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Note

Rapid method for the determination of polycyclic aromatic hydrocarbons in environmental samples by combined liquid and gas chromatography*

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Polycyclic aromatic hydrocarbons (PAHs) are formed in different combustion processes from many kinds of organic materials and are widespread throughout the environment. The carcinogenic properties of certain PAHs have long been recognized. PAHs have been detected in trace amounts in a wide variety of matrices, varying from exhaust gases, smoke, airborne particulates, surface and drinking waters and foodstuffs to soils and sediments. Many procedures have therefore been developed for the determination of PAHs, varying in complexity and in the instrumentation and techniques used. For clean-up and enrichement of PAH fractions liquid extraction[1,2] thin-layer chromatography (TLC)[3–5], liquid–solid column chromatography on different adsorbents[5–12] and high-performance liquid chromatography (HPLC)[13–15] have been employed.

TLC or adsorption chromatography alone does not have a sufficient resolving power to isolate completely each individual component. Several workers[2,8,12] have used gel permeation chromatography combined with HPLC or liquid–solid column chromatography to separate PAHs according to ring size. This technique is effective, but is time consuming and not suitable for rapid analysis. The other disadvantage of this technique is that it needs a large volume of solvent.

The most powerful method is pre-separation by HPLC[13], but microfine bonded HPLC phases are expensive, and such techniques are often not possible and the instruments may not be generally available in routine laboratories.

The detection and identification of PAHs have been carried out by UV and fluorescence spectroscopy[1,2,5,16] and more recently mostly by capillary gas chromatography[9,10,13,17–19] and gas chromatography–mass spectrometry (GC–MS)[20,21].

The methods described for PAH analysis so far require expensive instrumentation and are time consuming and expensive to run on a routine basis. For this reason we have attempted to devise a method that is rapid, utilizing equipment and materials

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that are available in most laboratories. After initial clean up by liquid chromatography (LC), the resulting PAH fraction is analysed by glass capillary GC. This procedure has distinct advantages of ease of operation and low cost.

EXPERIMENTAL AND RESULTS

Liquid chromatographic clean-up and concentration of PAHs was carried out by adsorption chromatography in two steps on silica gel and alumina. For these procedures a simple technique was developed using a short glass adsorption column (10 cm × 1 cm I.D.) connected to a 10-ml glass syringe by PTFE tubing. The syringe served to force the solvent through the adsorbent bed.

The columns were dry packed with the adsorbents and wetted with 5 ml of *n*-hexane. Woelm silica gel (30–60 μm) activated at 180°C for 6 h and Woelm alumina N (30–60 μm) activated at 350°C for 12 h were used as adsorbents.

Gas chromatography

A Carlo Erba Fractovap 2452 gas chromatograph equipped with a flame-ionization detector (FID), a Grob-type split–splitless injector and a 20 m × 0.3 mm I.D. glass capillary column coated with OV-1 stationary phase was employed.

Reagents

Analytical-reagent grade *n*-hexane and methylene chloride (Reanal, Budapest, Hungary) were washed with concentrated sulphuric acid and reacted with potassium permanganate, then distilled. Analytical-reagent grade acetone (Reanal) was used as received. C_{14}–C_{36} *n*-alkanes (Poly-Science, Evanston, IL, U.S.A., purity >98%) were used as internal standards.

PAH standards were obtained from different sources and were used as received.

Sample preparation

Sediment samples were dried, then Soxhlet extracted with benzene for 8–16 h. The extracts were cautiously evaporated to dryness and weighed. The dry extracts were dissolved in measured amounts of benzene, giving solute concentrations of 5–10 wt.-%.

Procedure

The scheme of the analytical procedure is given in Fig. 1.

A 0.2-ml volume of the benzene solution was applied to the top of the silica gel column. By using 40 ml of *n*-hexane for the elution of aliphatics and other weakly adsorbed compounds, then methylene chloride for the elution of aromatics, a rough group separation of aromatics was carried out. The more polar (heteroatom-containing) compounds retained on the silica gel were removed with 20 ml of acetone before reactivation.

The methylene chloride fraction was evaporated to dryness under reduced pressure and the residue was taken up in 0.2 ml of methylene chloride and applied to the alumina column. Based on preliminary experiments with model mixtures, a solvent programme was developed that produced a cut between two-ring and three-ring aromatics. A 10-ml volume of methylene chloride–*n*-hexane (1:4) yielded an eluate containing the remaining aliphatics and aromatics, including two-ring systems.

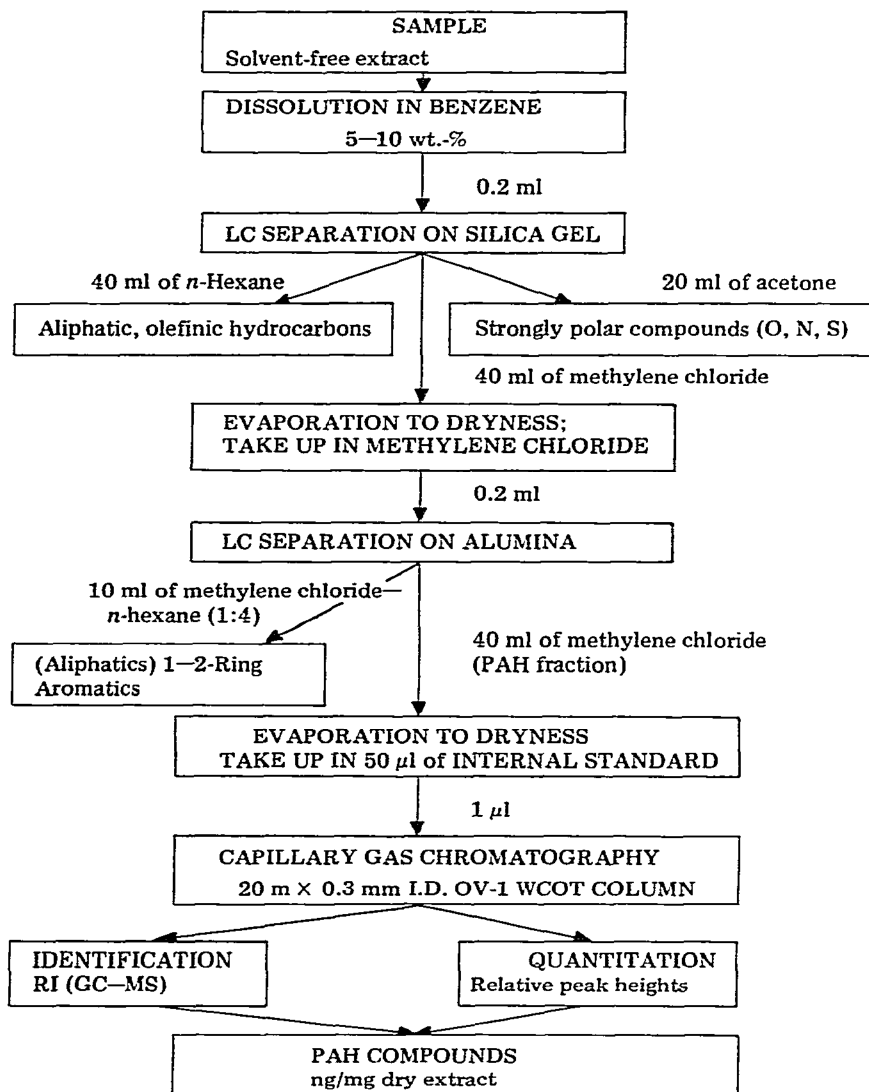

Fig. 1. Analytical scheme for PAH assay.

Subsequent elution with 40 ml of methylene chloride yielded an eluate containing three-ring and higher polyaromatics.

The above PAH fraction was evaporated to dryness and taken up in 50 μl of cyclohexane containing a known amount of selected *n*-alkanes as internal standards. A 1-μl volume of this solution was injected on to the OV-1 capillary column and chromatographed under conditions selected by using a model mixture of 14 PAH standards. The gas chromatogram of a sediment extract is shown in Fig. 2.

Identification of the major PAH components was carried out by using PAH standards and calculating retention indices. For confirmation of retention data and

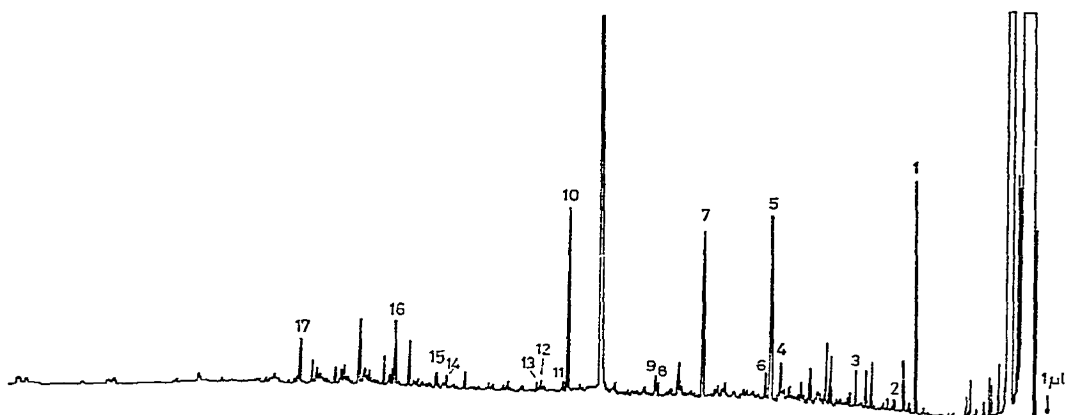

Fig. 2. Gas chromatogram of PAHs isolated from a sediment extract. GC conditions: 20 m × 0.3 mm I.D. glass capillary column coated with OV-1; FID; carrier gas, hydrogen at a flow-rate of 33.3 cm/sec; oven temperature, 40°C for 3 min. then increased at 25°C/min to 140°C and at 4°C/min to 300°C; injector temperature, 250°C; detector temperature, 300°C. Peaks: 1 = n-$C_{14}H_{30}$; 2 = fluorene; 3 = phenanthrene; 4 = fluoranthene; 5 = n-$C_{20}H_{42}$; 6 = pyrene; 7 = n-$C_{22}H_{46}$; 8 = 1,2-benzanthracene; 9 = chrysene; 10 = n-$C_{26}H_{54}$; 11 = benzofluoranthene; 12 = 3,4-benzopyrene; 13 = perylene; 14 = indeno[1,2,3-*cd*]pyrene; 15 = 1,12-benzoperylene; 16 = n-$C_{32}H_{66}$; 17 = n-$C_{36}H_{74}$.

identification of unknown components, GC–MS measurements were also carried out by using a Finnigan Model 3200E GC–MS system combined with an on-line computer (Model 6100).

Quantitation of PAHs was accomplished by comparing the peak height of an individual PAH with that of a selected *n*-alkane internal standard. The correlation between the heights of a PAH and an *n*-alkane peak was determined by injection of samples containing a measured amount of PAH standards.

Recoveries of the major PAH compounds in the LC separation steps were determined by using the mixture of PAH standards in the separation procedure. Blank tests were carried out by injecting directly the PAH standard mixture on to the capillary column without the LC separation steps. The recoveries measured are given in Table I. In the calculation of the results the recoveries measured for the individual PAHs were also taken into account. PAH concentrations are given in nanograms per milligram of dry extract.

The repeatability of the complete analytical scheme was investigated for a selected sediment extract. The results obtained for four replicate analyses are given in Table II. The relative standard deviations for the individual PAHs varied between 3 and 20%. Taking into account the number of different operations involved, the repeatability is adequate.

CONCLUSION

Assay of the major PAH compounds in environmental samples can be carried out efficiently and rapidly following the scheme shown in Fig. 1. Clean-up and concentration of the PAH fraction require simple apparatus and small amounts of

TABLE I

RECOVERIES OF PAH COMPOUNDS IN LC FRACTIONATION

PAH standard	*Peak height (LC+GC)**	*Relative standard deviation (%)*	*Peak height (GC)***	*Peak-height ratio****		*Recovery (%)*
				LC+GC	*GC*	
Phenanthrene + anthracene	157.9	8.3	157.5	0.685	0.695	98.5
Fluoranthene	57.2	7.6	64.0	0.495	0.57	86.8
Pyrene	103.5	3.3	105.5	0.895	0.93	96.2
1,2-Benzanthracene	55.7	2.3	64.0	0.54	0.63	85.7
Chrysene	94.2	4.0	100.5	0.915	0.99	92.4
3,4-Benzofluoranthene	60.2	3.9	61.5	0.83	0.75	110.6
3,4-Benzopyrene	52.1	4.0	58.0	0.715	0.71	100.7
Perylene	32.0	2.6	40.5	0.44	0.49	89.8
1,2,5,6-Dibenzanthracene	19.5	3.0	28.5	0.265	0.35	75.7
Indeno[1,2,3-*cd*]pyrene	27.0	4.3	35.0	0.37	0.43	86.0
1,12-Benzoperylene	39.7	8.3	45.0	0.545	0.55	99.0

* Average of four measurements.
** Average of two measurements.
*** With respect to the peak height of the *n*-alkane internal standard.

TABLE II

REPEATABILITY OF ANALYTICAL SCHEME FOR PAH ASSAY FOR A SEDIMENT EXTRACT

Results are nanograms per milligram of dry extract.

PAH component	*Repeated analyses (ng/mg)*				*Average value (ng/mg)*	*Relative standard deviation (%)*
	1	*2*	*3*	*4*		
Phenanthrene + anthracene	49.8	45.9	50.1	51.2	49.25	4.69
Fluoranthene	53.7	57.4	54.0	57.1	55.55	3.55
Pyrene	20.2	22.4	19.2	21.4	20.80	6.71
1,2-Benzanthracene	15.2	15.8	14.2	12.5	14.43	10.00
Chrysene	18.2	17.0	16.9	16.8	17.23	3.80
3,4-Benzofluoranthene	19.2	18.1	21.6	16.6	18.88	11.16
3,4-Benzopyrene	19.3	16.8	19.9	15.4	17.85	11.84
Perylene	18.8	14.8	21.2	13.6	17.10	20.60
Indeno[1,2,3-*cd*]pyrene	92.7	74.5	107.6	97.6	93.10	14.89
1,12-Benzoperylene	62.7	62.4	75.5	69.9	67.63	9.30

solvents. A GC separation furnishes sufficiently resolved peaks for identification and quantitation. The time required for an analysis is 2–3 h. The reproducibility and accuracy are adequate for environmental investigations.

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