CHROMSYMP. 200

INSTRUMENT FOR POLYCYCLIC AROMATIC HYDROCARBON ANALYSIS OF AIRBORNE PARTICLES BY CAPILLARY GAS CHROMATOGRAPHY WITH LASER-INDUCED FLUORESCENCE DETECTION

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SUMMARY

The proposed method is based on the idea that by combining thermal desorption injection, capillary chromatographic separation and fluorescence detection, the pre-treatment (extraction and clean-up) normally preceding gas chromatographic analysis of particulate polycyclic aromatic hydrocarbons can be omitted without sacrificing too much in terms of detectability and resolution. The advantages of the method are that only a small volume of air is necessary, as most of the sample can be injected in the same analysis, and that the time and cost per analysis are reduced. This allows measurements with good resolution in time and space as well as the use of small, light-weights sampling equipment, *e.g.*, for use in exposure studies in factories.

INTRODUCTION

In conventional gas chromatographic (GC) analysis of polycyclic aromatic hydrocarbons (PAHs), a time-consuming and elaborate pre-treatment of the samples is often necessary because of the complexity of the sample. This is a drawback, making it difficult to perform more extensive mappings of PAH profiles in time and space. By using a PAH-selective detector, this problem may be circumvented. Fluorescence is a semi-selective detector for PAHs, and such a detector has been used for this purpose by Burchfield *et al.*[1]. In their work as well as in that of others[2–4], where gas-phase fluorescence was used for the detection of PAHs, a conventional UV lamp was the excitation source. By using a laser as the source of the excitation the small cell size necessary for capillary chromatography can be used without sacrificing sensitivity and thus, allows better chromatographic resolution.

Sample injection is performed by thermal desorption, giving a good yield and sample economy (up to 50% of the sample may be injected at one time). This allows the use of small sampling volumes (1–100 l) and thus simplifies the sampling process, *e.g.*, in portable sampling equipment for exposure studies in the workplace.

EXPERIMENTAL

A schematic diagram of the experimental set-up is shown in Fig. 1.
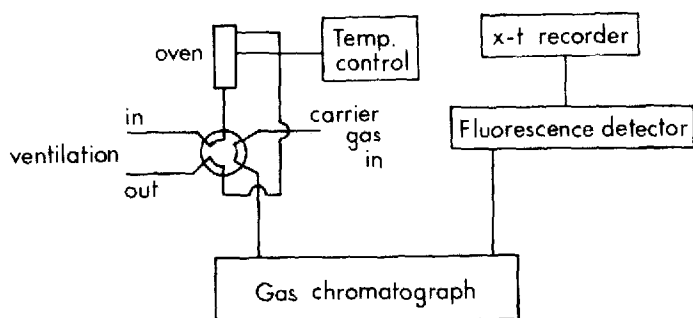
Fig. 1. Experimental set-up.

The sample is collected on a 37 mm diameter glass-fibre filter. About 25 % of the filter is cut out, inserted into the oven and thermally desorbed in an inert atmosphere (nitrogen) at 400°C for 10 min. The cut is made in the form of a sector in order to obtain a representative piece of the filter. The desorbed components are transported by the carrier gas (nitrogen, 3 ml/min) to the column (SE-54, fused silica, 200 μm, 25 m), where they are condensed at room temperature. The various hydrocarbons are separated on the column by temperature-programmed GC (40 to 120°C in 4 min, then up to 285°C at 5°C/min) and passed into the gas-phase fluorescence detector. A schematic diagram of the detector is given in Fig. 2.
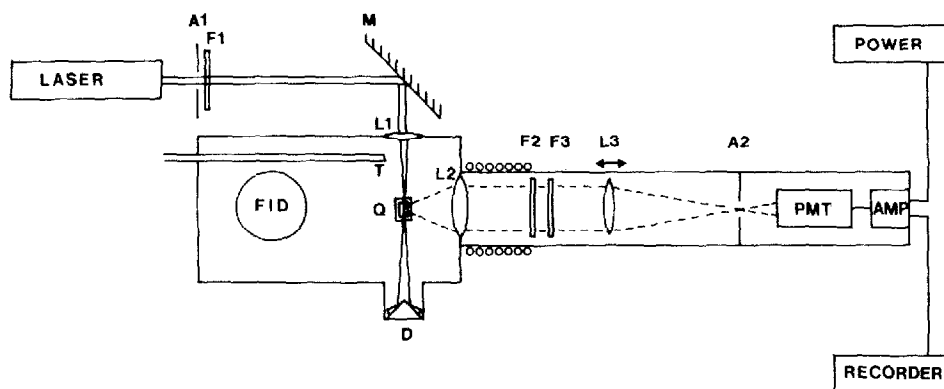

Fig. 2. The fluorescence detector.

The column is connected to a heated 4-μl flow-through quartz cell. Light from a He–Cd laser (Liconix 4110 HuV, 325 nm, 1 mW) is filtered and then focused in the cell with the mirror, M. Fluorescent light is collected at right-angles to the excitation beam with lens L2 ($f = 25$ mm, diameter 1 in.). After filtering, an image of the cell is produced by L3 at the adjustable aperture, A2. With this arrangement, scattered and fluorescent light from the walls of the cell is kept away from the light flux reaching the photomultiplier tube (PMT) (Hamamatsu R268). After amplification, the current from the PMT is fed to a strip-chart recorder.

In an attempt to optimize the filtration of the fluorescent light and to investigate the possibility of discriminating between peaks with similar retention times, gas-phase fluorescence spectra of 16 PAHs were recorded by a procedure similar to that used by Cooney et al.[2], in which the PMT is replaced by an optical multi-channel analyser (OMA)(Tracor Northern TNIDARSS).

In this instrument, a recording is made of the complete spectra of the incoming light. The recording is made simultaneously at all wavelengths and stored in a multi-channel memory (256 channels, 1.9 nm resolution) as a mean exposure during an operator-selected time interval. Because the retention times in the GC system for the PAHs are known, it was possible to "freeze" the spectra of different PAHs as they were emerging from the flow-through cell.

RESULTS

Two questions of major concern about the usefulness of the method are the detectability of different PAHs when excited at 325 nm and the interferences caused by other fluorescing compounds. Another problem that needs to be investigated is the possibility of chemical reactions on the filter during the thermal desorption.

The detectability was investigated by applying known amounts of standard solutions containing 28 different PAHs on to filter pieces that were analysed. These PAHs are listed in Table I; those marked + had a fluorescence yield stronger than 5% of the yield of fluoranthene.

Table I shows that 88% of the compounds with retention times longer than that of fluoranthene have a suitable response. It can also be seen that the detector has a very poor response to benzo[cd]pyrenone. This is interesting as this compound is eluted from many columns at the same time as benzo[a]pyrene. The fluorescence spectra of the fluorescent compounds were recorded with the OMA and are presented in Fig. 3. These spectra are neither corrected for the spectral response of the OMA nor normalized, but can still serve as a guide to optimum filtration in the detector.

TABLE I

COMPOUNDS INVESTIGATED

| No.	Compound	Response	No.	Compound	Response
1	Acenaphtylene	—	15	9,10-Dimethylanthracene	+
2	Acenaphthene	—	16	Benzo[a]fluorene	+
3	Dibenzofuran	—	17	Benzo[b]fluorene	+
4	Fluorene	—	18	Benzo[a]anthracene	+
5	9-Methylfluorene	—	19	Triphenylene	—
6	Dibenzothiophene	—	20	Benzo[e]pyrene	+
7	Phenanthrene	—	21	Benzo[a]pyrene	+
8	Anthracene	+	22	Benzo[cd]pyrenone	—
9	Acridine	—	23	Perylene	+
10	Carbazolie	—	24	3-Methylcholanthrene	+
11	2-Methylanthracene	+	25	Dibenz[a,c]anthracene	+
12	1-Methylphenanthrene	—	26	Dibenz[a,h]anthracene	+
13	Fluoranthene	+	27	Benzo[ghi]perylene	+
14	Pyrene	+	28	Coronene	+
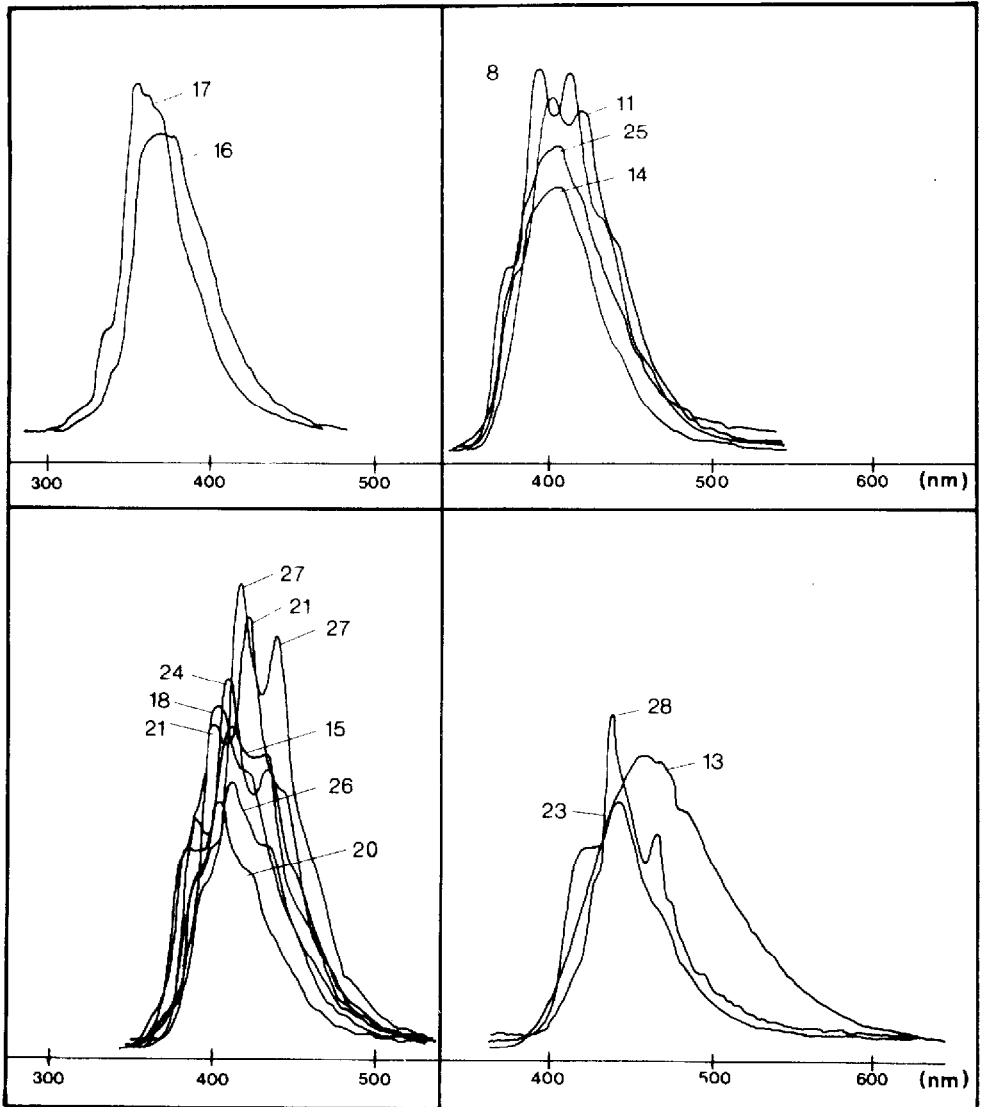
Fig. 3. Fluorescence spectra of 16 PAHs, grouped with respect to wavelength at emission maxima. Numbers refer to Table I.

In Fig. 4 a chromatogram obtained after injection of about 10 ng of each of the 28 PAHs in Table I is shown. Owing to laser problems, no detection limit experiments were performed, but the chromatogram in Fig. 4 indicates that a detection limit (signal-to-noise ratio = 1) of the order of 0.1–0.5 ng can be obtained, even under non-ideal conditions for most of the compounds.

In order to study possible artifacts and interferences with the proposed method, workplace samples were collected and analysed in parallel with conventional capillary GC techniques. In this technique the filters were Soxhlet extracted for 24 h with acetone.
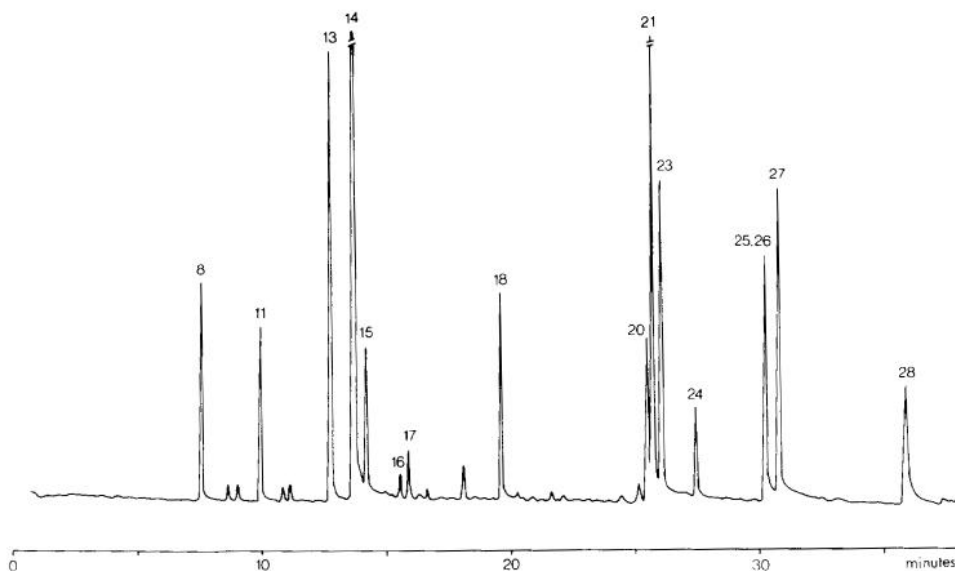
Fig. 4. Chromatogram showing the detector response to different PAHs. Numbers refer to Table I.

2-Methylanthracene and 1-methylpyrene were added as internal standards, and the extract was diluted with water and shaken with cyclohexane. The cyclohexane phase was then subjected to a liquid–liquid extraction with dimethylformamide (DMF)–water (9:1), and a subsequent back-extraction of PAHs from the DMF phase by addition of water and cyclohexane. After concentration, the cyclohexane phase was analysed on a Carlo Erba gas chromatograph with a glass capillary column (SE-54).
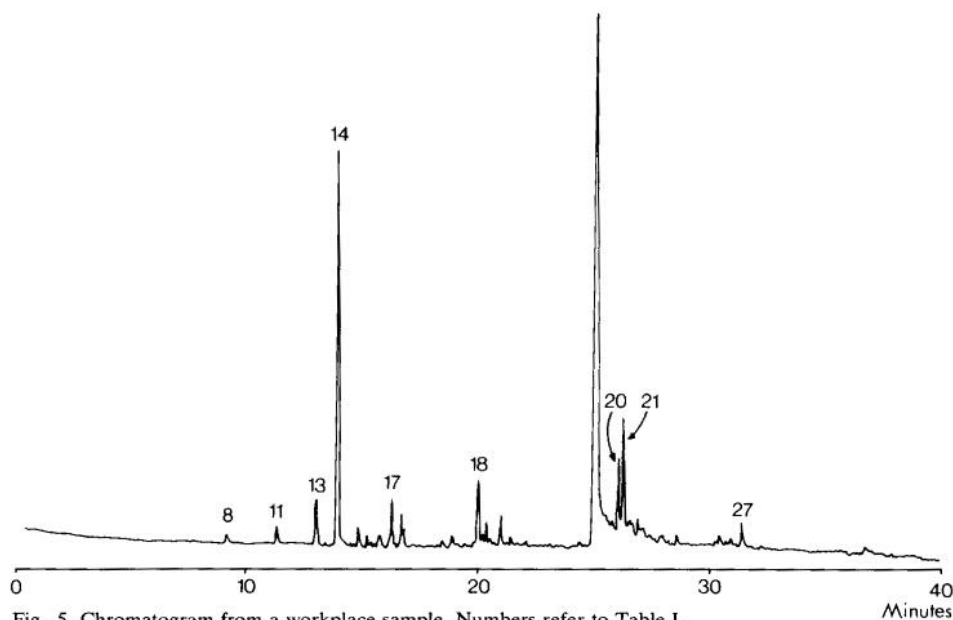

Fig. 5. Chromatogram from a workplace sample. Numbers refer to Table I.

A problem in the comparison was that the sensitivities of the two methods are different. Only the heavy loaded samples could be analysed with the conventional method. When these samples were analysed with the proposed method, it was necessary to excise and analyse not more than about 1% of the filter in order to avoid saturating the column. This was a large source of error in the comparison, but despite this, 75% of the peaks agreed to within ±25%. Occasionally, some peaks differed by up to 3.2 times, and one compound, benzo[b]fluorene, was systematically found in about 100 times higher concentrations with the proposed method. An interference from another fluorescent compound cannot be excluded.

Fig. 5 shows an example of the chromatogram of a typical workplace sample. This sample was collected at a graphite electrode plant, and the chromatogram corresponds to 34 l of sampled air, containing about 1–15 ng of the different compounds.

DISCUSSION

The method has been tested on only a few samples from a graphite electrode plant. Before any final conclusions can be drawn about the applicability of the instrument, it must be tested on far more samples from many different sources. However, the results obtained so far indicate that the method may be a useful complement to conventional analysis.

ACKNOWLEDGEMENTS

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