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EVALUATION OF ORGANIC POLLUTANTS IN THE OPEN AIR AND ATMOSPHERES IN INDUSTRIAL SITES USING GRAPHITIZED CARBON BLACK TRAPS AND GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC ANALYSIS WITH SPECIFIC DETECTORS

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SUMMARY

A method for evaluating the organic content of the atmosphere, involving the use of personal samplers, is described. A comparison of the performances of Tenax GC and Carbopack B is given in terms of sample recovery. Apparatus including selective columns, specific detectors and combined gas chromatography–mass spectrometry is also described.

Practical examples of the analysis of organic air pollutants trapped in the open air and the atmosphere in a chemical plant are discussed. A comparison of the results of complete gas chromatography and of the total hydrocarbon content is also made.

INTRODUCTION

The evaluation of organic pollutants in air involves techniques of various degrees of complexity, depending on the nature of the compounds involved, from the total hydrocarbon content including methane (using a simple flame-ionization detector), through the measurement of organic substances other than methane, the determination of lower alkanes and alkenes, and finally to the individual analysis of single organic substances.

The last type of measurement is essential when the situation in industrial sites has to be evaluated, because one needs to know the health hazards that specific compounds may have for persons continuously exposed to polluted atmospheres. In this context, the use of "personal samplers" has been proposed in order to obtain a better knowledge of the nature and amounts of actual and potential poisons inhaled in particular environments such as chemical plants and laboratories and in industrial sites where volatile organic substances have to be used.

On the other hand, the occurrence of photochemical oxidants in the open air and the recognition of the important role played by reactive hydrocarbons and other

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organic substances in the formation of photochemical smog make measurements of specific air pollutants important for research purposes and for optimizing air pollution control.

Because of the low concentrations of each component usually found in the atmosphere, sample enrichment is necessary in both instances, and various workers have sought the best enrichment procedures, ensuring that trapping is as complete as possible and that there is complete release of the organic compounds from the traps. Different approaches have been followed, mainly the use of cold traps at very low temperatures[1-6] and of traps working at room temperature[7-13]. Different kinds of trapping materials have also been studied, such as porous polymers alone[6-10] or coated with liquid phases[14,15], strong adsorbents such as active charcoal and successive solvent extraction[11], or moderately strong adsorbents such as graphitized carbon black[12,13]. However, cold traps obviously cannot be used in personal samplers, while traps operated at room temperature are also much more useful for monitoring organic pollutants in the open air, especially if automatic sampling and analysis is desired. The main problem is to find an adsorbent that is capable of trapping the highest number of substances, even though large volumes of air have to be sampled, and at the same time that is able to release higher boiling compounds on heating at moderately high temperatures.

With such severe limitations, both strong and weak adsorbents should be excluded, and only intermediate adsorbents or porous polymers remain to be considered. From preliminary results, Tenax GC (Enka, Arnhem, The Netherlands) and Carbopack B (Supelco, Bellefonte, Pa., U.S.A.) appeared to be the best materials for such purposes.

GENERAL CHARACTERISTICS OF TENAX GC AND CARBOPACK B

Tenax GC ($18.6 \text{ m}^2/\text{g}$) is a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide, the most important properties of which are its high operating temperature without appreciable bleeding and the capability of eluting a large number of compounds with good transmission of even highly polar or basic molecules. However, the resolution of Tenax GC as a packing material for chromatographic columns is very low and the selectivity is also poor in comparison with other adsorbents. Water is readily eluted from Tenax. The most interesting feature of Tenax, however, is its capability of eluting many compounds of different natures and molecular weights in a relatively short time. This porous polymer has been used mainly as a trapping material for enriching air or water samples[16]. It should be noted that, owing to its peculiar characteristics, Tenax was chosen for the chromatographic column in the Viking project[17].

Carbopack B is a graphitized carbon black adsorbent ($90 \text{ m}^2/\text{g}$) and has a large variety of applications as a column material in gas chromatography. It has been used in isotope separations[18] and in the analysis of sulphur compounds in air at the parts per billion level[19]. When suitably modified with small amounts of liquid phases, it shows a high selectivity for isomeric hydrocarbons[4] and complete transmission of alcohols, carboxylic acids and amines[20,21]. Columns made of Carbopack B offer good permeability and extremely high performance. The thermal stability of Carbopack B is without limit in practice and it does not show any bleeding, even at extremely high temperatures.

EXPERIMENTAL

Trapping procedure, measurement of breakthrough volumes and sample recovery

The traps are glass tubes, length 12 cm, I.D. 4 mm and O.D. 6 mm, with a 9-cm portion occupied by the trapping material, plugged with glass-wool on each side. The amount of material in each trap is 0.28 g of Tenax GC and 0.45 g of Carbopack B. Carbopack B is in the size range 80–100 mesh and Tenax GC 60–80 mesh.

Trapping in the open air is carried out with an electrically operated pump. Its pumping capacity is such that sampling with up to six traps simultaneously is possible, with a flow-rate in each trap of 30 ml/min. Sequential sampling is also possible for monitoring; a scheme of the trapping system is shown in Fig. 1. The sampling funnel is placed at about 10 m from the ground in the open air. A PTFE tube is used to connect the traps to the funnel.
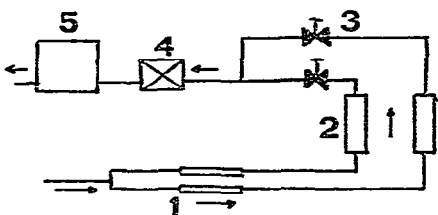

Fig. 1. Scheme of the trapping system. 1 = Traps; 2 = rotameters; 3 = needle valves; 4 = pump; 5 = flow counter.

Personal sampling is effected by using an Aircheck Personal Pump (SKC, Pittsburgh, Pa., U.S.A., Model 222-351). This pump is equipped with a digital flow meter and has a regulatable pumping capacity ranging from about 30 to 200 ml/min. The dimensions of the trap are as described above. Breakthrough volumes of test compounds are measured by injecting a known amount of the sample into the trap at room temperature, allowing extra-pure nitrogen to pass through the trap at the flow-rate desired until 0.5, 1.5 or 5.0 l have passed through, then closing the trap and heating it at 300° for 10 min.

A special four-way valve operating at temperatures up to 400° is used (Valco, Houston, Texas, U.S.A.). Injection is made by passing the carrier gas through the trap before entering the column. A scheme of the injection device that is also used when the organic compounds from traps have to be analyzed is shown in Fig. 2.

The chromatograms are compared for quantitative evaluation with that obtained by injecting the test mixture directly through the trap at 300°. In this way, one knows the amount lost or irreversibly retained by the trap. A Hewlett-Packard Model 3380A digital integrator is used for calculations.

Analytical equipment

It is important to note that with the device shown in Fig. 2, no loss of chromatographic resolution is observed for compounds scarcely retained in the column, as shown in Fig. 3.
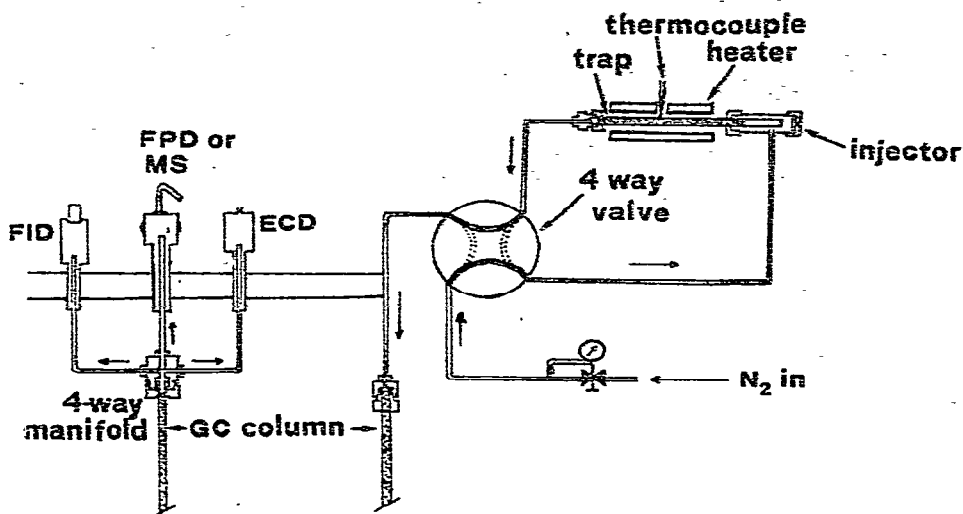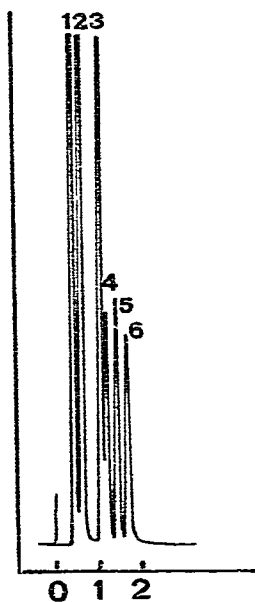
Fig. 2. Injection and detection system.

Fig. 3. Chromatogram obtained by injection through the trap, showing that dead volumes do not affect resolution. Peaks: 1 = methane + ethane; 2 = propane; 3 = isobutane; 4 = butene-i; 5 = *n*-butane; 6 = *trans*-butene-2.

A Carlo Erba Model GI gas chromatograph was modified at the injection port as described and a four-way manifold was used at the column exit to divide the gas stream into three portions, so that three detectors (flame-ionization, FID; electron-capture, ECD; and flame-photometric, FPD) could be used, as shown in Fig. 2. An analogous apparatus was used by McLeod *et al.*[22]. A similar chromatograph,

equipped with the same injection device, is coupled to an AEI MS12 mass spectrometer with an FID placed in parallel according to the technique described previously[23]. The apparatus for trapping and analyzing low-boiling compounds was shown in a previous paper[4].

The total organic content less methane is monitored using an automatic apparatus constructed in our laboratory. It consists of a modification of the apparatus described elsewhere[24] and is shown schematically in Fig. 4. One of the two detectors is directly fed with ambient air, sampled at the location of the traps, while the other is placed at the end of a chromatographic column (stainless steel, 2.0 m long, 4 mm I.D., 6 mm O.D., packed with Porapak Q, 80–100 mesh) where the same sample of air is injected every 5 min.
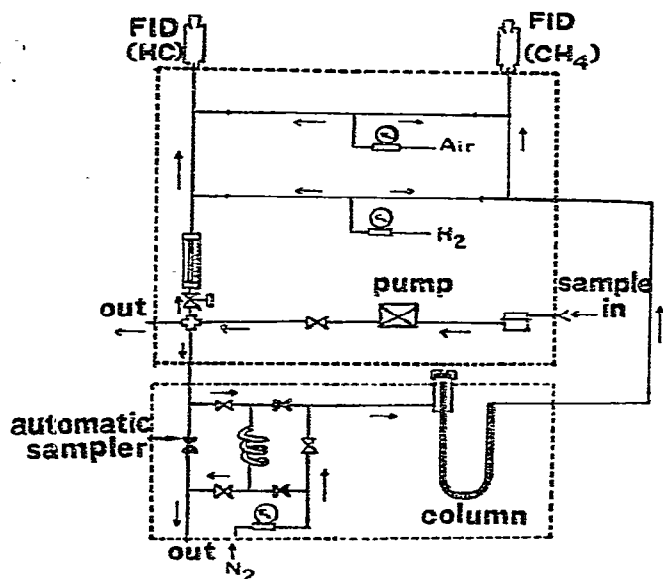

Fig. 4. Scheme of the apparatus for monitoring total hydrocarbon content and methane in air.

The column is operated at room temperature so that the methane peak is separated from any other peak. Further, owing to the large difference in the concentrations of methane and other single organic substances, it is possible to regulate the electrometer attenuation so as to detect the methane peak only. From calibration graphs, by subtracting the methane concentration, that of the total organic content is obtained.

A highly selective column was devised for the purposes of this work. The column should be able to work either at room temperature, yielding good separation factors for light compounds, or at higher temperatures to separate aromatic compounds up to C_{10}–C_{12}. It should also be able to elute polar compounds.

The column chosen was made of stainless steel, 1.80 m long and 2 mm I.D., packed with Carbopack C (Supelco), coated with 0.4% SP1000. Such a stationary phase, based on the unique properties of gas–liquid–solid chromatography, shows a pronounced selectivity for isomeric hydrocarbons and, owing to the polarity of the

liquid modifier, gives symmetrical peaks for hydrogen-bonding compounds. It should be noted that a polar liquid phase on graphitized carbon black enhances the separation of isomers and decreases the retention times[25]. The percentage of SP1000 is such that the first monolayer is incomplete, so that the separation is best for the effect of lateral interactions.

RESULTS AND DISCUSSION

Sample recovery

In Table I, the recoveries of various compounds attained with Carbopack B and Tenax GC are compared. The choice of the compounds examined was made with the aim of screening most of the types of organic compounds likely to be present in air pollutants. The list of compounds is obviously incomplete, but gives a fair idea of the trapping and releasing properties of the adsorbents considered.

There are two reasons why a particular compound injected in the trap could be incompletely recovered: (i) the compound is hardly adsorbed and is eluted from the trap by the air passing through it during the trapping step, or (ii) the compound is strongly adsorbed and is not released when the trap is heated. Thus, there is a critical region where the trap is most efficient for each adsorbent. The results in Table I show

TABLE I

RECOVERY (%) OF ORGANIC COMPOUNDS FROM AIR SAMPLES USING CARBOPACK B AND TENAX GC TRAPS

Compound	Carbopack B			Tenax GC		
	0.5-l sample	1.5-l sample	5.0-l sample	0.5-l sample	1.5-l sample	5.0-l sample
Methanol	3	0	0	1	0	0
Ethanol	3	0	0	1	0	0
Methyl chloride	1	0	0	3	1	0
Acetone	5	1	0	68	2	0
Chloroform	100	54	1	100	84	5
Diethylamine	100	80	50	80	50	1
Isobutanol	100	100	25	100	95	16
n-Pentane	100	100	100	100	50	9
Cyclohexane	100	100	100	100	50	9
n-Hexane	100	100	100	100	100	20
Ethyl acetate	100	100	100	100	100	35
n-Butanol	100	100	100	100	100	35
Benzene	100	100	100	100	100	35
Toluene	100	100	100	100	100	100
—*	—	—	—	—	—	—
n-C$_{13}$	65	65	65	100	100	100
n-C$_{14}$	46	46	46	100	100	100
n-C$_{15}$	25	25	25	100	100	100
n-C$_{16}$	8	8	8	100	100	100
n-C$_{17}$	1	1	1	100	100	100
n-C$_{18}$	0	0	0	100	100	100

* Styrene, ethylbenzene, xylene, pyridine, chlorophenol, alkanes, alkenes from C_7–C_{12} had 100% recovery in any case.

that Carbopack B and Tenax GC are comparable in this respect. However, benzene and n-hexane are completely retained by Carbopack B in the trapping step, but pass through Tenax GC; and the same occurs for the alkanes from n-pentane to isooctane. It is worth noting that significant differences are observed for light compounds. Acetone is recovered better from Tenax GC, while for butanol and diethylamine Carbopack B is more efficient.

Such differences may be explained by the strong retention of hydrocarbons on graphitized carbon black. For polar compounds, the specific active sites present on the carbon black surface increase the retention. The small number of carbon atoms and the low polarity are responsible for the low retention of acetone on Carbopack B. Tenax, which elutes amines linearly[17], i.e. without appreciable irreversible adsorption, allows these compounds to pass through the trap.

The same reasons that favour Carbopack B for the range C_4–C_8 favour Tenax GC if compounds above C_{12} are considered. However, it should be noted that such compounds are seldom present in the open air or in industrial sites, as will be shown later with examples of field measurements. They are, however, major constituents of the organic fraction of atmospheric dust, but this is a different problem.

For the sake of comparison in the real use of the adsorbents, the following experiment was carried out. Two traps of the same length and diameter, one of Tenax GC followed by Carbopack B according to the direction of the air stream, and the other of Carbopack B followed by Tenax GC, were used for parallel air sampling, 1.5 l of air being sampled in each trap. During the trapping step, the compounds that were not retained by Tenax GC passed into the second part of the trap and were retained by the Carbopack B. In a similar manner, in the other trap compounds that were not retained by Carbopack B were subsequently retained by Tenax GC.

The traps in tandem were then separated and their organic contents injected into the column, giving the four chromatograms shown in Fig. 5. Calculations were made by considering the total peak areas of chromatograms A + B and C + D as 100%. The two total areas were closely correlated, showing that the sampling and injection procedure is highly reproducible.

From this experiment, it was also found that Carbopack B behaves as a better trapping and releasing material than Tenax GC (83% recovery compared with 75%). Only acetone, as expected from the results in Table I, is better retained by Tenax GC, while cyclohexane and pentane are partly lost by Tenax GC and completely retained by Carbopack B in the trapping step.

In addition, the chromatograms in Fig. 5 show that there is a discrepancy between the breakthrough volumes measured with the method described and the actual retention and releasing properties of the adsorbents in field measurements. In fact, both of the materials lose some of the C_8–C_{10} fraction, and this could not be forecast from the results in Table I. A possible explanation of this effect is that sampling is carried out under extremely dilute conditions, which are completely different from those which occur when breakthrough volumes are being measured. In this instance, the samples injected in the traps are much more concentrated.

Sampling and analysis of atmospheric pollutants

A 5.0-l volume of air from suburban open air was sampled with a Carbopack B trap at a flow-rate of 30 ml/min. A cold trap[4] was used at the same time for the
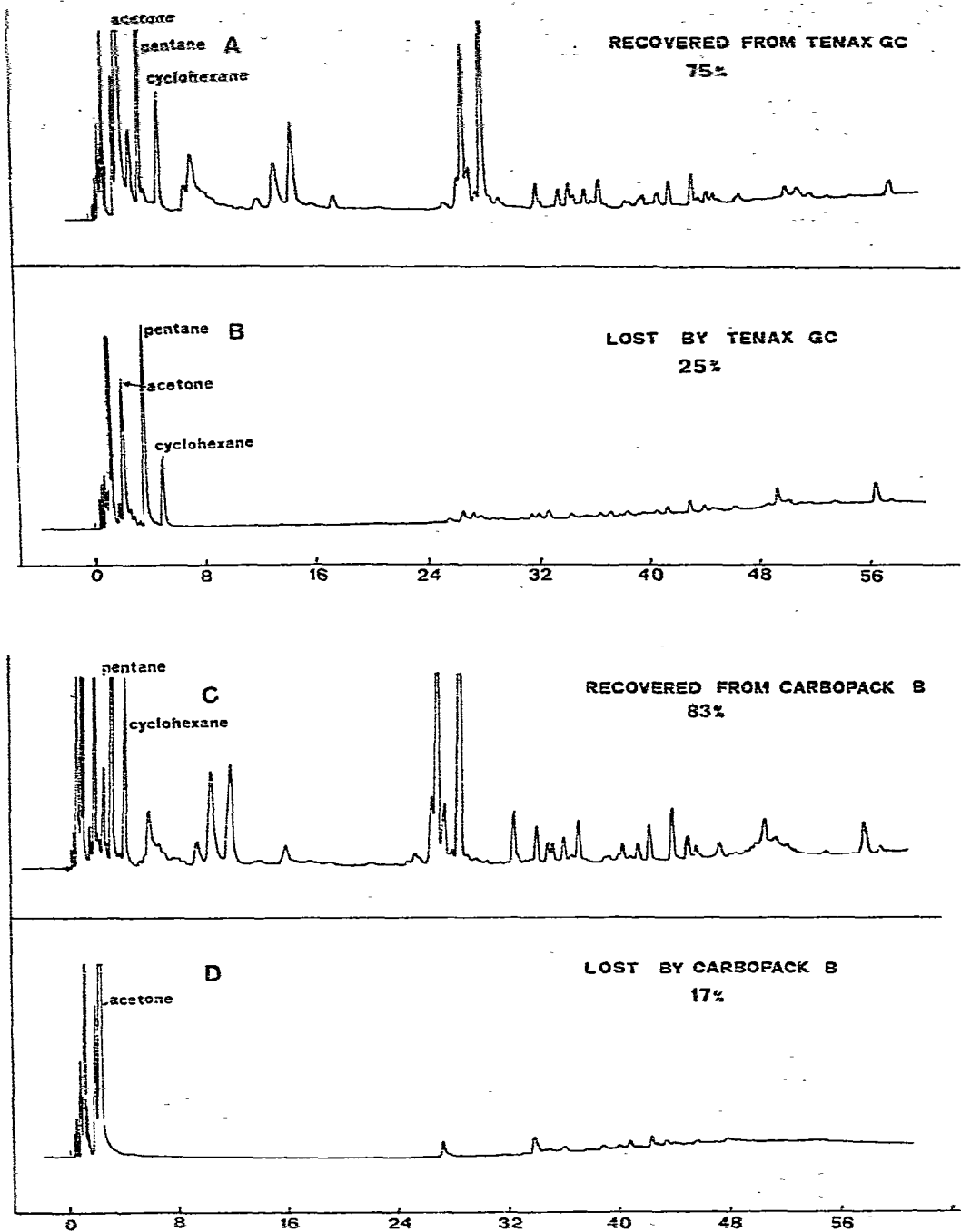
Fig. 5. Chromatograms showing losses and recovery from an actual air sample using Tenax GC and Carbopack B.

analysis of C_2–C_4 compounds and the total non-methane organic compounds (THC) were also monitored. The THC trace obtained is shown in Fig. 6 together with that obtained with a sample from an urban site. The area within the broken line corresponds to the time period when the traps were operated.

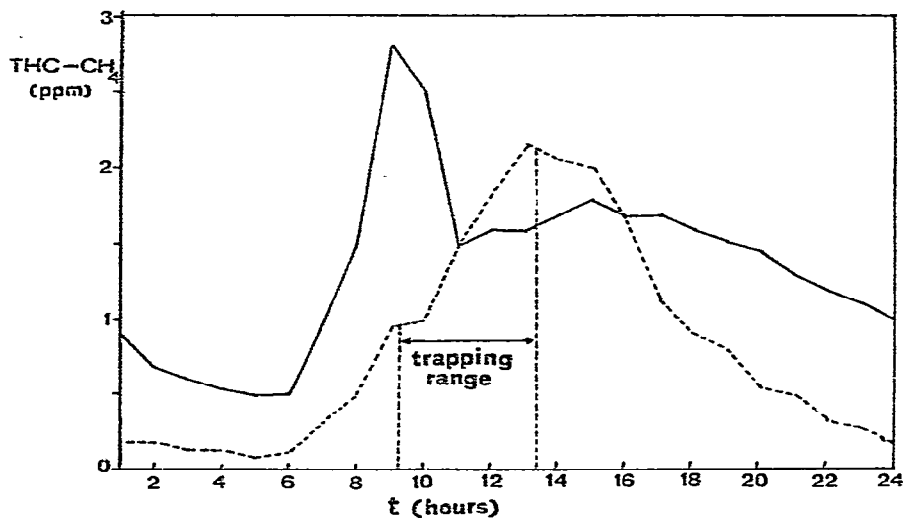The analysis was then run using the FPD, ECD and FID as parallel detectors

Fig. 6. Total hydrocarbon content during 24 h monitored in typical urban (———) and suburban (– – –) areas.
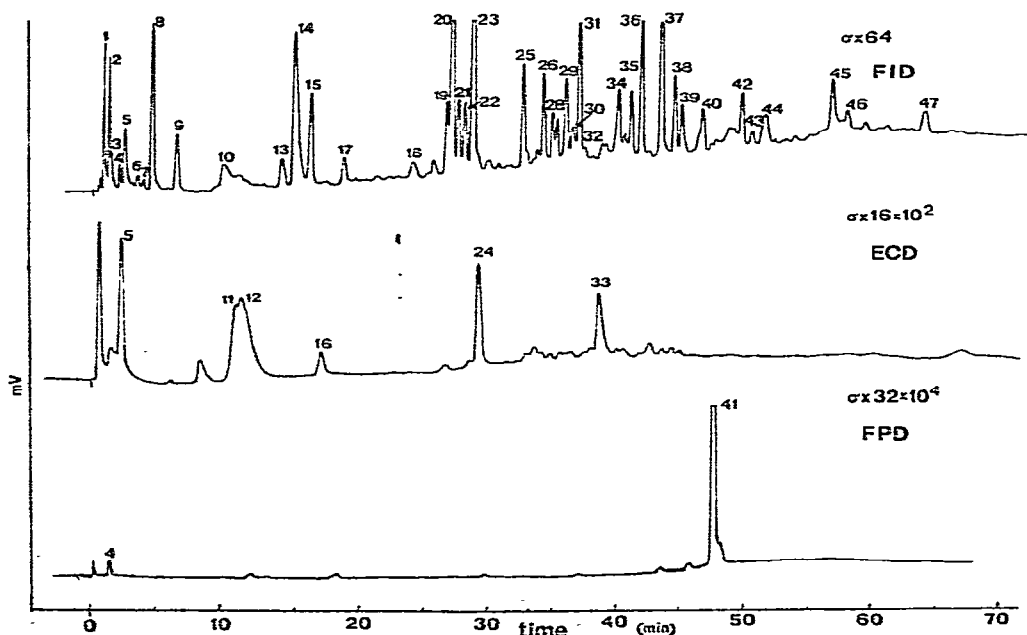
Fig. 7. Triple detector chromatogram showing the analysis of a sample of air taken in suburban open atmosphere. Peak Nos. as in Table II. Sampling material: Carbopack B.

and the resulting chromatogram is shown in Fig. 7. Most peaks were identified by MS. The potentiality of specific detection is shown by the identification of benzo-thiophene and halogenated compounds, which was effected on the basis of retention times. The amount of these compounds is so low that when other compounds were present in the same region of the chromatogram mass spectrometric identification was impossible.

Another feature of the chromatogram is that, in spite of its complexity, major peaks corresponding to single compounds were obtained, showing a high selectivity. This can also be seen from peaks Nos. 30, 31 and 32, which gave identical mass spectra, and which were identified as the three xylenes from the retention times. The separation achieved for the other aromatic compounds is also worthy of note. Only two pairs of peaks overlapped.

Table II lists the compounds identified, together with the approximate amounts found. The accuracy of the determinations was 10–20 % based on the absolute amounts present.

Parallel sampling and analysis of the light fraction were also carried out, using a technique described elsewhere[4]. The analysis was effected with the triple detector system and the qualitative and quantitative results are reported in Table III.

It is interesting to note the noticeable amount of methylene chloride found, which indicates the importance of halogenated compounds in air pollution.

Table IV shows the results for the balance of the components. From a comparison of the data in Tables II and III, it can be seen that the C_2–C_5 fraction is only 25 % of the total, showing that a complete analysis up to C_{10} is needed for a reasonable screening of air pollutants. The aromatic fraction is present in about the same percentage as the C_2–C_5 hydrocarbons, in good agreement with the data available from the literature[26]. The concentration of the heavier organic compounds is obtained by subtracting the peaks corresponding to the light fraction from the total integration of the chromatogram in Fig. 7.

The unidentified fraction is the sum of the minor peaks, present in low amounts, for which mass spectrometric identification was impossible. The fraction lost probably corresponds in part to compounds heavier than C_{10}, but the discrepancy may also be due to errors in the analytical measurements. However, repetitive measurements always gave a lower figure for the total amount found by gas chromatography with respect to the direct THC values, showing that the first hypothesis is more feasible. The non-hydrocarbon fraction comprises about 14 % of the total organic compounds, confirming the strong prevalence of petroleum products in organic air pollutants.

No evidence for the presence of terpenes has been found; in fact, the suburban area where sampling was carried out is a long distance from forest areas. The presence of some ketones and halogenated compounds is probably due to some small factories located 1–2 km from the sampling point.

Sampling and analysis in industrial sites

Carbopack B traps were used for sampling organic substances in a chemical plant where solvents are used in process syntheses. A 1-l volume of air was sampled in the area of the plant where workers usually spend most of their working day, in order to obtain a representative sample of inhaled air. The sampling rate was ap-

TABLE II

ANALYSIS OF ORGANIC COMPOUNDS IN OPEN AIR

Peak No.	Retention time (min)	Identified as (MS)	Amount (ppb CH_4)
1	0.72	Butene-1 + cis-butene-2 + isobutane	25
2	1.13	n-Butane + trans-butene-2	16
3	1.35	1,3-Butadiene	7
4	2.02	Methyl mercaptan	4
5	2.37	Acetone + CH_2Cl_2*	16
6	3.42	C_5 unsaturated hydrocarbon	2
7	3.88	i-C_5 hydrocarbon	1
8	4.48	n-C_5 hydrocarbon	40
9	6.45	Cyclohexane	17
10	10.0	—	50
11	11.20	—*	5
12	11.80	Carbon tetrachloride*	5
13	14.66	Dietyl ketone	11
14	15.64	Benzene	74
15	16.88	C_6 unsaturated hydrocarbon	33
16	18.00	Trichloroethylene*	<1
17	19.54	n-C_6 hydrocarbon	8
18	25.03	Butanol	6
19	27.63	Methylcyclohexane	19
20	27.99	C_7 unsaturated hydrocarbon	90
21	28.55	C_7 unsaturated hydrocarbon	21
22	29.06	Toluene	20
23	29.61	C_7 hydrocarbon	100
24	29.80	1,3-Dichloropropane*	6
25	33.59	Dimethylcyclohexane	30
26	35.19	C_8 unsaturated	26
27	35.91	Ethyl butyl ketone	15
28	36.25	Styrene	13
29	36.96	Ethylbenzene	21
30	37.50	m-Xylene	11
31	37.98	p-Xylene + isopropylbenzene	41
32	38.44	o-Xylene	3
33	39.81	—*	4
34	41.04	n-C_9 hydrocarbon	20
35	42.07	Ethyltoluene	19
36	42.83	1,3,5-Trimethylbenzene	18
37	44.38	1,2,4-Trimethylbenzene	54
38	45.46	1,2,3-Trimethylbenzene	22
39	46.05	Ethyldimethylbenzene	18
40	47.67	Methylisopropylbenzene	18
41	48.67	Benzothiophene*	3
42	50.77	1,2,3,5-Tetramethylbenzene	13
43	51.57	1,2,3,4- + 1,2,4,5-Tetramethylbenzene	4
44	52.59	—	18
45	57.74	—	18
46	58.99	—	4
47	65.05	—	19

Total: 988

* Detected with specific detectors and identified with standards.

TABLE III

ANALYSIS OF LIGHT ORGANIC COMPOUNDS IN THE OPEN AIR (COLD TRAP)

All peaks identified with standards.

Peak No.	Retention time (min)	Identified as	Amount (ppb CH₄)
1	3.00	Ethene	15
2	3.23	Ethane	7
3	7.45	Propene	8
4	7.84	Propane	5
5	21.07	Isobutane	10
6	35.08	n-Butane	35
7	32.12	1,3-Butadiene	10
8	37.0	trans-Butene	5
9	47.45	Dichloroethane*	150
10	50.82	—	35
11	61.25	2-Methylbutene	14
12	67.54	Isopentane	10
13	77.70	n-Pentane	40
14	80.25	—	35
15	90.20	—*	<1
		Total:	376

* Detected with ECD.

TABLE IV

BALANCE OF THE COMPONENTS IN THE OPEN AIR

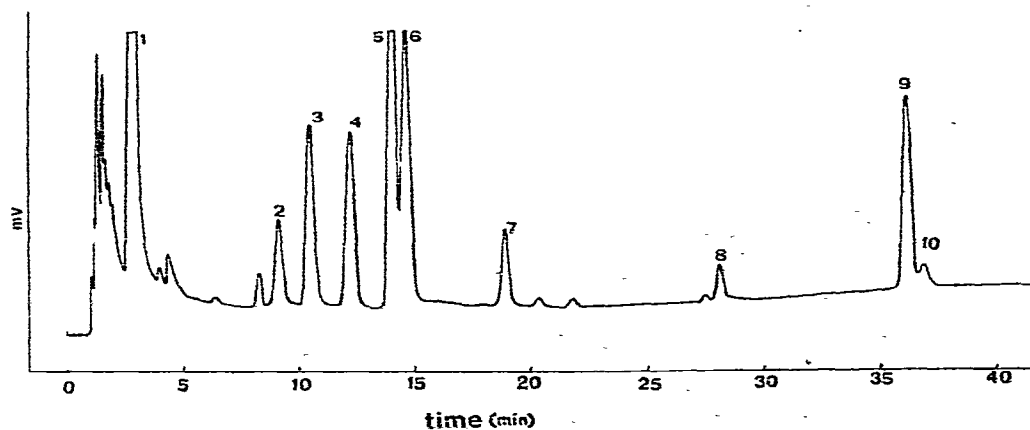| Fraction	Amount (ppb)
THC (non-methane)	1550
Light organics (cold trap)	375 (26%)
Heavier organics trapped and recovered	1076 (74%)
Total organics trapped	1451
Unidentified (minor peaks)	336 (23.1%)
Lost	98 (6.3%)

Fig. 8. Chromatographic analysis of an air sample taken inside a chemical plant. Peaks as in Table IV. Sampling material: Carbopack B.

proximately 100 ml/min. Particular emphasis was placed on a search for aromatic solvents. The chromatogram obtained is shown in Fig. 8 and peak identification is reported in Table V.

The GC–MS analysis was made 2 h after sampling, and a parallel sampling was made with an identical trap, which was processed 1 week later. The same chromatogram was obtained without significant changes, which indicates that traps can be stored prior to analysis without problems unless very reactive and unstable compounds are present in the trap. The trap was closed at the terminals during storage. The amount of acetone was estimated knowing that about 95% is lost during the trapping step.

TABLE V

ANALYSIS OF AIR SAMPLE FROM A CHEMICAL PLANT

Chromatograms in Fig. 7.

Peak No.	Identified as	Amount (ppm)
1	Acetone	≈ 50
2	C_6 unsaturated	1.0
3	C_6 unsaturated	2.2
4	Ethyl isopropyl ketone	2.0
5	Diethyl ketone	3.6
6	Benzene	2.9
7	Hexane	0.7
8	Toluene	0.3
9	Styrene	2.6
10	Ethylbenzene	0.12

CONCLUSION

The results show that the analytical procedure involving the use of Carbopack B or Tenax GC traps for sampling at room temperature can be used to evaluate the air quality with reliable results. It should be noted that the total amount of organic pollutants unidentified is relatively high (23%), but also that the practical value of this figure is limited, because it includes only very minor components.

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