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GAS CHROMATOGRAPHIC METHOD FOR THE ANALYSIS OF MAJOR POLYNUCLEAR AROMATICS IN PARTICULATE MATTER

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SUMMARY

A chromatographic method has been developed and applied to the determination of polycyclic aromatic hydrocarbons (PAHs) present in sediments in the Rhondda Fawr Valley. The procedure involves Soxhlet extraction followed by a purification process including both column and thin-layer chromatography. Identification was achieved by fluorescence analysis coupled with gas–liquid or gas–solid chromatography. The quantitation of PAHs was made employing gas chromatography. The method enables the routine analysis of at least nine PAHs present in the environment. Good cross checks were obtained with gas chromatography–mass spectrometry.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are well known for their carcinogenic activity[1,2]. They can occur as very complex mixtures[3,4] and are wide-spread throughout the environment[5], being detected in trace quantities in a wide variety of matrices varying from foodstuffs[6,7] to sediments and soils[3,8,9]. Oils[10] and tars[11,12] also have been shown to be a source of PAHs. PAHs have also been detected in medicinal oils for pharmaceutical use[13].

It is recognised that the major route of PAHs into the atmosphere is via their formation during the partial combustion of organic matter[14]. A typical synthesis of 3,4-benzpyrene is by an initial pyrolysis in the 400°–750° range, resulting in the formation of smaller unstable molecules or radicals which react further to produce the more complex structures[15,16]. Thus emission of carcinogenic materials directly into the atmosphere gives cause for concern especially where fossil fuels are partially combusted[5].

Evidence is also available which indicates their indigenous formation in certain plants and micro-organisms[17,18].

PAHs belong to a most extensively studied group of compounds. Analytical procedures vary in complexity and many different clean-up techniques have been employed. Quantitation and identification has been effected by spectral and gas or liquid chromatographic techniques[3,19–24]. Capillary column gas chromatography–mass spectrometry (GC–MS) produces the highest resolution and will no doubt

continue to be the most effective technique for complete environmental analysis, *e.g.* for the alkyl- and hydro-derivatives of PAHs. However, the nature of the analytical procedure depends mainly on (1) the equipment available, cost being the limiting factor here; and (2) analysis time, rapid analyses being required for routine work.

These parameters impose limitations in the procedure employed. Several workers have used gel permeation chromatography to separate PAHs according to ring size[3,22,25]. This technique is effective, but is a time-consuming process and not practicable for rapid analysis. The technique of capillary GC–MS is not readily available, and microfine bonded high-performance liquid chromatography (HPLC) phases are exceedingly expensive. Due to the low vapour pressure of some PAHs, special high-temperature liquid phases must be employed for gas-liquid chromatography (GLC), which also impose a cost limit on the overall procedure. Therefore, we have attempted to produce a method which is rapid, utilising equipment and materials which are readily available in most laboratories. The procedure evolved is quantitative, although limited to the more common PAHs. After initial clean-up, the resulting PAH fraction is analysed quantitatively by GC, identification of the compounds being effected by the combination of GC retention data and fluorescence spectroscopy. According to Sawicki *et al.*[26] it is possible, through judicious selection of the proper wavelength, to obtain the true fluorescence spectrum of a particular polynuclear in a mixture of PAH. However, this is not generally applicable as reported by O'Haver and Parks[27]. These workers discuss methods for resolving partially or severely overlapping spectra. In the case of a complex environmental extract there may be a large number of PAH fluorophores and the fluorescence spectrum will be idefinite[28]. The successful application of fluorescence spectroscopy to the identification of PAHs depends on good separation of the hydrocarbons[12], and even thin-layer chromatography (TLC) in very complex cases may not be sufficient to give a clear-cut fluorescence spectrum. However, if PAHs can be resolved into simple mixtures, then, by varying the excitation wavelength, the fluorescence emission spectra of the components may be clearly defined. The great sensitivity of the technique enables the detection of as little as 0.001 μg/ml of PAH compounds[29], particularly in deoxygenated dilute solutions, where the elimination of oxygen quenching of the relatively long-lived PAH excited singlets can lead to the enhancement of fluorescence intensity by factors of up to four[21]. Consequently, the proposed method combines the high resolution of GC with the great sensitivity of fluorescence analysis for identification of the compounds, the relatively pure PAHs being trapped as they elute from the analytical GC column[30]. Each fraction is then subjected to fluorescence analysis.

EXPERIMENTAL

Reagents

Reagents used were: cyclohexane, methylene chloride, hexane, acetone; alumina, basic type H, 100–150 mesh (B.S.S.) from Laporte Industries (Widnes, Great Britain); Kieselgel, Merck Kieselgel G, type 60 from BDH (Poole, Great Britain). The purification of these materials before use is discussed below (see *Contamination*).

Equipment

A Pye 104 gas chromatograph equipped with an FID head, a Pye Series 104

preparative trapping system, and an Aminco Bowman spectrophotofluorimeter were employed.

Slit Arrangement for measurement of fluorescence emission spectra

Slit widths (mm) used were: Xenon light source, 5.0; Light incident on sample, 5.0; Light emergent from sample, 0.1; Photomultiplier slit, 0.5.

Phase preparations and analytical conditions for GC

Gas–liquid chromatography. 5% Dexsil 300 GC (purchased from Analabs) on Chromosorb W NAW (60–80 mesh) was prepared on a w/w basis. The dissolved liquid phase was coated onto the support *via* slow rotation in a Morton flask. After about 20 min the excess solvent was removed by rotary evaporation. The phase was dried and packed by vibration and suction. The column was conditioned for 14 h at 360° with a nitrogen flow-rate of 50 ml/min.

Analytical conditions were as follows.

Column: glass, 3 ft. × 4 mm I.D. Carrier gas, nitrogen; flow-rate, 40 ml/min. Temperature programme: 100° for 2 min, programming at 10°/min, then 340° for 7 min. Hydrogen flow-rate, 60 ml/min. Air flow-rate, 300 ml/min. Injection port heater, 5. Outlet heater, 330°. Chart speed, 5 mm/min; 10-mV recorder. Attenuation, 5×10^2.

Gas–solid chromatography (GSC). GSC has been applied to the analysis of PAHs[31–34]. Their low vapour pressure excludes the use of normal liquid phases, thus only the more unconventional phases are satisfactory. However, investigations in this laboratory show that most inorganic salt-coated support phases exhibit bad tailing characteristics and/or rapid column deterioration, both being undesirable. Of the phases investigated 2% rubidium chloride on Chromosorb G NAW (60–80 mesh) exhibited a separation comparable with the GLC column used, both with respect to peak shape and reproducibility over a long period of use.

Separation by adsorption leads to changes in elution order compared to that by partition[34].

Column preparation was as follows. Rubidium chloride was dissolved in distilled water and coated on to the support as described previously. The phase was fired at 450° for 12 h, sieved carefully (60–80 B.S.S.), and then packed by vibration and suction. The column was conditioned at 380° for 1 h, with a nitrogen flow-rate of 60 ml/min, before use.

Analytical conditions were:

Column: glass, 5 ft. × 4 mm I.D. Carrier gas (nitrogen) flow-rate: 60 ml/min. Temperature programme: for 3 min at 100°, programming at 15°/min, then 360° for 7 min. The other conditions are the same as for GLC.

PAH standards

The standard compounds were purchased from Koch-Light (Colnbrook, Great Britain), and their purity assessed by GLC. They were found to be of satisfactory quality, and hence the compounds were used without further purification. Standard compounds were: anthracene, fluoranthene, 3,4-benzpyrene, pyrene, 2,3-benzofluorene, 1,2,3,4-dibenzanthracene, phenanthrene, chrysene, perylene, coronene, benzo(*ghi*)perylene, triphenylene.

Fig. 1 shows the separation of standard compounds by GLC [5% Dexsil 300 GC on Chromosorg W NAW (60–80 mesh)], while Fig. 2 shows their separation by GSC [2% rubidium chloride on Chromosorb G NAW (60–80 mesh)]. All solutions analysed by GC were made up in cyclohexane. The response shown in these figures corresponds to an injection quantity in the range 40–100 ng of standard compound.

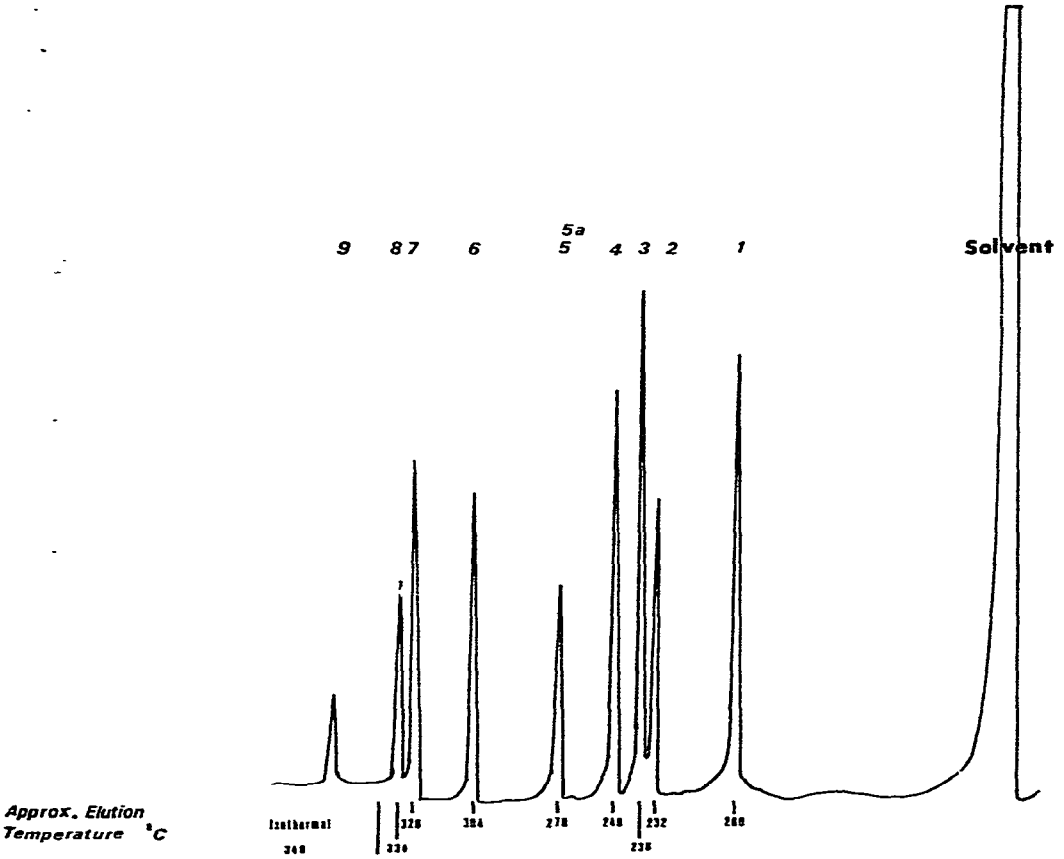

Fig. 1. GLC separation of standard compounds. Peak identification: see text.

Elution order of standard compounds

The order of elution was as follows: 1 = anthracene and phenanthrene, 2 = fluoranthene, 3 = pyrene, 4 = 2,3-benzofluorene, 5 = chrysene, 5a = triphenylene, 6 = 3,4-benzpyrene and perylene, 7 = 1,2,3,4-dibenzanthracene, 8 = benzo-(*ghi*)perylene, 9 = coronene.

Procedure

Fig. 3 shows the analytical scheme employed.

Sample drying

Loss of PAHs was observed from spiked samples when either (1) freeze drying,

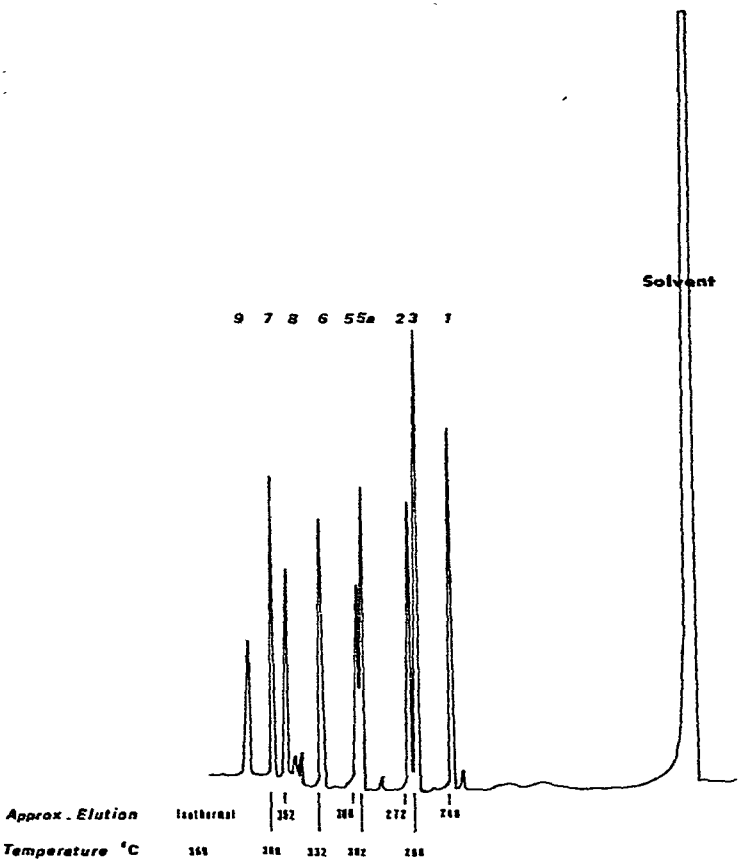

Fig. 2. GSC separation of standard compounds. Peak identification: see text.

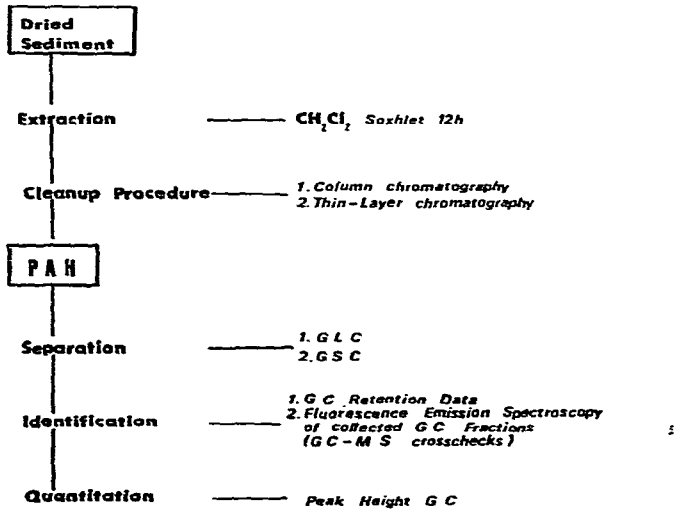

Fig. 3. Analytical scheme.

or (2) oven drying at 30–35° were employed. Losses were as high as 70% with method 2. Sediments were dried as far as possible by suction filtration on a medium glass frit. A portion was weighed and then dried for 12 h at 30°. From this an estimate of the per cent water content could be obtained. About 100–150 g of partially dried sediment was weighed to one decimal place and mixed intimately with an excess of anhydrous sodium sulphate until homogeneous. The mixture was Soxhlet extracted for 12 h using methylene chloride. The results can thus be expressed both on a dry and wet weight basis.

Analytical method

The crude extract was concentrated by rotary evaporation to about 10–15 ml. Chromatographic alumina (type H, 100–150 mesh, basic), activated at 600° for 12 h was subsequently deactivated via equilibration with 5% (w/w) of water through shaking for 30–40 min. The chromatographic column (21 × 2.5 cm I.D.) was slurry packed (20 g alumina) using hexane solvent. The extract was quantitatively applied to the column in hexane–methylene chloride (70:30). This solution was percolated through the column and elution with 150 ml hexane ensured complete recovery of the PAH fraction. The eluate was reduced to 1 ml by evaporation using a rotary evaporator and finally a slow stream of nitrogen (concentrate 1).

A second column (21 × 1 cm I.D.) was slurry packed (10 g alumina) and concentrate 1 quantitatively applied in hexane. Hexane (200 ml) was used to elute the PAH fraction, the eluate being concentrated to an accurately known volume, usually 2–5 ml (concentrate 2).

TLC plates (20 × 20 cm, 250 μm thick, Merck Kieselgel G Type 60) were activated at 100–120° for 30 min, being cleaned before use as described below. An accurately known volume (100 or 200 μl) of concentrate 2 was applied to the origin as a band. A Hamilton syringe and Camag bandspreader were used for this purpose. Standard PAH compounds, particularly anthracene, pyrene, 1,2,3,4-dibenzanthracene and coronene were spotted onto each TLC plate at least 4 cm away from the band origin (to prevent cross contamination), and the plate scored at a height of about 13 cm above the origin. The plate was developed by ascending elution in hexane and the compounds visualised by illumination with 366-nm light for a minimum period.

The standards selected above represent maximum and minimum R_F values for the PAHs chosen for analysis under these conditions. The region which had R_F values intermediate between those of the standards was quantitatively transferred to a column and the PAHs eluted with methylene chloride. This solution was finally evaporated to dryness under a stream of nitrogen, and the resultant material dissolved in a known volume of cyclohexane. The solution was then analysed by GC.

All elutions must be carried out in the dark to avoid partial decomposition of the PAHs.

Gas Chromatography

Two of the cleaned samples were subjected to GC–MS and the major GC peaks identified. The procedure was merely used as a cross check of the identification for the method described below, which is based on retention data and fluorescence analysis. The latter was used for other samples, since the two methods indicated the same compounds to be present.

Peak identification. A chromatogram of the sample was obtained using GLC and the peaks were tentatively identified by co-injection with a mixture of standard compounds. The procedure was repeated using GSC. The peaks which were enhanced in the two cases gave a strong indication as to their identity, and these peaks were further examined using spectrophotofluorescence.

Collection of fractions from the gas chromatograph. The GC instrument was modified to trap the tentatively identified peaks using a commercial Pye Series 104 manual preparative kit with a 25:1 stream splitter. To trap a fraction, the glass U-tube was placed into position before the emergence of the peak. After complete emergence, the trap was replaced by another and the process repeated for other peaks of interest. Unrequired material was also trapped. These traps are advantageous in that they are both small and inexpensive. The material was transferred to a glass vial with portions of cyclohexane, which was evaporated by a slow stream of nitrogen to a volume of less than 0.2 ml. This solution was then subjected to fluorescence analysis, emission spectra being recorded.

Quantitation. Quantitative analysis was performed during the peak identification procedure via peak height as measured from peak base to apex in the environmental chromatogram and comparison with standard calibration curves. The injection quantity may then be varied accordingly to ensure trapping of sufficient material to obtain a clear fluorescence spectrum. The numerical results for the environmental samples are expressed in terms of the corresponding standard compound.

Contamination

All efforts were made to ensure the cleanliness of both apparatus and reagents used during the procedure.

Glassware. Glassware was thoroughly cleaned using the following method: (1) hot teepol wash, (2) thorough rinsing in water, (3) chromic acid bath dip overnight, (4) thorough rinsing in water, (5) acetone wash. The apparatus was then washed in methylene chloride immediately before use.

Solvents. All solvents used in any stage of the procedure, whether for washing of apparatus or employment in the analysis, were doubly fractionated. All plastic Winchester bottle tops were inlaid with methylene chloride washed aluminium foil, thus avoiding plasticizer contamination.

Chromatographic systems. Alumina was fired overnight at 600°; this both activated the material and destroyed by oxidation and volatilisation organic material which may have been present. In order to ensure complete removal of organics, the first 60 ml hexane percolated through the chromatographic columns was rejected.

All TLC plates were pre-eluted with methylene chloride before use in the analytical procedure. The plates were scored 1–2 cm below the solvent front and dried. Only then were they used for environmental samples.

Two other sources of contamination were possible: (1) the Soxhlet thimbles, (2) the anhydrous sodium sulphate used for sample drying. The former was eliminated by exhaustive extraction with methylene chloride before use, and the latter by firing at 600° overnight.

Procedural blanks. In order to assess the quality of the contamination prevention procedures adopted, procedural blanks were included (at least one with each batch of materials cleaned). These were subjected to GLC at a higher sensitivity

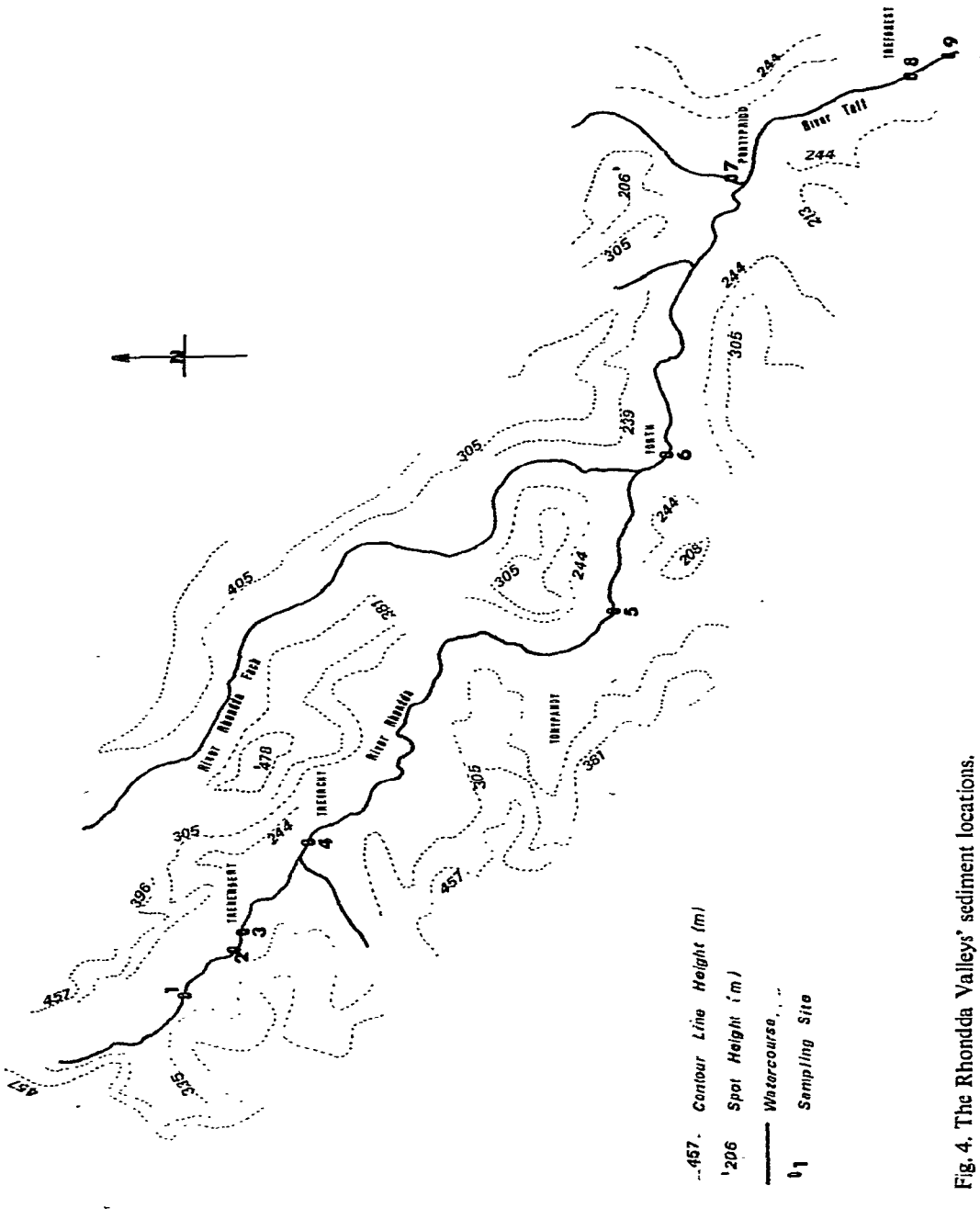

Fig. 4. The Rhondda Valleys' sediment locations.

(usually by a factor of 3) than that used for the environmental concentrates. In almost all cases, there was negligible background contamination.

Sampling

Location. Sediment samples were taken along the river courses in the Rhondda Fawr Valley, South Wales. The nature of the industrial development of the valley prompted the choice of the area for sampling. During the nineteenth and early twentieth centuries, rich coal veins were discovered in the area and mining became a major industry. The rivers were used to wash the crude coal, with the result that their sediments consist wholly or partially of fine coal dust. Even though most of the coal mines have long since ceased to be operative, the scars of the mining era remain, both visually in terms of spoils tips and, perhaps more insidiously, in the form of trace element contamination[35]. Fig. 4 shows the location of the sediment sites sampled.

Sampling procedure and storage. The sediments were obtained with a grease free, solvent washed, metal scoop and stored in cleaned dark glass bottles, the caps of which had been inlaid with aluminium foil to prevent plasticiser contamination. They were stored at 0° and extracted as soon as possible, the extracts also being stored at 0° until analysed.

RESULTS

The recovery of the method was assessed by processing known quantities of the standards through the clean-up procedure. Table I shows the percentage recovery for triplicate determinations.

TABLE I

RECOVERY OF THE METHOD

1,2,3 = Determination No.; $\bar{x}$ = arithmetic mean; σ = standard deviation.

Compound	*Recovery (%)*			$\bar{x}$	σ
	1	*2*	*3*		
Anthracene	85.2	87.5	84.8	85.8	1.5
Fluoranthene	86.3	88.4	85.6	86.8	1.5
Pyrene	88.7	90.3	87.8	88.9	1.3
2,3-Benzofluorene	86.8	87.6	89.9	88.1	1.6
Chrysene	89.7	87.6	88.7	88.7	1.1
3,4-Benzpyrene	87.8	88.0	86.8	87.5	0.6
1,2,3,4-Dibenzanthracene	85.7	86.6	85.7	86.0	0.5
Benzo(*ghi*)perylene	86.3	87.2	88.0	87.2	0.9
Coronene	88.6	88.0	86.3	87.6	1.2

Chromatograms for site 7 (Pontypridd) are shown in Fig. 5 and are typical of those obtained for all sites. Table II shows the distribution of PAHs throughout the sampling sites. The figures are obtained by GLC quantitation and do not take percentage recoveries into consideration. Figures for both wet and dry weight of sediment are given.

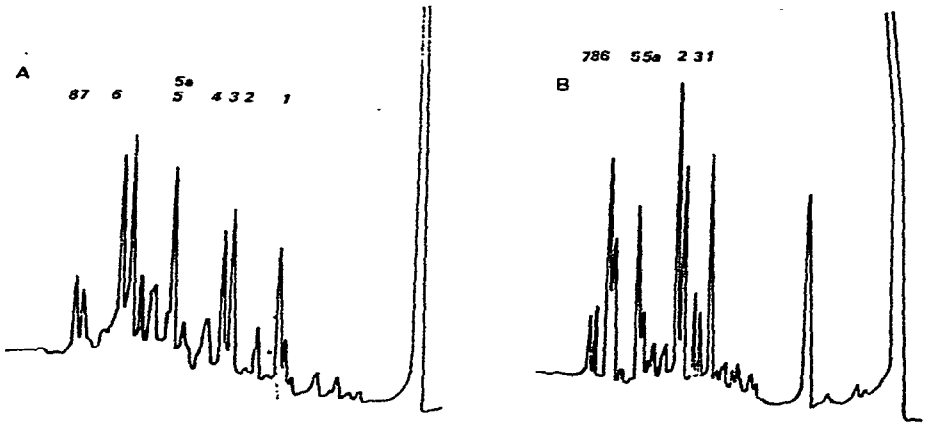

Fig. 5. GLC (A) and GSC (B) traces of site 7 (Pontypridd).

TABLE II

DISTRIBUTION OF PAHs IN RHONDDA FAWR SEDIMENTS

Sampling date: November 20th, 1975.

Compound	*Site No.*								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
μg PAH per g sediment (dry weight basis)									
Anthracene	12.4	5.3	11.2	7.8	7.5	12.8	0.6	17.6	1.8
Fluoranthene	13.4	12.4	11.0	6.5	10.2	10.4	0.6	13.8	1.6
Pyrene	10.9	8.7	6.1	5.1	8.8	11.3	0.7	21.3	1.9
2,3-Benzofluorene	3.6	3.0	2.1	1.8	2.0	3.2	0.2	7.1	0.6
Chrysene (triphenylene)	15.2	25.9	17.8	35.5	56.8	14.9	1.1	24.1	2.5
3,4-Benzpyrene	9.7	11.9	3.9	7.2	10.2	29.3	2.7	6.0	5.0
1,2,3,4-Dibenzanthracene	2.2	6.1	0.6	5.4	7.3	—	0.4	—	1.1
Benzo(*ghi*)perylene	3.6	6.5	1.4	4.2	6.0	2.9	0.6	—	1.3
Coronene	—	—	—	—	—	—	—	—	—
μg PAH per g sediment (wet weight basis)									
Anthracene	8.4	3.9	8.7	5.9	4.9	9.4	0.6	12.8	1.3
Fluoranthene	9.1	9.2	8.5	5.0	6.6	7.6	0.5	10.1	1.1
Pyrene	7.4	6.5	4.7	3.9	5.7	8.3	0.6	15.5	1.4
2,3-Benzofluorene	2.4	2.2	1.6	1.3	1.3	2.3	0.2	5.2	0.4
Chrysene (triphenylene)	10.3	19.2	13.8	27.2	36.8	11.0	0.9	17.5	1.8
3,4-Benzpyrene	6.6	8.8	3.0	5.5	6.6	21.6	2.4	4.4	3.6
1,2,3,4-Dibenzanthracene	1.5	4.6	0.4	4.1	4.7	—	0.4	—	0.8
Benzo(*ghi*)perylene	2.4	4.8	1.1	3.2	3.9	2.1	0.5	—	0.9
Coronene	—	—	—	—	—	—	—	—	—

Fig. 6 presents the fluorescence emission spectra obtained for standard compounds compared with those for the GLC fractions collected for site 7 (Pontypridd). These spectra may be taken as the typical case and confirm the presence of PAHs in these sediments.

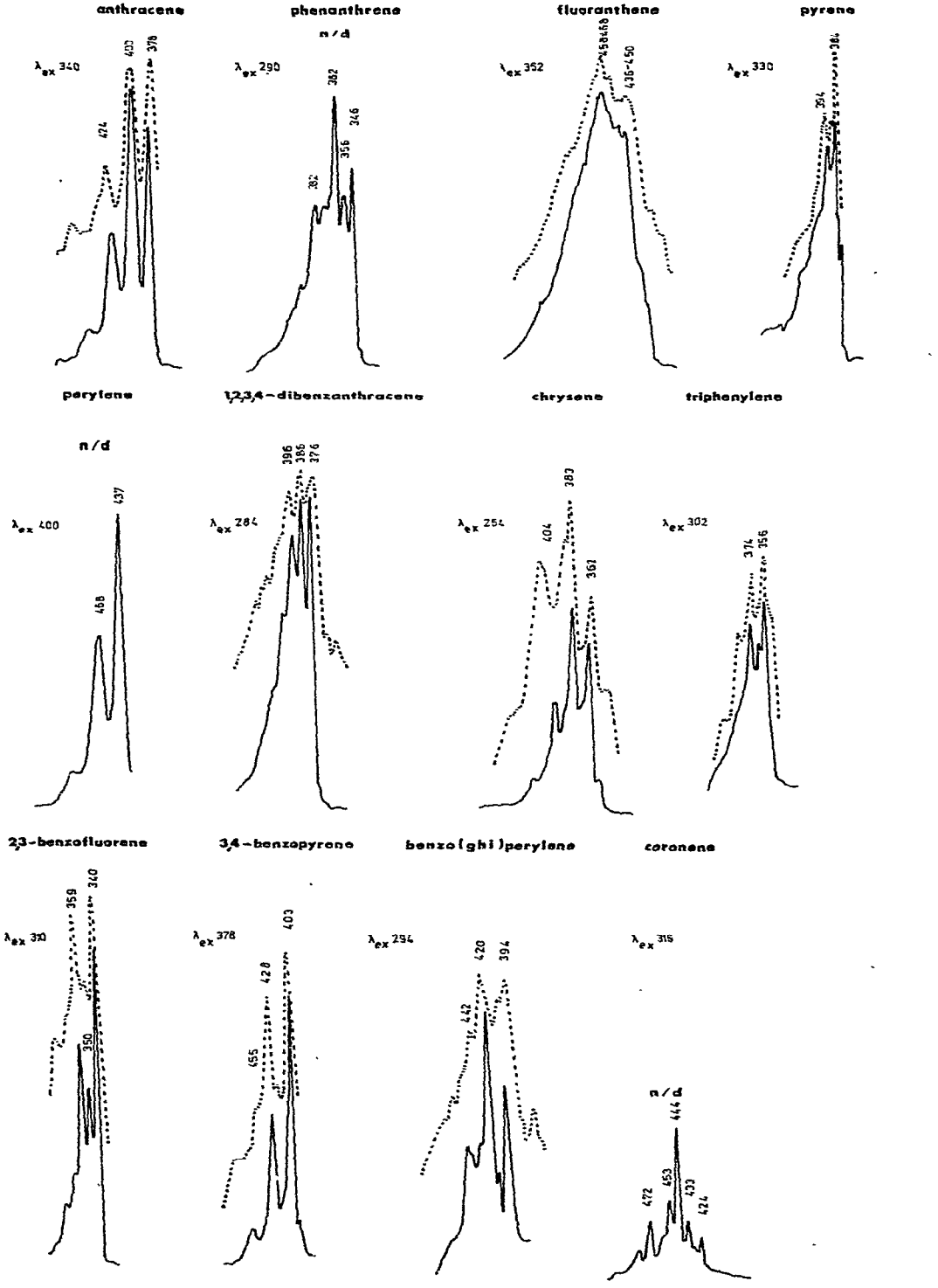

Fig. 6. Fluorescence emission spectra: ———, standard compounds; — — —, trapped fractions for site 7 (Pontypridd). n/d = Not detected as site 7 (see also Table V). λ_{ex} = Exitation wavelength (nm); emission wavelengths of the major peaks are in nm and measured to an accuracy of ±2 nm.

DISCUSSION

This work shows the ubiquity of PAHs throughout the sediments of the watercourses in the Rhondda Fawr Valley. Intercomparison of the figures based on sediment dry weight is more reliable when considering PAH distribution since wet weight does not take the water–sediment ratio into account. This ratio can vary extensively for each sample giving rise to an inconsistent basis for the resulting analytical figures, leading to an invalid comparison. The drying of the sample was thus considered to be a most important parameter as the objective of environmental analyses lies in the intercomparison of sample site values, with a view to the possible location of pollution sources.

TABLE III

RESOLUTION OF STANDARD COMPOUNDS BY GC

+ = Resolved; − = unresolved.

Compounds	*GLC*	*GSC*
Anthracene + phenanthrene	−	−
Chrysene + triphenylene	−	+
3,4-Benzpyrene + perylene	−	−

Complete resolution of PAHs is an exceedingly difficult task, requiring highly sophisticated and costly apparatus[36]. The method proposed will not separate certain PAHs (Table III) and therefore it is probable that several GC peaks in the environmental chromatogram will consist of a number of unresolved components. This also may be true of other cases[20,22]. In our work, each peak is quantitated in terms of the corresponding standard compound as identified by co-injection. Although fluorescence spectroscopy, coupled with GC retention data, has unambiguously confirmed the presence of the particular compound in the collected GLC fraction, the quantitative estimation actually indicates the total PAH present in that peak, in terms of the selected standard. This leads to inconsistencies when comparing quantitation by GSC to that by GLC. Table IV compares the concentration of PAHs for site 7 when

TABLE IV

QUANTITATION BY GC (μg PAH PER g SEDIMENT, DRY WEIGHT BASIS, SITE 7)

Compound	*GLC*	*GSC*	
Anthracene	0.6	0.8	
Fluoranthene	0.6	0.9	
Pyrene	0.7	0.8	
2,3-Benzofluorene	0.2	−	
Chrysene	1.1	1.3	1.8
Triphenylene		0.5	
3,4-Benzpyrene	2.7	3.2	
1,2,3,4-Dibenzanthracene	0.4	0.5	
Benzo(*ghi*)perylene	0.6	0.7	

computed by GLC and GSC. It should be noted that 2,3-benzofluorene may not elute from the GSC column, probably because of decomposition. Thus no figure for its concentration can be given in Table IV.

The detection of the compounds shown in Table III at the sample sites was effected by fluorescence spectroscopy and the results are shown in Table V. However, further complications can arise since other PAHs, which lie outside the scope of this paper, may also be present but were not investigated by fluorescence analysis in the collected GLC fractions, *e.g.* benzo(*e*)pyrene which would elute in the "benzpyrene fraction" (3,4-benzpyrene, benzo(*e*)pyrene and perylene).

TABLE V

DETECTION OF COMPOUNDS BY FLUORESCENCE IN UNRESOLVED GC FRACTIONS

d = Detected; nd = not detected.

Compound	*Site no.*								
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Phenanthrene	nd	nd	nd	nd	nd	nd	nd	nd	nd
Triphenylene	nd	nd	d	nd	nd	nd	d	d	d
Perylene	nd	nd	nd	nd	nd	nd	nd	nd	nd

These difficulties in quantitation not only occur with the GC methods but also with spectral techniques such as UV and fluorescence[3,24,29]. With such techniques there is a high probability of finding partially or severely overlapping spectra, with more than one compound contributing to the overall intensity. This gives rise to erroneous concentration levels if taken to apply to a single compound. Quantitative fluorescence analysis also suffers from the limitations of oxygen quenching and therefore a standard degassing procedure is important[21,29].

CONCLUSION

Care must be taken when comparing results from different analytical techniques[20]. It is, therefore, essential to apply the same technique of quantitation to a particular area with a view to survey work, and a generally standardised quantitation procedure is badly required in this field.

The complexity of the matrix studied herein, containing a vast number of organic compound classes such as waxes, fatty acids, phenols, pigments, porphyrins and aliphatic hydrocarbons, is adequately overcome by the clean-up procedure, which should therefore be applicable to other matrices such as air particulate matter and water extracts. The resultant GLC chromatograms are sufficiently well defined to allow collection of fractions which produce easily interpreted fluorescence emission spectra, whilst the inorganic salt-coated phase shows excellent separation characteristics for most of the PAHs investigated.

The procedure may be limited to the more common PAHs in the environment, but has distinct advantages in ease of operation and low cost. Typical "extract-to-analysis" time being in the range 5–6 h.

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