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QUALITATIVE AND SEMI-QUANTITATIVE ANALYSIS OF THE NON-POLAR ORGANIC FRACTION OF AIR PARTICULATE MATTER

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SUMMARY

A simple method is presented for the rapid analysis of the non-polar organic fraction of air particulate matter (quality control of air). The method is based on heat desorption of the volatile organic material directly in the injector of a gas chromatograph, followed by separation of the compounds on a high-resolution glass capillary gas chromatographic column. Complete analysis can be performed in as little as 5 h.

INTRODUCTION

Although the organic fraction of air particulate matter (aerosols) is smaller than the inorganic fraction, it is important because of the presence of carcinogenic polynuclear aromatic hydrocarbons (PAHs). The currently popular analytical method is based on a minimum of 24 h aerosol collection on a paper or a glass fibre filter and Soxhlet extraction, which also takes *ca.* 24 h to be quantitative. Fractionation of the extract on thin layers is often necessary. These methods are lengthy and cannot pinpoint an emission source of short duration. There is also no solvent capable of extracting all organic material in one step. The extraction efficiency of solvents is very variable, and instances where in 6 h 90% is extracted by one solvent and only 50% by another have been described[1,2]. Also, it is never certain that all material has been extracted, and errors can easily be introduced because of solvent contamination. Many solvents are extremely hard to obtain absolutely pure and always leave a small residue, especially on evaporation of the large volumes necessary for Soxhlet extraction.

An alternative method is heat desorption of the volatiles coupled to gas chromatographic (GC) analysis.

EXPERIMENTAL

Sampling

Samples were collected on the roof of the laboratory. A high volume sampler with a Becker DT 25 pump with a capacity of 15 m^3/h was fitted with circular glass

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fibre filters (Whatman GF/A) of 11 cm diameter. The filters were first purified by heating overnight at 350° and were tested in blank runs.

Preparation of samples

The total suspended particulates (TSP) collected are determined by weighing before and after the collection period. Before weighing, the filters are dried in a $CaCl_2$-filled desiccator and then equilibrated for 10 min in the weighing room atmosphere. The unused outer ring of the filter is cut off and the remainder is weighed again. A strip of this filter, the size of which depends on the amount of TSP, is cut out with clean scissors for analysis. Weighing indicates exactly what fraction of the filter has been cut for subsequent semi-quantitative analysis.

Analysis

The piece of filter strip with air particulate matter is introduced in a glass injector insert[3] with an I.D. of 2.5 mm. For quantitative analysis 1 μl of a dichloromethane solution of squalane (20 ng/μl) is spotted on the filter strip. The injector insert is placed in the heated injector block and connected with Teflon shrinking tubing to a capillary column mounted in the cool oven. With some practice this takes only *ca.* 30 sec. The gas flow, which was initially set at the desired rate, is cut off during this operation. The gas flow cut-off valve is reopened and 5 min are allowed for the removal of all volatiles from the strip to the head of the column. The oven temperature is then brought quickly to 160° and then programmed at 2°/min to 225°. A schematic drawing of the arrangement described is shown in Fig. 1.

Gas chromatography

The GC analysis was optimised by using different capillary columns, *e.g.* Pyrex and soda-lime glass columns with different internal diameters, with and without deactivation and with a film thickness ranging from 0.1 to 1 μm.

SE-30 was always used as the stationary phase but significant differences in polarity were observed; the film thickness of the stationary phase is the most sensitive parameter in this respect.

The best results, especially for quantitative analysis, were achieved on columns of 30 m length, 0.4–0.6 mm I.D., coated statically[4] with an SE-30 film of thickness 0.5–0.6 μm. The polyaromatics benzo[*e*]pyrene (B*e*P) and benzo[*a*]pyrene (B*a*P) are then separated from the added squalane standard. With stationary films of thickness 0.1–0.4 μm the polyaromatics elute relatively faster than the hydrocarbons and B*e*P or B*a*P can overlap with squalane (retention shifting in the direction of hexacosane).

A film thickness of 0.7–1 μm retards the PAHs, which then elute together or after heptacosane. With a film thickness of 0.9 μm, squalane cannot be used as internal standard because it overlaps with benzo[*k*]fluoranthene (peak number 16).

The resolution of B*e*P and B*a*P is not improved by using narrow-bore capillary columns, owing to the heat desorption injection. With normal injection techniques, *e.g.* solid-state injector, even sharper separations than the ones shown in the figures are possible. Other GC details are: injector temperature, 350°; hydrogen flow-rate 4 ml/min; Varian Model 3700 chromatograph (equipped with a flame ionization detector, FID) with sensitivity setting at $4 \cdot 10^{-11}$.

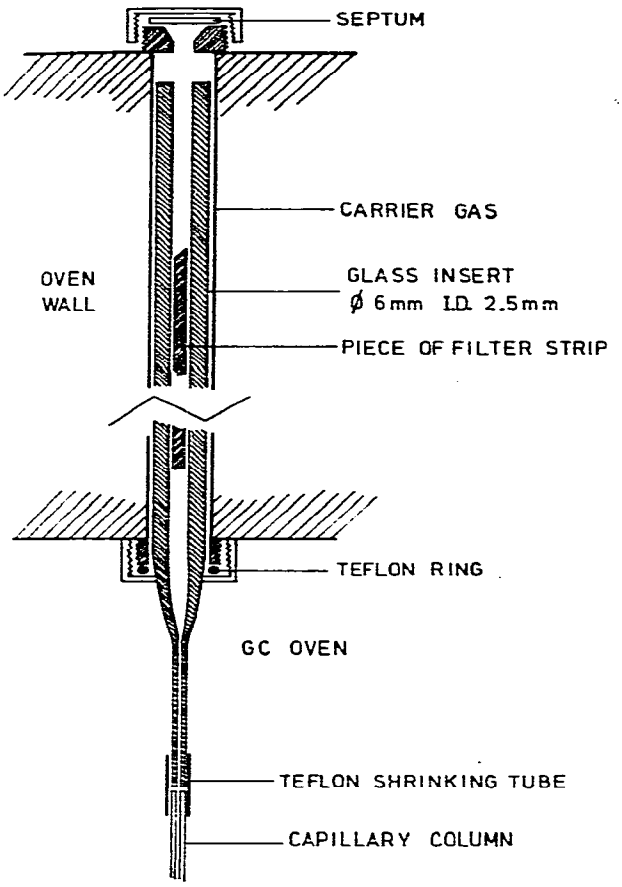

Fig. 1. Glass insert with collection filter-strip shown in final position in the Varian Model 3700 gas chromatograph.

Semi-quantitative analysis

Quantitation of B*a*P was obtained by comparison of peak areas with the standard squalane peak (20 ng). The response of the FID signal for squalane and B*a*P is practically the same as was ascertained experimentally (0.98).

RESULTS AND DISCUSSION

Comparison with extraction

A 24 h collection filter was cut into strips. The major portion was extracted with methylene chloride for 24 h and a small part used as described above. The extraction analysis is shown in Fig. 2B, and Fig. 2A shows the results of the heat desorption method for the same filter. The two results are practically identical, but the heat desorption method is much faster and it can be carried out with a very small sample. The same filter can also be used for several analyses.

Depending on the origin of the air particulate matter, the matrix dust may be a stronger adsorbent than in our case and then thermal desorption may present

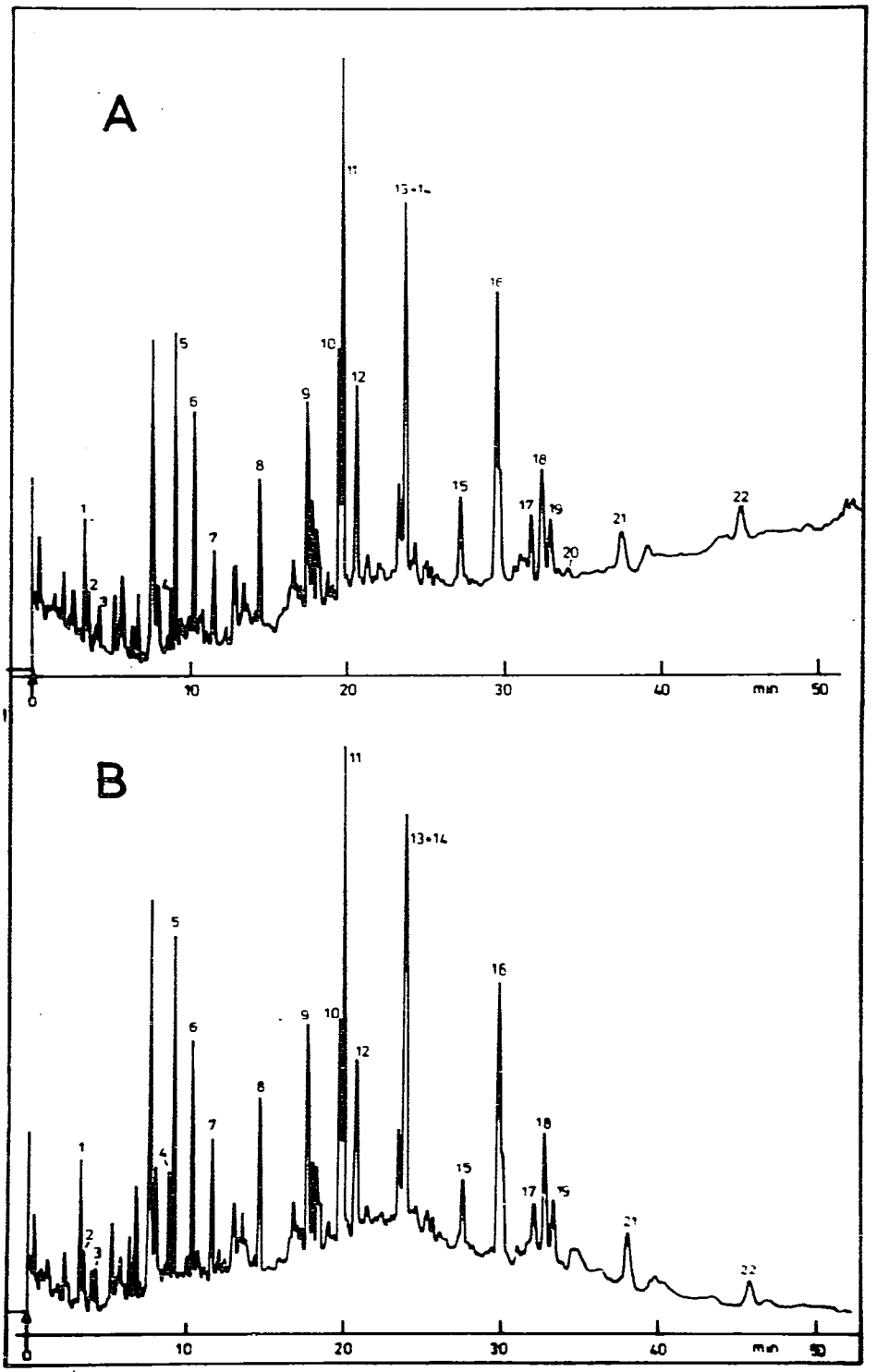

Fig. 2. Comparison of (B) extraction and (A) heat desorption. Column 30 m × 0.6 mm I.D.; SE 30. d_F = 0.9 μm. Peaks: 1 = phenanthrene; 2 = anthracene; 3 = n-C_{18}; 4 = n-C_{20}; 5 = fluoranthene; 6 = pyrene; 7 = n-C_{21}; 8 = n-C_{22}; 9 = n-C_{23}; 10 = benz[a]anthracene; 11 = chrysene; 12 = n-C_{24}; 13 = n-C_{25}; 14 = diethylhexylphthalate; 15 = n-C_{26}; 16 = benzo[k]fluoranthene; 17 = n-C_{27}; 18 = benzo[e]pyrene; 19 = benzo[a]pyrene; 20 = perylene; 21 = n-C_{28}; 22 = n-C_{29}.

difficulties. There is no proof for this, but the possibility must be kept in mind. Checking against extraction results is therefore recommended.

The possibility of contamination is much smaller with the heat desorption method than with procedures based on extraction, but precautions must still be taken. The filters should be heated overnight at 350° just before use. Keeping them in envelopes in a laboratory drawer led to contamination by dibutyl phthalate and by a range of hydrocarbons from C_{17} to C_{30}. The same hydrocarbons are found in air particulate matter. The source of these contaminations is unknown.

Another contamination source at the start of our research was the filter support in the high volume sampler, which was made of plastic and had thus to be replaced by a metal support. Filters should be touched only with metal tweezers and scissors, because human skin excretes large amounts of squalene (concentrations up to 500 ng were detected) which are adsorbed on the filter paper: the concentration of squalene in skin is *ca.* 475 μg/g dry weight[5].

Normally a filter strip of 2 mm × 4.5 cm (1.5–2% of the total filter) is introduced in the injector insert. However, larger portions can be used if they are folded. This needs practice, and it is better to use an insert of at least 3 mm I.D. If wide-bore capillary columns are used the separation efficiency is not affected. In this way 10% of a filter can be analysed, which is of help in detecting emission sources of short duration.

Reproducibility of the heat desorption method

A test mixture was spotted eight times on a piece of a blank glass fibre filter which was analysed by heat desorption as described above. The heights of different peaks were compared and the reproducibility was shown to be good. Reproducibility on actual filter samples is equally good, as shown by the results discussed in the next paragraph. Fig. 3 shows the quantitative analysis of the polyaromatic B*a*P in air particulates collected in March 1977. For profiling the sample, a first run was done with *ca.* 1/50 of a 4 h collection filter. For quantitation, 1/44 of the filter was analysed on a soda-lime column and the concentration of B*a*P was found to be 6.30 ng per m^3 air (detail A in Fig. 3). Next, 1/69 of the same filter was analysed on a Pyrex capillary column. In this case the B*a*P concentration was 6.23 ng per m^3 air. Note the shift of peaks 17, 18 and 19 in Fig. 3 compared with Fig. 2 (film thickness difference).

Homogeneity of the particulate deposit on the filter

As the analysis uses only part of a collection filter it is necessary to ensure that the filter is covered homogeneously by particulates. For this determination a 24 h collection filter was cut twice diagonally, and four strips of about 1.5–2 mm width and 5 cm long (half the diameter) were cut from each quarter. The strips represent about 1 cm^2 or 1/70 of the total filter. Analysis of the strips gave results completely in accord with Fig. 3. A comparison of the heights of different peaks is shown in Table I. The last two column present the mean value and the standard deviation. The results show that the homogeneity is satisfactory and that complete analysis can be carried out on 1/70 of a 24 h collection filter.

Identification of compounds

Most of the components in the chromatograms have been described before

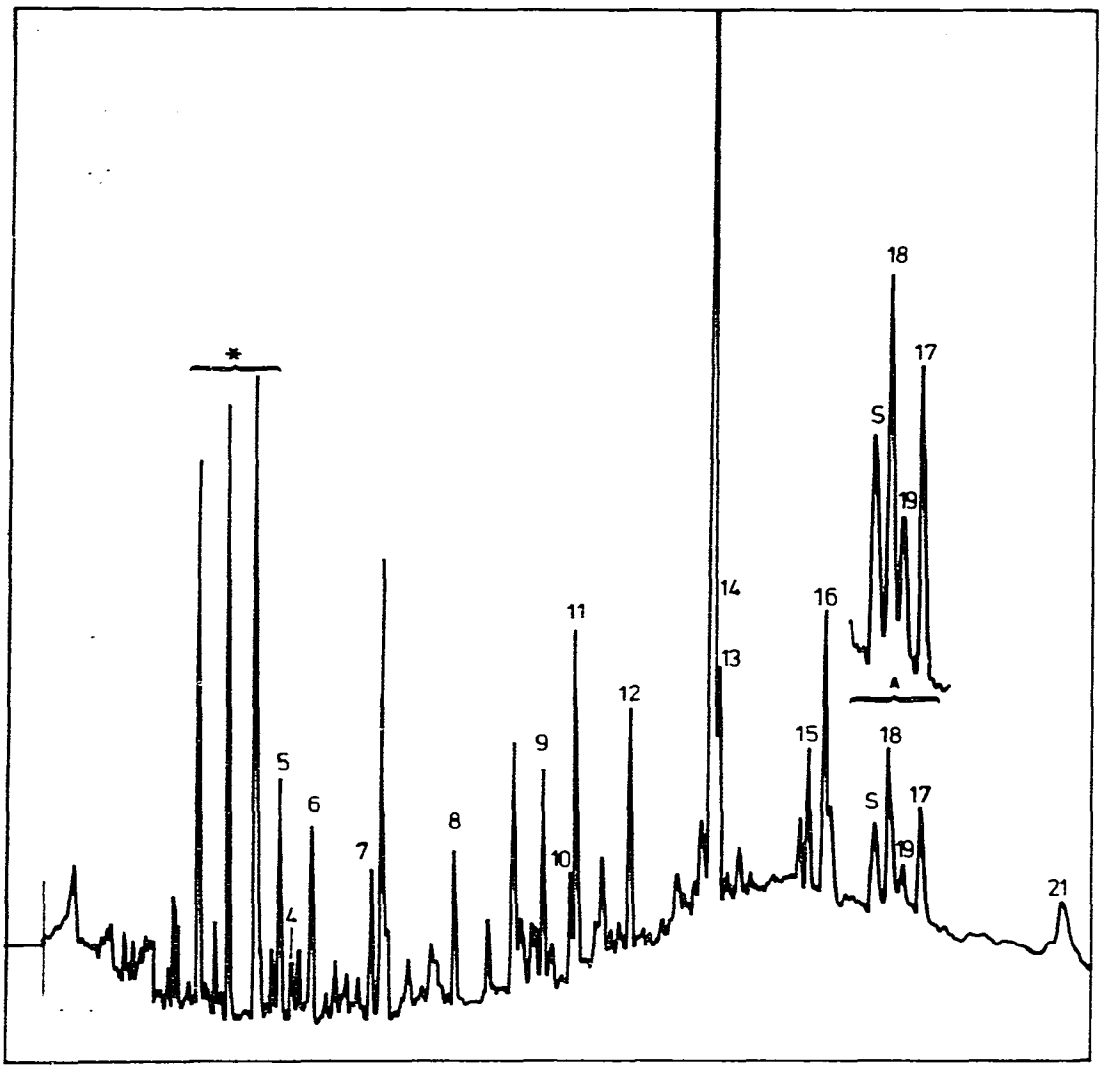

Fig. 3. Semi-quantitative analysis of benzo[*a*]pyrene. Column 30 m × 0.4 mm I.D.; SE-30, d_f = 0.6 μm. Peaks as in Fig. 2. S, squalane internal standard; A, detail used for semi-quantitative analysis; *, contamination peaks of laboratory drawer.

TABLE I

HOMOGENEITY OF PARTICULATE DEPOSIT ON FILTER

Peak	*Run*				$\bar{G}$	$\bar{S}$	%
	1	*2*	*3*	*4*			
5/4	2.46	2.42	2.88	2.57	2.58	0.21	8.07
6/5	0.77	0.79	0.83	0.79	0.79	0.025	3.17
6/7	1.50	1.46	1.57	1.84	1.59	0.17	10.76
8/10	1.06	1.09	—	1.07	1.08	0.022	2.05
8/12	1.17	1.12	—	1.04	1.11	0.07	5.9
11/10	1.87	1.88	—	—	1.88	0.01	0.38
12/15	1.63	1.77	—	1.93	1.78	0.15	8.43
18/19	2.24	2.59	2.33	2.52	2.42	0.16	6.72
21/19	1.32	1.26	1.29	1.21	1.27	0.047	3.69

in the literature. We have used GC–mass spectrometry for confirmation and identification. Details of this work and new results in this field are reported[6].

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