*-Pentadecane
37	1-Ethyl-4-methylbenzene	91	Dimethylbenzaldehyde[a]
38	1-Ethyl-3-methylbenzene	92	2-Methylnaphthalene
39	Limonene[a]	93	*n*-Hexadecane
40	1,3,5-Trimethylbenzene	94	1-Methylnaphthalene
41	Isododecane	95	Benzothiazole[a]
42	1-Ethyl-2-methylbenzene	96	*n*-Heptadecane
43	Isododecane	97	Dimethylnaphthalene
44	1,2,4-Trimethylbenzene	98	Diphenyl
45	Octenal[a]	99	2,6-Dimethylnaphthalene
46	1-Isopropyl-4-methylbenzene	100	1,6-Dimethylnaphthalene
47	Isododecane	101	1,8-Dimethylnaphthalene
48	Isododecane	102	*n*-Octadecane
49	Isododecane	103	Methyldiphenyl
50	*n*-Butylbenzene	104	Acenaphthene
51	Propylmethylbenzene	105	*n*-Nonadecane
52	sec-Butylbenzene	106	Dibenzofuran[a]
53	1,2,3-Trimethylbenzene	107	Fluorene
54	Isotridecane	108	*n*-Eicosane

[a] Reacts with sulphuric acid.

A more detailed comparison of chromatograms A and B (Fig. 5) leads to the following conclusions. In the first part of both chromatograms, a quantitative increase is observed with increasing molecular weight for every homologous series, caused by gradually diminished losses (due to decreased volatility). Maximum amounts are attained where no further losses occur and total adsorption starts. After this point, the amounts decrease, reflecting the decreasing concentrations of the respective substances in the air.

It may be interesting to examine which part of chromatogram A in Fig. 5 has some quantitative meaning. The answer is given by chromatogram B, where only small amounts of undecanes are found whereas dodecanes are not detected. This means that, for the alkanes, chromatogram A after undecane is quantitatively meaningful. The corresponding limit for the alkylbenzenes shows an important shift to the left and is found after the ethyldimethylbenzenes, in the area where tridecane would be eluted. We think that this apparently different behaviour of alkanes and aromatics is due simply to the polarity of the column, since the substances forming the respective limits, *i.e.* undecane and the ethyldimethylbenzenes, have very similar boiling points.

With special care we tried to identify the substances that react with sulphuric acid (indicated with [a] in Table I), but we could not establish detailed structures for all of them. We have very little knowledge as yet of the origin and significance of these compounds. Work is under way to determine whether, or to what extent, they occur locally or temporarily.

Some special interest may be directed towards oxygenated compounds such as aromatic aldehydes and acetophenone, since they may represent oxidation products of alkylated aromatics. There remains some suspicion that they might be formed through oxidation of adsorbed aromatics on the charcoal during the long exposure period. A piece of evidence against this doubt is the fact that on the second filter only benzaldehyde, but no less volatile homologues, are found. This probably means that part of the more volatile benzaldehyde has passed the first filter whereas its less volatile derivatives were totally adsorbed. In the case of formation on the charcoal we would expect the aldehydes to be distributed over both filters, without regard to their volatility.

It is obvious that detectors capable, for instance, of specifically detecting traces of metal compounds but with low sensitivity for hydrocarbons would be extremely helpful in gaining more information from our analysis. At present, however, most specific detectors either lack sensitivity or bring about dead volumes that are too great to be used for high-resolution chromatography.

QUANTITATIVE ANALYSIS

As discussed above, GC analysis of the solution obtained from a charcoal filter may be used to estimate certain substances, provided that they have been adsorbed from the air totally or almost totally. This means that these substances should not be found on a second adsorbent filter, or only in a relatively small amount.

An attempt to apply this principle leads to the conclusion that quantitative analysis in a single run is not possible over the whole spectrum of volatile organic compounds in air. While the most volatile components will pass through the filter, less volatile ones will not be adsorbed in sufficient amounts to allow determination. Thus the spectrum has to be divided into sections for which an optimum air volume with respect to the capacity of the filter has to be selected.

As an example, estimation of the most volatile substances may be shown. 250 l of air (*i.e.* 100 times less than used to obtain Fig. 5) were sampled on 25-mg charcoal filters for 1.5 h. 4 μl of a 1 : 1000 solution of 1-chlorooctane (internal standard) in carbon disulphide were added to the filter with a syringe before extraction with carbon disulphide. Repeated extraction of the first and second filter produced solutions from which chromatograms, as shown in Fig. 6, were obtained.

A first unexpected observation was that chromatograms A and B are not influenced when the first extraction is extended from 0.5 h to 1 or 2 h. Thus the considerable amounts of air constituents found in the second extract (B) cannot be transferred into the first extract by extending the first extraction period. The explanation for this phenomenon must be that some dissolved material is vaporized together with the solvent and is again adsorbed on the charcoal. This process of desorption and re-adsorption leads to a stable equilibrium after 10–15 min. The more charcoal in the filter, the greater is the percentage of material remaining on the charcoal during

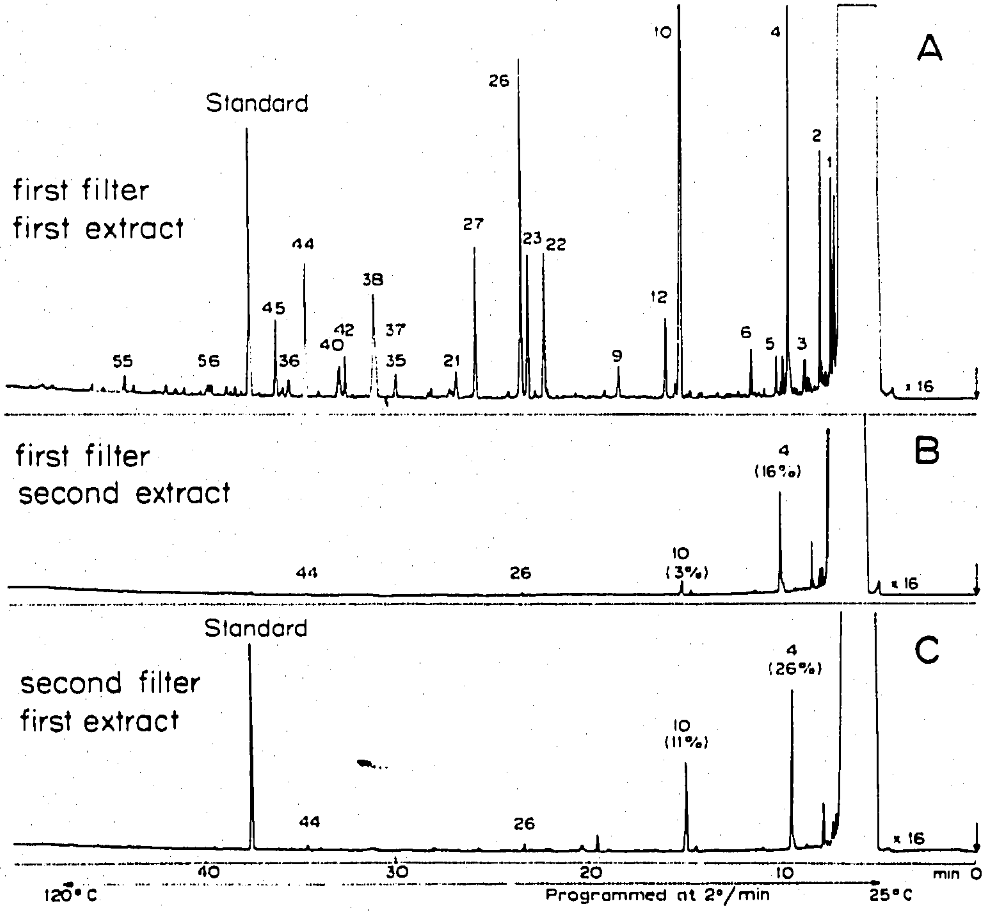


Fig. 6. Quantitative analysis of lower molecular weight organic compounds in the atmosphere. Corresponding substances and concentrations are listed in Table II. For column, conditions and calculation, see text.

the first extraction step. This is a further important reason for keeping the amount of adsorbent as low as possible (see the section SAMPLING).

TABLE II

CONCENTRATION OF SOME C_6–C_{12} ORGANIC COMPOUNDS IN THE ATMOSPHERE OF ZÜRICH

Numbers correspond to those in Fig. 6.

No.	*Compound*	*Concentration, p.p.b.*
1	2-Methylhexane	28[a]
2	*n*-Heptane	34[a]
4	Benzene	54[a]
5	2-Methylheptane	3.4[a]
6	*n*-Octane	3.4[a]
10	Toluene	39[a]
11	Tetrachloroethylene	10
9	*n*-Nonane	1.7
22	Ethylbenzene	8.7
23	1,4-Dimethylbenzene	9.0
26	1,3-Dimethylbenzene	21
27	1,2-Dimethylbenzene	9.3
21	*n*-Decane	1.6
35	*n*-Propylbenzene	1.5
37	1-Ethyl-4-methylbenzene	*ca.* 3.5
38	1-Ethyl-3-methylbenzene	*ca.* 5.5
42	1-Ethyl-2-methylbenzene	2.6
40	1,3,5-Trimethylbenzene	2.1
44	1,2,4-Trimethylbenzene	9.0
36	*n*-Undecane	0.95
56	Ethyldimethylbenzene	0.74
55	*n*-Dodecane	1.3

[a] Values corrected for losses as seen from B and C, Fig. 6.

It is a consequence of the above equilibrium that for very volatile sample components, *e.g.* benzene, the solutions of at least two extraction steps have to be analysed and the determined amounts added.

It can be seen from chromatogram C that the fundamental conditions for quantitative determination are well fulfilled for the xylenes and heavier substances. For toluene (no. 10), an exact determination is still possible by adding the relatively small amount found on the second filter to the result. For benzene, however, the same procedure yields a much less exact result since both corrections, as seen from chromatograms B and C, are relatively large. Better results are obtained from reduced air volumes.

The concentrations given in Table II were obtained in the following way. A chromatogram was run from a synthetic solution containing known amounts of all substances to be determined including the internal standard. Since identical chromatographic conditions were used for synthetic and natural samples, the amounts of every substance could be expressed by the ratio of the peak height of the respective substance to that of the internal standard. Results for the natural samples were then calculated by comparing the peak height ratios. This procedure has the advantage that neither the volumes of the carbon disulphide solutions (synthetic and natural) nor the volumes injected for chromatography have to be known. Since no stream splitting is used, quantitative reproduction of the chromatograms is excellent.

Fig. 6A and Table II strikingly resemble an analysis of gasoline, the only difference being that, in the most volatile part, the alkanes appear in a reduced amount compared with the aromatics. We suppose that the higher molecular weight alkanes in the atmosphere originate from diesel engines and oil burners. We do not know yet whether these two sources can be distinguished analytically. We know, on the other hand, that in winter the alkanes are present in relatively higher concentrations, probably reflecting the increased activity of oil burners.

We are now extending our quantitative measurements over the area of Zürich with the aim of learning more about the local, seasonal and meteorological variations of the air composition.

ACKNOWLEDGEMENT

This work was generously sponsored by F. J. Burrus & Cie., Boncourt, Switzerland.

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