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POLAR ORGANIC FRACTION OF AIR PARTICULATE MATTER

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SUMMARY

Air particulate matter collected on glass-fibre filters was extracted with dichloromethane and subsequently with methanol. The methanol extract was derivatized and analysed by capillary-column gas chromatography and gas chromatography–mass spectrometry. About 20 components, mostly polyols, were identified. It is speculated that these polyols originate through microbiological action in the atmosphere.

INTRODUCTION

Most studies on the organic fraction of air particulate matter have been devoted to qualitative and quantitative aspects of the apolar or hydrocarbon fraction. The polynuclear aromatic hydrocarbons (PAHs) and specifically the benzopyrenes have attracted much attention because they are carcinogenic. The isolation of this apolar fraction involves the collection of the air particulate matter on a filter and extraction of the filter with a solvent such as benzene or cyclohexane. The yield of this (apolar) fraction is usually 10–15% of the total suspended particulates (TSP) collected.

Studies on the extraction efficiency of different solvents or solvent combinations was carried out by Stanley *et al.*[1], who found that up to 30% of the TSP can be extracted. The composition of the extractable material will therefore roughly be 1:1 polar–apolar. We separated these two fractions by successive extractions of the collection filters with dichloromethane and methanol, and this paper is concerned with the chemical composition of the polar (methanol-extractable) fraction. A rapid heat desorption procedure for the semi-quantitative analysis of the apolar fraction of TSP is published[2].

EXPERIMENTAL

Sampling

TSP was collected during 24 h on the roof of the laboratory by filtering air

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through Whatman GF/A 11-cm glass-fibre filters with a Becker DT 25 high-volume sampler pump with a capacity of 15 m^3/h.

The filters were previously heated at 300° and tested for their suitability in a test gas chromatographic (GC) run.

Extraction of the filters

To prevent the concentration of solvent impurities on evaporation, it is essential to carry out the extraction with a minimum volume of solvent. This was achieved by using an elongated beaker with a coarse sintered-glass filter bottom to hold the TSP collection filter, hanging it above the boiling solvent and under the reflux condenser. The extraction temperature is then the boiling point of the solvent and only a small volume (*ca.* 25 ml) of solvent is needed.

The 11-cm diameter filter with the collected TSP is rolled into a cigarette shape and placed in the filter beaker, which is placed in a pear-shaped flask with a capacity of 100 ml containing 25 ml of the extraction solvent. Heat is applied with an oil-bath (100°) and passage of a slow stream of nitrogen through a capillary ensures easy boiling and prevents oxidation.

It was ascertained experimentally that vigorous operation of the above set-up for 6 h leads to virtually complete extraction.

The filters were extracted in this manner first with dichloromethane and then with methanol. Methanol also extracts inorganic material, mainly sulphates and nitrates, which partly crystallize out and can be removed by filtration.

The clear, brown methanol extract is evaporated and further dried in an oven at 70° until the weight remains constant. The yield of the polar organic fraction is 10–15% of the weight of TSP.

Derivatization of the polar fraction of TSP

The methanol extract cannot be gas chromatographed as such and has to be derivatized.

Silylation was carried out with N,N-bistrimethylsilyltrifluoroacetamide (BSTFA) (50 μl of reagent for 1 mg of extract) for 30 min at 70°. Excess of reagent was removed with a stream of nitrogen before GC. The procedure was repeated until the chromatogram showed no further changes.

Methylation according to the usual procedures was tried but without success. Good results were obtained by the method of Hakomori[3]:

$$CH_3\text{–}SOCH_3 + NaH \rightarrow CH_3\text{–}SOCH_2^- Na^+ + H_2$$
$$CH_3\text{–}SOCH_2^- + ROH + CH_3I \rightarrow ROCH_3 + I^- + CH_3\text{–}SOCH_3$$

Dimethyl sulphoxide and sodium hydride were made to react under nitrogen at 50–60°. Excess of methyl iodide is necessary in order to neutralise unreacted base. The reaction mixture was diluted with water and extracted with chloroform, which was then dried and evaporated.

Chromatography and spectrometry

All separations were obtained by glass capillary gas chromatography or (GC)[2].

following previously described procedure[4]. The chromatograph was a Varian 1400 with a flame-ionization detector.

Identification by means of GC combined with mass spectrometry (GC–MS) is routinely carried out in the helium–charge exchange (He–CE) and normal chemical ionization (CI) modes. The He–CE spectra are identical with the ones obtained by electron impact (EI) and lead to typical fragmentation patterns. The CI spectra normally give the molecular weight through the quasi-molecular ions. This combination allows the identification of many compounds.

Mass spectra were obtained with a Finnigan 3200 quadrupole spectrometer in the above modes. The spectra were manipulated with a Finnigan 6000 data system.

RESULTS AND DISCUSSION

The $(GC)^2$ trace of the silylated extract is shown in Fig. 1. This promising chromatogram did not lead to expected results, as the trimethylsilyl ethers of the compounds under discussion do not give molecular ions, even with isobutane as the reaction gas. Only two peaks could be identified through the spectral patterns and by comparison with literature data: treitol (peak 1) and inositol (peak 2). This identification was confirmed by co-chromatography of authentic reference compounds. The other peaks give mass spectra similar to those of peaks 1 and 2.

Methylation as described above gave better results. The GC and MS techniques were optimized by using meso-inositol as the reference compound. The

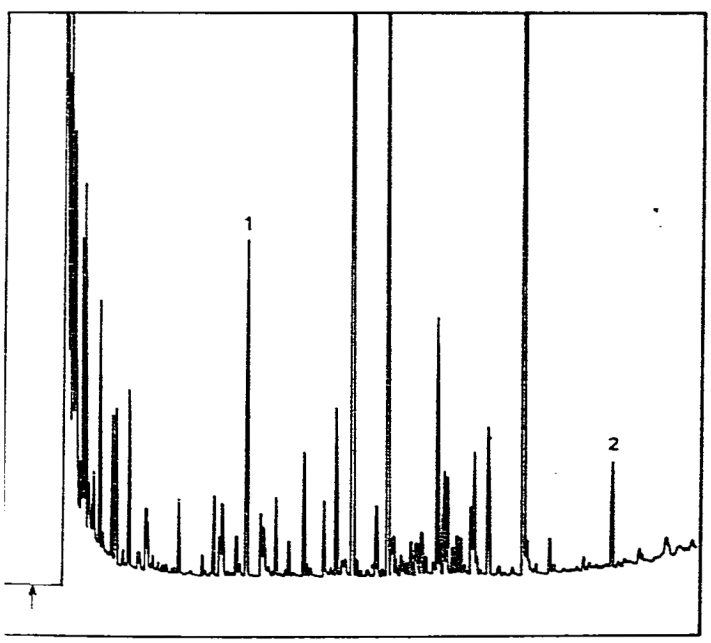


Fig. 1. Gas chromatogram of the silylated polar fraction of particles collected from air. Glass capillary column (50 m × 0.5 mm) coated statically with a 0.6-μm layer of SE-30. Injector at 240°, detector at 230°. Programmed from 120° to 230° at 2°/min. Carrier gas (hydrogen) flow-rate, 5 ml/min. Chart paper speed, 0.5 cm/min. Total time, 50 min. Sensitivity of Varian 1400 chromatograph, 10^{-11}. Peaks: 1 = treitol; 2 = inositol.

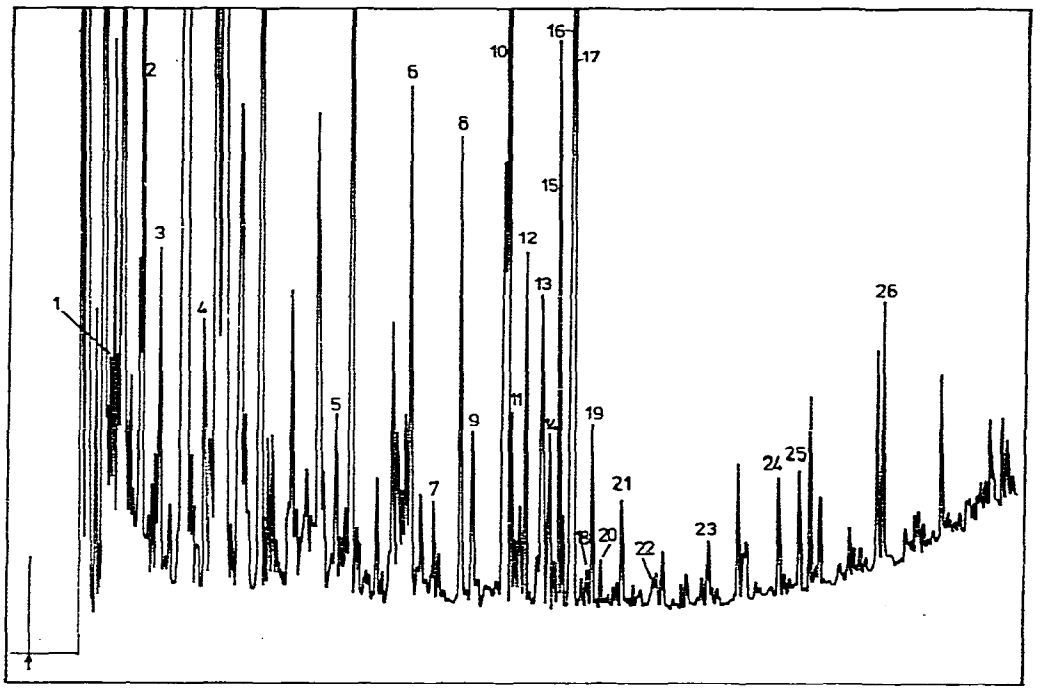


Fig. 2. Gas chromatogram of the methylated polar fraction of particles collected from air. Soda-glass capillary column (90 m × 0.5 mm) coated statically with a 0.6-μm layer of SE-30. Injector at 240°, detector at 230°. Programmed from 80° to 230° at 2°/min. Carrier gas (hydrogen) flow-rate, 5 ml/min. Chart speed, 0.5 cm/min. Total time, 75 min. Peak numbers as in Table I.

trace of the permethylated extract is shown in Fig. 2. The chromatogram up to about peak 5 is contaminated by large peaks of side reaction products from the dimethyl sulphoxide, which can also be (hexa)methylated. Nevertheless, a large number of the other peaks could be identified. A list of compounds identified is presented in Table I; the numbers correspond to the numbers on the chromatogram.

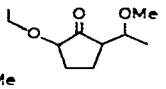
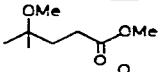
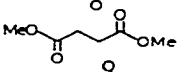
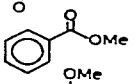
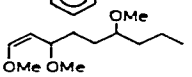
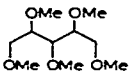
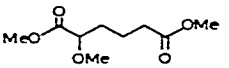
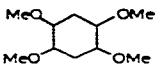
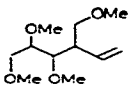
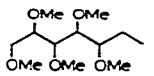
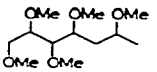
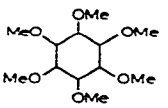
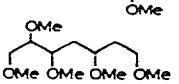
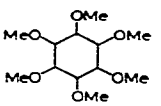
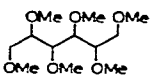
Peaks marked with one asterisk in Table I were only tentatively identified. A double asterisk indicates that the MS pattern was clearly correlated with the proposed structure, according to MS theory and as described in refs. 5–8. A triple asterisk indicates that the mass spectra correspond fully with published reference spectra. A more detailed description of the MS data would lengthen this paper needlessly; further information on particular spectra can be obtained from the author.

The main point of interest in Table I is that most of the compounds in the polar fraction are polyols. It is probable that the unidentified compounds above peak 6 in Fig. 2 are similar in nature. The origin of these polyols is not clear. Photochemical or microbiological processes on primary compounds emitted in the atmosphere do not seem evident. Photochemical degradation of hydrocarbons in the gas phase does not lead to polyols but mostly to lactones[9]. Polyols are found in soil, supposedly as the reaction products of the microbiological degradation of alkanes. The reaction pathway is not clear as microbiological degradation is mostly represented as a β-oxidation leading to acids. The literature does not mention mechanisms for

TABLE I

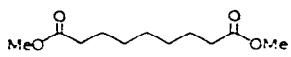
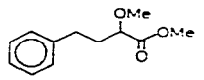
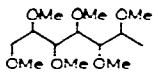
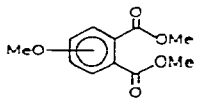
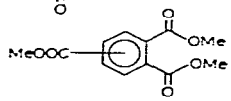
COMPOUNDS IDENTIFIED IN THE METHYLATED FRACTION

Me = Methyl.

Product	*Structure*	*Name*	*Identification (see text)*
1		2-Ethoxy-5-(1-methoxymethyl)-cyclopentanone	*
2		4-Methyl-4-methoxymethyl valerate	**
3		Dimethyl succinate	***
4		Methyl benzoate	***
5		1,3,6-Trimethoxy-1-nonene	*
6		1,2,3,4,5-Pentamethoxypentane	**
7		2-Methoxydimethyl adipate	**
8		1,2,4,5-Tetramethoxycyclohexane	**
9		3-Methoxymethyl-4,5,6-tri-methoxy-1-hexene	*
10		Methylated polyol	—
11		1,2,3,4,5-Pentamethoxyheptane	*
12		1,2,3,4,6-Pentamethoxyheptane	*
13		Hexamethoxycyclohexane	**
14		1,2,3,5,7-Pentamethoxyheptane	*
15		Hexamethoxycyclohexane	***
16		Hexamethoxyhexane	***
17	—	Methylated polyol	—
18	$C_{11}H_{23}COOMe$	Methyl dodecanoate	***

(Continued on p. 138)

TABLE I *(continued)*

Product	*Structure*	*Name*	*Identification (see text)*
19		Dimethyl azelate	***
20		2-Methoxy-4-phenylmethyl-butyrate	**
21		1,2,3,4,5,6-Hexamethoxyheptane	*
22	—	Isomeric with 21	*
23		3-Methoxydimethylphthalate	**
24		Benzenetricarboxylic acid trimethyl ester	**
25	—	Isomeric with 24	**
26	$C_{15}H_{31}COOMe$	Methyl palmitate	***

microbiological polyol formation. In favour of microbiological intervention is the fact that the *n*-alkanes most abundant in the apolar TSP fraction are in C_{18}–C_{34} range. These higher alkanes are known to be much more resistant than lower alkanes to microbiological attack. The volatility of the lower alkanes must also be considered, however, in addition to the Gaussian distribution curve for the C_{18}–C_{34} alkanes, peaking at C_{22}–C_{25}. This needs to be explained.

Whether microbiological activity is important in air particulates is still an open question. Much research has been carried out on the effect of pollutants on air microorganisms[10] but the possible reverse effect has hitherto escaped attention.

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