

IMPROVED EVALUATION OF POLYNUCLEAR HYDROCARBONS IN ATMOSPHERIC DUST BY GAS CHROMATOGRAPHY*

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In a previous paper¹ it has been reported that gas chromatography can be applied to the determination of polynuclear hydrocarbons in airborne particles.

The possibilities of gas chromatography for the evaluation of these compounds has been the object of further work and several aspects have been considered.

New liquid phases have been evaluated in order to obtain a sharper separation of certain compounds and programmed temperature chromatography has been used. It has also been shown that an electron capture detector may be used for the determination of polynuclear hydrocarbons and the relative response evaluated.

EXPERIMENTAL

A commercial gas chromatography apparatus (Fractovap C. Erba, Milano, model PAID/f) equipped with either a flame ionisation or an electron capture detector and a linear temperature programmer was used.

All measurements were carried out with glass capillary columns described previously². The characteristics of the column are given in Table I.

TABLE I
COLUMN CHARACTERISTICS

<i>Liquid phase</i>	<i>Type</i>	<i>No. of theoretical plates</i>	<i>Length (m)</i>
(a) SE-30	Methylsilicone, Applied Sc. Lab.	20,000	30
(b) SE-52	Methylphenylsilicone, Applied Sc. Lab.	40,000	50
(c) XE-60	Cyanoethylmethylsilicone, Applied Sc. Lab.	20,000	35

The working conditions for these columns were: injector temperature 300°C; carrier gas: nitrogen at inlet pressure 0.3 atm. for (a) and (c) and 0.6 atm. for (b); splitter ratio 1:100, sample size 0.1–1.0 μg for each compound.

The retention volumes of some polynuclear hydrocarbons relative to chrysene obtained under isothermal conditions ($t = 200^\circ$) are reported in Table II.

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TABLE II

RETENTION VOLUMES RELATIVE TO CHRYSENE AT 200°C, WITH GLASS CAPILLARY COLUMNS COATED WITH DIFFERENT LIQUID PHASES

Compound	SE-30	SE-52	XE-60
Anthracene	13	12	12
Fluoranthene	31	27	29
Pyrene	36	32	33
1,2-Benzfluorene	48	44	42
3-Methylpyrene	54	53	52
Benz(<i>m,n,o</i>)fluoranthene	82	79	81
1,2-Benzanthracene	98	97	98
Chrysene	100	100	100
Naphthacene	—	214	224
7,12-Dimethyl-1,2-benzanthracene	236	—	—
3,4-Benzfluoranthene	263	242	248
1,2-Benzpyrene	310	312	325
3,4-Benzpyrene	310	333	330
Perylene	321	363	336
20-Methylcholanthrene	400	—	—
1,3,5-Triphenylbenzene	415	455	315

The SE-30 column is not very specific and, as previously reported, some compounds are only slightly separated. Better results are obtained with an SE-52 column as a mixture of 1,2-benzpyrene, 3,4-benzpyrene and perylene give well defined peaks, and good resolution is also obtained for chrysene and 1,2-benzanthracene. These separations are of practical importance because of the toxic properties of these compounds.

The elution order and the elution time for the column coated with the more polar liquid XE-60 is approximately the same as for the SE-52 column. It cannot, however, be used at temperatures higher than 200°.

SE-52 has a low vapour pressure at high temperatures and does not bleed significantly up to 300°. It was found very useful for programmed temperature chromatograms. For a complete evaluation of polynuclear hydrocarbons, as is usually required in air pollution investigations, it is of interest also to determine compounds in a boiling point range higher than those reported in Table II; for this purpose programmed temperature chromatography was found very convenient. A good separation is realised for each compound and the analysis of a mixture of hydrocarbons, ranging in boiling point from naphthalene to coronene, is obtained as shown in Fig. 2.

RETENTION INDICES OF POLYNUCLEAR HYDROCARBONS

In order to make the data obtained in programmed temperature gas chromatography of general use and more suitable for the identification of polynuclear hydrocarbons found in complex mixtures, the retention indices, as described by KOVATS³, were calculated.

In Fig. 1 the retention indices of polynuclear hydrocarbons are plotted against temperature, measured from a series of isothermal chromatograms run at different temperatures in the range 180–250°. These values have been calculated from the retention times of *n*-alkanes having from 16 to 28 carbon atoms.

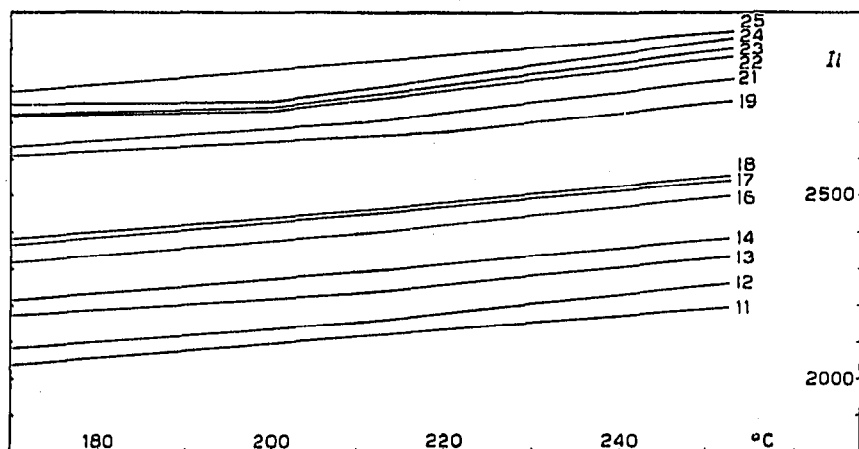


Fig. 1. Variation of retention index with the temperature. The numbers correspond to the compounds of Table III.

The retention indices are slightly affected by temperature variation. A change of less than 1% is observed for an increase of 10°.

The retention indices for programmed temperature chromatograms (I_{pr}) have been computed from the retention temperatures (T_r) according to VAN DEN DOOL AND KRATS⁴. These values are collected in Table III and are in good agreement with the corresponding values of the isothermal indices (I_t) measured at a temperature $0.92 T_r$, as is shown from the deviation, which is less than 12 units. The agreement between these figures indicates that both under isothermal conditions and at programmed temperatures, the identification of polynuclear hydrocarbons can be performed with a high degree of reliability.

APPLICATION OF THE ELECTRON CAPTURE DETECTOR

Many polynuclear hydrocarbons show a high affinity for free electrons and consequently, as reported by LOVELOCK^{5,6}, an electron capture detector can be employed for their chromatographic determination.

The interesting feature of a detector based on this principle is that its response to various hydrocarbons is quite different and thus its use can be very successful in the analysis of mixtures containing a large number of compounds, such as are usually observed in extracts of atmospheric dusts.

The weight response of some polynuclear hydrocarbons relative to benz-(m,n,o)-fluoranthene, measured with the electron capture detector, operating at 15 V D.C., is reported in Table IV.

These values differ widely and thus may be used to differentiate a certain component if the response ratio of the change in current in the flame ionisation and the electron capture detectors can be measured.

It should be pointed out, however, that the figures reported in Table IV are only indicative, because the response of an electron capture detector is greatly affected by geometrical characteristics and by the applied potential.

Fig. 3 shows the chromatogram of an atmospheric dust sample extracted according to the procedure described previously¹ and obtained with a flame ionisation and an electron capture detector.

TABLE III

RETENTION INDICES, ON SE-52, AT PROGRAMMED TEMPERATURES FROM 100° TO 300°C WITH PROGRAMMING 2.5°C/MIN.

<i>n</i>	<i>Compound</i>	<i>T_r</i>	<i>I_{pr}</i>	<i>I_{i(0.92T_r)}</i>	$\frac{\delta}{I_{i(0.92T_r)} - I_{pr}}$
1	Naphthalene	102	1173		
2	Azulene	105	1212		
3	Diphenyl	109	1262		
4	Acetylnaphthalene	113	1313		
5	Acenaphthalene	116	1350		
6	Fluorene	124	1460		
7	<i>trans</i> -Stilbene	137	1620		
8	Phenanthrene	143	1695		
9	Carbazole	154	1838		
10	Anthracene	160	1850		
11	Fluoranthene	174	1988	1977	— 11
12	Pyrene	178	2040	2032	— 8
13	1,2-Benzfluorene	185	2125	2137	+ 12
14	3-Methylpyrene	189	2173	2176	+ 3
15	1-Methylpyrene	189	2173		
16	Benz-(<i>m,n,o</i>)-fluoranthene	199	2297	2297	0
17	1,2-Benzanthracene	204	2358	2356	— 2
18	Chrysene	207	2397	2394	— 3
19	Naphthacene	219	2543		
20	1,2-Benzfluoranthene	227	2648		
21	3,4-Benzfluoranthene	228	2655	2665	+ 10
22	1,2-Benzpyrene	234	2728	2728	0
23	3,4-Benzpyrene	235	2742	2738	— 4
24	Perylene	237	2766	2759	— 7
25	1,3,5-Triphenylbenzene	244	2853	2852	— 1
26	1,2,5,6-Dibenzanthracene	258	3008		
27	1,2,3,4-Dibenzanthracene	261	3048		
28	1,12-Benzperylene	278	3230		
29	1,2,3,4-Dibenzpyrene	281	3270		
30	Coronene	282	3283		

TABLE IV

WEIGHT RESPONSE FOR SOME POLYCYCLIC HYDROCARBONS WITH FLAME IONISATION (HF) AND ELECTRON CAPTURE (EC) RELATIVE TO BENZ-(*m,n,o*)-FLUORANTHENE

<i>Compound</i>	<i>HF</i>	<i>EC</i>	<i>EC/HF</i>
Anthracene	0.75	0.06	20.2
Fluoranthene	0.76	0.09	32.5
Pyrene	0.84	0.40	124.3
1,2-Benzfluorene	1.00	0.02	5.5
3-Methylpyrene	0.97	0.27	69.2
Benz-(<i>m,n,o</i>)-fluoranthene	1.00	1.00	250.0
1,2-Benzanthracene	0.90	0.87	267.2
Chrysene	0.85	0.00 ₅	1.5
3,4-Benzpyrene	1.53	2.15	343.5
1,2-Benzpyrene	0.66	0.75	310.0
3,4-Benzfluoranthene	1.01	0.67	180.2
Perylene	1.80	0.01	1.5

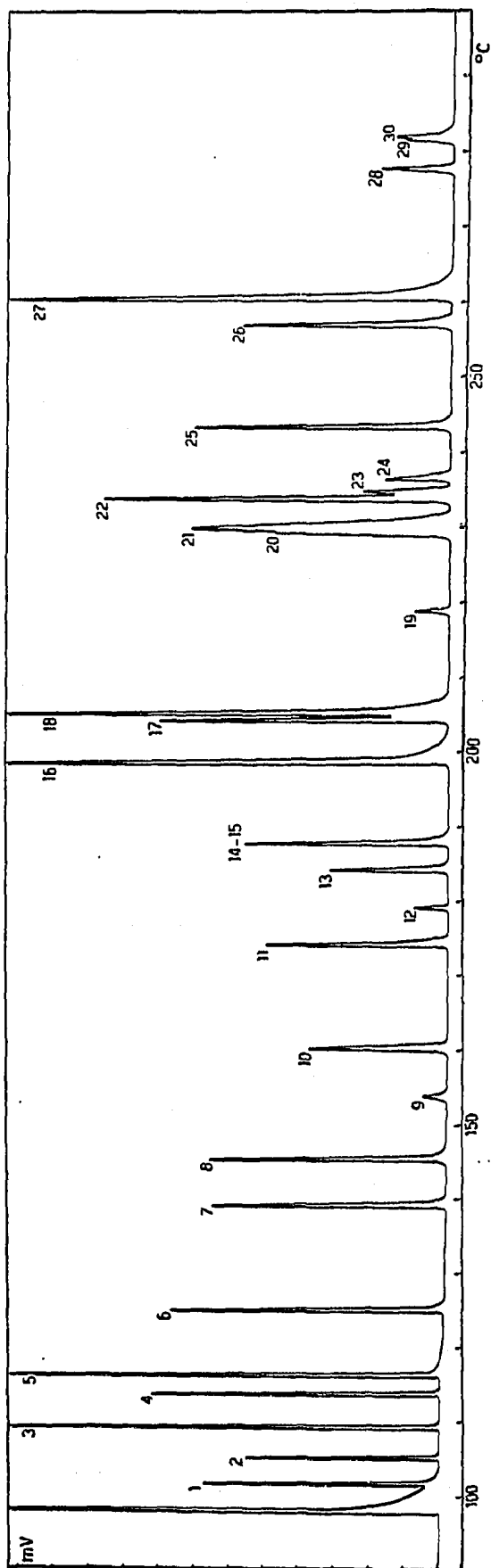


Fig. 2. Programmed temperature gas chromatogram of a polynuclear hydrocarbon mixture ($100^{\circ} - 300^{\circ}\text{C}$ at $2.5^{\circ}\text{C}/\text{min}$). Glass capillary column coated with SE-52. The number of each peak corresponds to the compound reported in Table III.

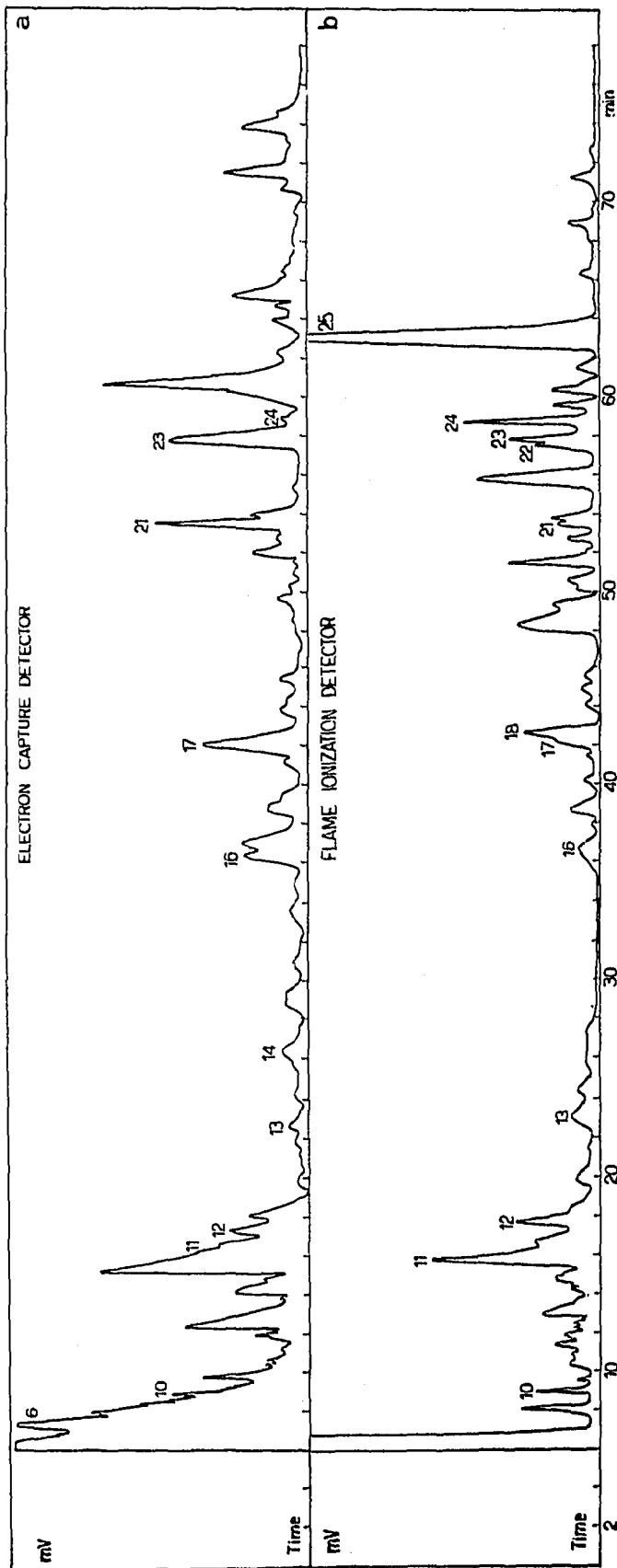


Fig. 3. Gas chromatogram of a representative sample of an atmospheric dust extract, obtained with EC (a) and HF (b) detectors. Programmed temperature $150 - 230^{\circ}\text{C}$ at $2.5^{\circ}\text{C}/\text{min}$ on a SE-52 column. Numbers of the identified compounds as in Table III.

In the chromatogram of the atmospheric dust sample (Fig. 3) the response of the electron capture detector is very different from that of the flame and at the same time shows many other unknown compounds as large peaks that are not detected by the flame detector because of being present in too small an amount.

SUMMARY

Mixtures of polynuclear hydrocarbons can be analysed by means of high efficiency glass capillary columns. Several liquid phases have been tried, SE-52 being the most effective.

The retention index of these hydrocarbons has been measured isothermally and under programmed temperature conditions. An electron capture detector has been applied to the determination of such hydrocarbons and its relative response is compared with the results obtained with a hydrogen flame ionisation detector.

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