

## GAS CHROMATOGRAPHIC DETERMINATION OF POLYNUCLEAR HYDROCARBONS IN DUST

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The determination of polynuclear hydrocarbons in urban airborne particles can be performed by chromatography on alumina or silica gel, elution with suitable solvents, and determination of the various components either by ultraviolet or fluorescence spectroscopy. Several procedures following this scheme have been suggested<sup>1-3</sup>. Though gas chromatography has been successfully applied to the analysis of aliphatic and aromatic hydrocarbons, no previous work has been carried out on the application of this technique to the determination of polynuclear hydrocarbons in air pollution investigations.

The determination of some polycyclic hydrocarbons by gas chromatography in cigarette smoke<sup>4</sup>, coal tar and mineral oil<sup>5,6</sup> has been reported.

The purpose of this work was the study of the operational conditions under which gas chromatography can be applied for the determination of polynuclear hydrocarbons in dust, to develop a method of analysis, and to evaluate the limitations and the advantages of the procedure. Attention has been also paid to the determination of alkanes as they have been found in noticeable amounts in urban dust.

The method has been developed with synthetic mixtures of polynuclear hydrocarbons and checked with air particulate samples obtained by a commercial high volume air sampler.

In order to find a rapid method for the determination of various components in atmospheric dust, some preliminary chromatograms were carried out directly on samples obtained by extraction of dust with cyclohexane and evaporation of the solvent. The large number of components found in dust, however, renders the chromatograms of the samples of little use, so that a preliminary fractionation is considered necessary. An efficient procedure for isolating the hydrocarbons consists in the use of successive extractions of the cyclohexane solution with methanol-water and nitromethane as suggested by HOFFMANN AND WYNDER<sup>7</sup>; in the former operation the cyclohexane phase is freed of hydrophilic compounds and in the latter the hydrocarbons are fractionated, the aromatics being extracted in the nitromethane phase.

## EQUIPMENT AND MATERIALS

The gas chromatographic investigation was carried out with a Carlo Erba Fractovap C (mod. PAID/f), equipped with a flame ionisation detector and a linear programmed

temperature system. All the chromatograms reported were carried out with a glass capillary column (35 m long, 0.35 mm I.D.) coated with SE 30 silicone rubber. The working conditions were: column temperature, 200°; injector temperature, 250°; carrier gas, nitrogen at inlet pressure of 0.25 atm; column flow rate, 1 ml/min; splitter 1:100 ratio; sample size 0.5-2  $\mu\text{l}$  of solution containing approximately from 0.5 to 2  $\mu\text{g}/\mu\text{l}$  for each component. The column efficiency measured from the *n*-hexacosane peak is about 10,000 theoretical plates.

The dust sample, kindly supplied by Prof. D'AMBROSIO of the Laboratorio Provinciale Milano, had been previously analysed by paper chromatography and by spectrophotometry.

The solvents employed (cyclohexane (R. P. Carlo Erba), nitromethane (A.S.D.) and methanol (R.P. Carlo Erba)) were purified by fractional distillation, collecting the fractions with a constant boiling point. Their purity was tested periodically by gas chromatography; 50 ml of each solvent was evaporated to a very small volume and injected into the gas chromatograph operating under the usual working condition; no other peaks were observed.

#### METHOD

Dust samples (0.5-1.0 g) were extracted in a Soxhlet extraction apparatus with 100 ml cyclohexane for about 5 h; after this time the liquid portion, condensed in the thimble, did not show any fluorescence when exposed to ultraviolet light. The thimble was previously extracted with acetone.

The extract was evaporated to a volume of about 5 ml and shaken with a 5 ml mixture of methanol-water (4:1). The methanol extract was shaken three times with 5 ml portions of cyclohexane to recover the hydrocarbons. The separation of the phases was carried out by centrifugation in 25 ml tubes. The combined cyclohexane fractions were extracted 6 times with 5 ml of nitromethane. The cyclohexane and the nitromethane solutions containing respectively the aliphatic and the polycyclic hydrocarbons were evaporated to dryness under reduced pressure. The residues were dissolved with small volumes of ether and concentrated in micro test tubes to about 10  $\mu\text{l}$ .

#### EXPERIMENTAL

Table I shows the relative retention volumes referred to chrysene ( $V_R = 1.0$ ) of polynuclear hydrocarbons obtained under the above described working conditions. A higher column temperature (230°) was used to elute a certain number of less volatile hydrocarbons. These values show that a fairly good separation is obtained for most hydrocarbons and their identification therefore might be performed by gas chromatography.

The response of the hydrogen detector is proportional to the concentration of the various hydrocarbons but no simple relationship exists between the number of carbon atoms of various molecules and the response of the detector. For example, a mixture of pyrene and fluoranthene with the same molecular weight at the same molar concentration yields elution peaks with different areas, the former being about 1.4 times the latter.

TABLE I

RELATIVE RETENTION VOLUMES AND WEIGHT RESPONSE FACTOR OF POLYNUCLEAR HYDROCARBONS

No.	Component	$V_R (200^\circ)$	$A/A_{St}$
1	Anthracene	0.13	—
2	Fluoranthene	0.31	1.20
3	Pyrene	0.36	1.61
4	1:2-Benzofluorene	0.48	—
5	1-Methylpyrene + 3-methylpyrene	0.54	0.82
6	Benzo[ghi]fluoranthene	0.82	—
7	1:2-Benzanthracene	0.98	—
8	Chrysene	1.00	0.72
9	7,12-Dimethyl-1:2-benzanthracene	2.36	—
10	2:3-Benzofluoranthene	2.63	0.78
11	3:4-Benzopyrene + 1:2-benzopyrene	3.10	0.60
12	Perylene	3.21	0.37
13	20-Methylcholanthrene	4.00	—
14	1,3,5-Triphenylbenzene	4.15	1.00
		$V_R (230^\circ)$	
15	1:2;5:6-Dibenzanthracene	5.28	
16	1:12-Benzoperylene	5.92	
17	1:2;3:4-Dibenzopyrene	13.6	
18	1:2;4:5-Dibenzopyrene	15.2	
19	Coronene	15.5	

In order to apply gas chromatography to quantitative determinations it has been found necessary to find a suitable internal standard and to evaluate a correction factor for each hydrocarbon.

Several attempts have been made to select a suitable internal standard; 1,3,5-triphenylbenzene (FLUKA), was found to meet the requirements for this purpose. Its retention volume under the conditions described ( $200^\circ$ ) is 4.15 and is therefore quite different from those of the aromatic hydrocarbons tested.

The correction factors, determined from the ratio of the peak areas of the tested hydrocarbon and the peak area of the internal standard ( $A/A_{St}$ ), at the same weight concentrations, are reported in Table I.

In artificial mixtures the determination of a hydrocarbon can be performed with an error of  $\pm 3\%$ .

Dust samples have been extracted according to the procedure described and a typical gas chromatogram of the nitromethane fraction containing aromatic hydrocarbons is shown in Fig. 1. A large number of peaks is obtained and it seems that in dust, besides the polynuclear hydrocarbons identified by spectrophotometry, other compounds of the same class are present. In Table II are reported the retention volumes of the components eluted from the column. The concentrations of the hydrocarbons identified have been determined by the method described here and the results are compared with the values obtained by spectrophotometry.

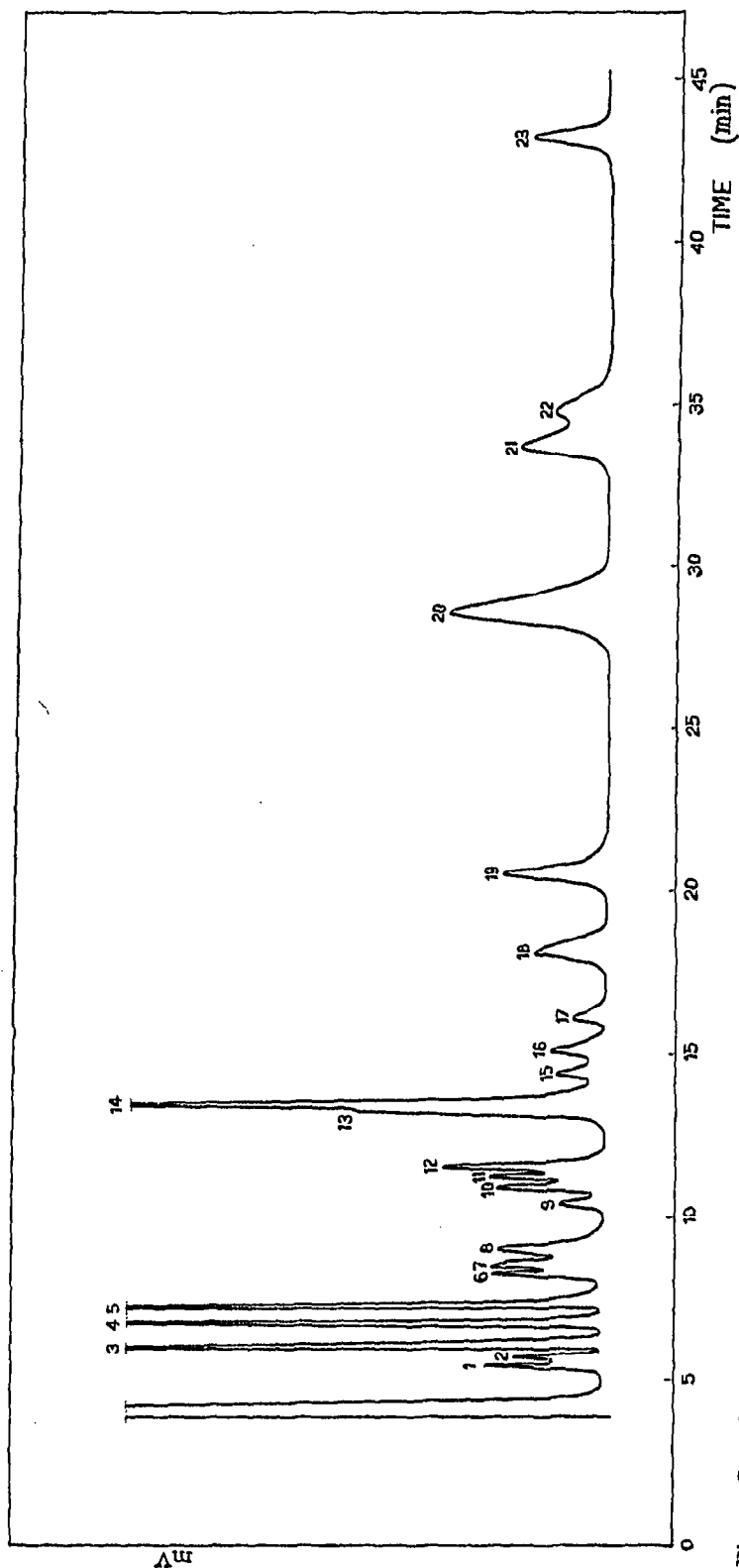


Fig. 1. Gas chromatogram of polynuclear hydrocarbons from a dust sample (nitromethane fraction). The peak numbers correspond to the components reported in Table II.

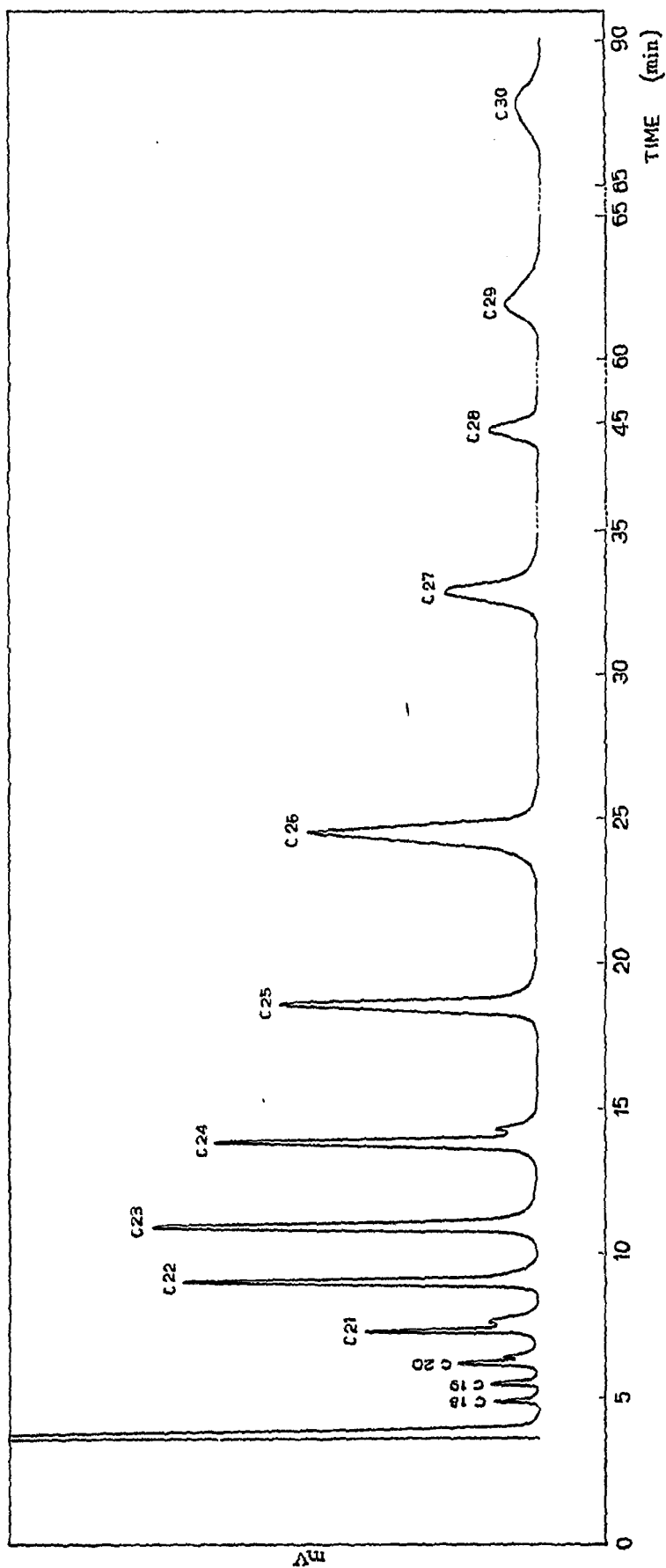


Fig. 2. Gas chromatogram of alkanes from a dust sample (cyclohexane fraction).

TABLE II  
SPECTROPHOTOMETRIC AND GAS-CHROMATOGRAPHIC DETERMINATION OF POLYNUCLEAR  
HYDROCARBONS IN DUST ( $\mu/\mu\text{g}$ )

No.	Components	$V_R(200^\circ)$	Sample A		Sample B		Sample C	
			GLC	SPCT	GLC	SPCT	GLC	SPCT
1	—	0.16						
2	—	0.19						
3	—	0.22						
4	Fluoranthene	0.31	115	126	76	60	32	46
5	Pyrene	0.36	114	130.4	78	70.5	37	49.6
6	—	0.45						
7	1:2-Benzofluorene	0.48	Trace	—	Trace	—	Trace	—
8	1-Methylpyrene + 3-methylpyrene	0.54	70	—	80	—	50	—
9	—	0.68						
10	—	0.73						
11	—	0.77						
12	Benzo[ghi]fluoranthene	0.82	Trace	—	Trace	—	Trace	—
13	1:2-Benzanthracene	0.98	620	133.2	410	134.9	315	80
14	Chrysene	1.00						
15	—	1.09						
16	—	1.18						
17	—	1.29						
18	—	1.50						
19	—	1.76						
20	2:3-Benzofluoranthene	2.63	364	—	277	—	313	—
21	3:4-Benzopyrene + 1:2-benzo- pyrene	3.10	282	241.5	245	262.3	205	181.2
22	Perylene	3.21	202	—	122	—	135	—
23	1,3,5-Triphenylbenzene	4.15						
24	1:12-Benzoperylene	5.92		49.6		58.3		41.3
		(230°)						
25	Coronene	15.5		10.4		10.8		9.5
		(230°)						

#### Analysis of the cyclohexane fraction

The cyclohexane fraction has been analysed by gas chromatography under the same working conditions, and a typical chromatogram of this fraction is shown in Fig. 2. In order to identify these peaks, a series of alkanes ( $C_{18}, C_{20}, C_{24}, C_{28}$ ) was chromatographed and the plot of the logarithm of the relative retention volume *versus* number of carbon atoms yielded a straight line. The retention volumes due to peaks of the cyclohexane fractions reported in Table III, fall on this line and correspond to alkanes from  $C_{18}$  to  $C_{30}$ , with even and uneven number of carbon atoms. These compounds seem to be normal components of the urban dust as have been found in most samples. As alkanes have been identified in cigarette smoke<sup>4</sup> and in coal tar<sup>6</sup> their presence in the dust might be attributed to these sources.

#### DISCUSSION

The method which has been suggested, consisting of a gas chromatographic determination of a cyclohexane extract preceded by an extraction of hydrophilic compounds, seems to be quite reliable for the determination of polynuclear hydrocarbons in air.

TABLE III  
RELATIVE RETENTION VOLUMES OF NORMAL PARAFFINS FROM DUST EXTRACT,  
CYCLOHEXANE FRACTION

<i>Fraction</i>	$V_R$	<i>Fraction</i>	$V_R$
C <sub>18</sub>	0.13	C <sub>25</sub>	1.50
C <sub>19</sub>	0.19	C <sub>26</sub>	2.08
C <sub>20</sub>	0.26	C <sub>27</sub>	2.90
C <sub>21</sub>	0.37	C <sub>28</sub>	4.00
C <sub>22</sub>	0.55	C <sub>29</sub>	5.50
C <sub>23</sub>	0.73	C <sub>30</sub>	8.05
C <sub>24</sub>	1.00		

The recovery of the polycyclic hydrocarbons from the dust is practically quantitative and a complete separation is achieved between the aliphatic and the aromatic fraction. Previous experiments performed using a short alumina column to isolate the polynuclear hydrocarbons from the dust extract did not yield satisfactory results since the high boiling alkanes were eluted together with some polynuclear hydrocarbons; the procedure moreover was time consuming.

The gas chromatographic procedure in comparison with the column adsorption-spectrophotometric method has the limitation that some pairs of hydrocarbons are not separated and yield a single elution peak. They are 1-methylpyrene and 3-methylpyrene, 1:2-benzanthracene and chrysene, 3:4-benzopyrene and 1:2-benzopyrene.

It should be pointed out, however, that by changing the liquid phase (as observed using an Apiezon column) some of these components can be separated.

It seems therefore that by carrying out a gas chromatographic analysis with two liquid phases, such as Silicone rubber S.E. 30 and Apiezon, a complete picture of the composition of polynuclear hydrocarbons in dust should be obtained.

It is convenient to perform the analysis of the nitromethane fraction at two temperatures, 200° and 230°. The use of a higher working temperature is required for the elution of compounds such as coronene; at this temperature the elution of the higher boiling components is rendered easier but a poor resolution for the hydrocarbons which boil at a lower temperature is obtained.

When enough information is available on the retention volumes of various hydrocarbons, chromatograms with programmed temperature can be performed with considerable success.

The agreement between the gas chromatographic and the spectrophotometric methods is fair with some hydrocarbons but not too satisfactory with others. Since both methods present some limitations, an extensive comparative investigation seems desirable.

At present the method which has been developed offers two main advantages: a high speed of analysis and the possibility of realizing a clear separation for various components. The time of analysis of the nitromethane fraction of the dust is less than two hours and might be shortened by carrying out the gas chromatogram at a programmed temperature.

The determination of polynuclear hydrocarbons may become a routine measurement, carried out by non-technical personnel. An interesting feature of the method is

the possibility of detecting and identifying other polycyclic hydrocarbons possibly present in the atmosphere and of following the probable changes. An extensive application of this method might be of a noticeable help in increasing our knowledge of the components of urban airborne particles.

#### SUMMARY

The gas chromatographic separation of polynuclear and paraffinic hydrocarbons is reported. A procedure for their separation from dust samples is described. The gas chromatographic results are compared with the spectrophotometric data, and the advantages and the limitations of both methods are discussed.

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