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CONCENTRATION AND DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN AQUEOUS SAMPLES ON GRAPHITIZED CARBON BLACK

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SUMMARY

A method is proposed for the determination of six polycyclic hydrocarbons in water samples, using a short column packed with graphitized carbon black (GCB). The adsorbed compounds are eluted by passing through the column toluene-benzene-acetonitrile (5:2:3). In order to choose the optimal eluent, the partition coefficients in GCB-liquid systems were studied in a static arrangement; to optimize the size of the concentration columns breakthrough curves were plotted.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has been bound, under a Consent Decree, to set maximum concentration limits in effluent waters for a group of "unambiguous priority pollutants"¹, and included in this list are several polycyclic aromatic hydrocarbons (PAHs). The EPA is now in the process of establishing upper concentration limits for these compounds and recommending analytical methods for their determination. In 1971 the World Health Organization set an upper limit of 200 ng/l for the total concentration of six PAHs in domestic water². Additional PAHs were known to occur in water samples but only these six could be easily separated by the analytical methods in use at that time³. Thus, these compounds, must be monitored at very low levels in water samples, levels so low that a concentration step must often precede the analysis in order to achieve sufficient concentrations for detection. The determination of PAHs present in water at the microgram per litre level or less has usually been carried out by removal of the PAHs from the water using liquid-liquid extraction⁴⁻⁷ or headspace sampling techniques^{8,9}. An alternative method is adsorption trapping, using a solid matrix such as carbon¹⁰, Tenax GC¹¹, XAD resins¹²⁻¹⁴, polyurethane foam^{15,16} or C₁₈ bonded phase¹⁷⁻¹⁹. These compounds are then desorbed and analysed by thin-layer chromatography^{20,21}, high-performance liquid chromatography (HPLC)²²⁻²⁵, gas chromatography²⁶⁻²⁹, or gas chromatography-mass spectrometry³⁰.

The liquid-liquid extraction techniques, the traditional methods for extraction and concentration of organic compounds from water, require the use of large volumes

of organic solvents followed by a tedious and time-consuming concentration step, and headspace sampling gives very low recoveries for all except the most volatile PAHs⁸.

As graphitized carbon black (GCB) has a high sorption capacity in the recovery of several classes of organic micropollutants³¹, we investigated the use of GCB in packing chromatographic columns that are employed to extract trace amounts of PAHs from aqueous samples.

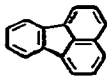
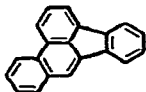
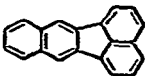
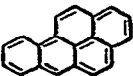
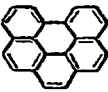
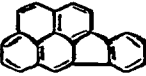
The chromatographic aspects (retention volumes and dynamic capacities) were characterized by plotting breakthrough curves. Partition coefficients between liquid systems and GCB were measured in order to evaluate the recovery.

EXPERIMENTAL

Materials

Fluoranthene, benzo[*def*]chrysene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene were obtained from Analabs, (North Haven, CT, U.S.A.) and benz[*e*]acephenanthrene and benzo[*k*]fluoranthene from Nanogens (Watsonville, CA, U.S.A.). These standards, which were available as powders, were dissolved in acetonitrile at 100 µg/ml. These compounds and their structures are listed in their order of elution in Table I.

TABLE I
POLYCYCLIC AROMATIC HYDROCARBONS STUDIED

No.	Formula	IUPAC name	Other names	Remarks
1		Fluoranthene	Benz[<i>a</i>]acenaphthene 1,2-Benzacephthene Idryl	
2		Benz[<i>e</i>]acephenanthrene	Benzo[<i>b</i>]fluoranthene 2,3-Benzofluoranthene 3,4-Benzofluoranthene	
3		Benzo[<i>k</i>]fluoranthene	8,9-Benzofluoranthene 11,12-Benzofluoranthene	Carcinogenic
4		Benzo[<i>def</i>]chrysene	Benzopyrene Benzo[<i>a</i>]pyrene 1,2-Benzopyrene 3,4-Benzopyrene	Carcinogenic
5		Benzo[<i>ghi</i>]perylene	1,12-Benzoperylene	Carcinogenic
6		Indeno[1,2,3- <i>cd</i>]pyrene	Indeno[<i>a,b-3,4a,4</i>]pyrene <i>o</i> -Phenyleneperylene 2,3- <i>o</i> -Phenyleneperylene 3,4- <i>o</i> -Phenyleneperylene	

Reagents

Acetonitrile and all of the solvents used were analytical-reagent grade products (Merck, Darmstadt, G.F.R.).

Column

A glass column (I.D. 50 mm) was packed with GCB (Carbopack B; Supelco, Bellefonte, PA, U.S.A.), surface area 100 m²/g, 80–100 mesh, pH 10.25 after suspension in water. Zettlemayer³² supposed that the oxygen- and sulphur-carbon surface complexes are burnt-off residues left over from the heating at 3000°C of carbon blacks carried out in the production of graphitic carbons.

Apparatus

A Du Pont 840 liquid chromatograph was used, with the following conditions: column, Perkin-Elmer HC-ODS, 25 cm × 0.26 I.D., 10- μ m C₁₈ packing, Part N 089-0716; mobile phase, 80% acetonitrile in water; flow-rate at room temperature, 0.6 ml/min; detector, photometric (254 nm).

Analytical procedure

GCB-liquid system partition coefficients. We chose organic phases in which the PAHs were readily more soluble and added measured amounts of PAHs and 200 mg of GCB to 100 ml of each solvent employed. The suspension obtained was shaken for 8 h in a thermostated room at 25°C in order to reach equilibrium; in this way the compounds examined were divided between the liquid phase and the solid adsorbent. The two phases were separated by filtration on a Gooch filter and the organic phase, after addition of an internal standard (4 methylpyrene), was gently dried, then dissolved in acetonitrile and analysed by HPLC.

Breakthrough plots. The breakthrough plot tests were carried out with aqueous samples (drinking and river waters) to which measured amounts (5 μ g/l) of the six PAHs were added and shaken for 30 min. They were then put in a glass tank and the glass chromatographic column was connected to the bottom of the tank by a tap with a PTFE stopper; the GCB in the column was retained by a glass-wool stopper. The flow of water out of the column was regulated at 4 ml/min by using a water pump. Each aqueous fraction, before and after the passage through the column, was extracted in a separating funnel with three 30-ml volumes of *n*-pentane. The three *n*-pentane extracts were combined and dried by passage over a bed of anhydrous magnesium sulphate. After adding an internal standard (4-methylpyrene) the extracts were evaporated just to dryness, the residues were dissolved in 1 ml of acetonitrile and the solutions were analysed by HPLC.

Recovery of PAHs. After elution, the glass column packed with GCD was detached from the apparatus and a brief flow of nitrogen was forced through it in order to remove traces of PAHs. The adsorbed compounds in the GCB were eluted by passing through the column aliquots of various solvents or solvent mixtures at a flow-rate of 1 ml/min. Each experiment was performed in triplicate.

RESULTS AND DISCUSSION

Table II gives the partition coefficients of the six PAHs for several GCB-organic solvent and GCB-water systems. The partition coefficients were measured in a static arrangement. Eight hours is sufficient to obtain equilibrium conditions.

Of the organic solvents examined, toluene gives a partition coefficient for compounds 1 and 2 that favours almost completely the organic solvent; in this solvent compounds 4, 5, 6 and to some extent 3 have comparable partition coefficients on GCB and in the liquid phase. With benzene alone, compound 1 has a partition coefficient that completely favours the liquid phase; in contrast, the other compounds show values increasingly favourable towards the solid phase. For all other solvents investigated only compound 1 has a partition coefficient intermediate between the liquid and solid phases.

TABLE II
PARTITION COEFFICIENTS IN GCB-LIQUID SYSTEM

<i>Liquid</i>	<i>Partition coefficient*</i>					
	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>
Toluene	0.0091	0.0096	0.0582	0.2593	0.2048	0.2105
Benzene	0.0095	0.1765	0.2270	3.6232	3.3448	3.5714
Dichloromethane	0.0200	5.8824	6.2893	9.7087	—	—
Acetonitrile	0.1000	3.0030	3.9230	—	—	—
<i>n</i> -Hexane	0.2000	7.1870	9.0025	—	—	—
Water	∞	∞	∞	∞	∞	∞

* Compounds 1-6 as in Table I.

Hence it is evident that for the recovery of the six PAHs from the adsorbent matrix elution has to be carried out with a solvent mixture. Table III gives the recoveries obtained using single eluents and mixtures for the desorption. The best recoveries of the six PAHs were obtained with toluene-benzene-acetonitrile (5:2:3).

The breakthrough capacities of the adsorbent are shown in Figs. 1 and 2.

TABLE III
RECOVERY (%) OF PAH COMPOUNDS WITH DIFFERENT ELUENTS

<i>Compound*</i>	<i>Eluent**</i>							
	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>	<i>VII</i>	<i>VIII</i>
1	25	36	80	101	104	97	100	97
2	10	20	20	80	101	91	101	109
3	9	22	19	81	96	87	100	107
4	10	15	17	38	60	41	71	103
5	5	10	13	30	58	20	49	58
6	0	9	10	32	49	18	52	53

* Compounds 1-6 as in Table I.

** I, 100 ml acetonitrile; II, 100 ml *n*-hexane; III, 100 ml dichloromethane; IV, 100 ml benzene; V, 100 ml toluene; VI, 100 ml toluene-acetonitrile (1:1); VII, 100 ml toluene-benzene-acetonitrile (4:4:2); VIII, 100 ml toluene-benzene-acetonitrile (5:2:3).

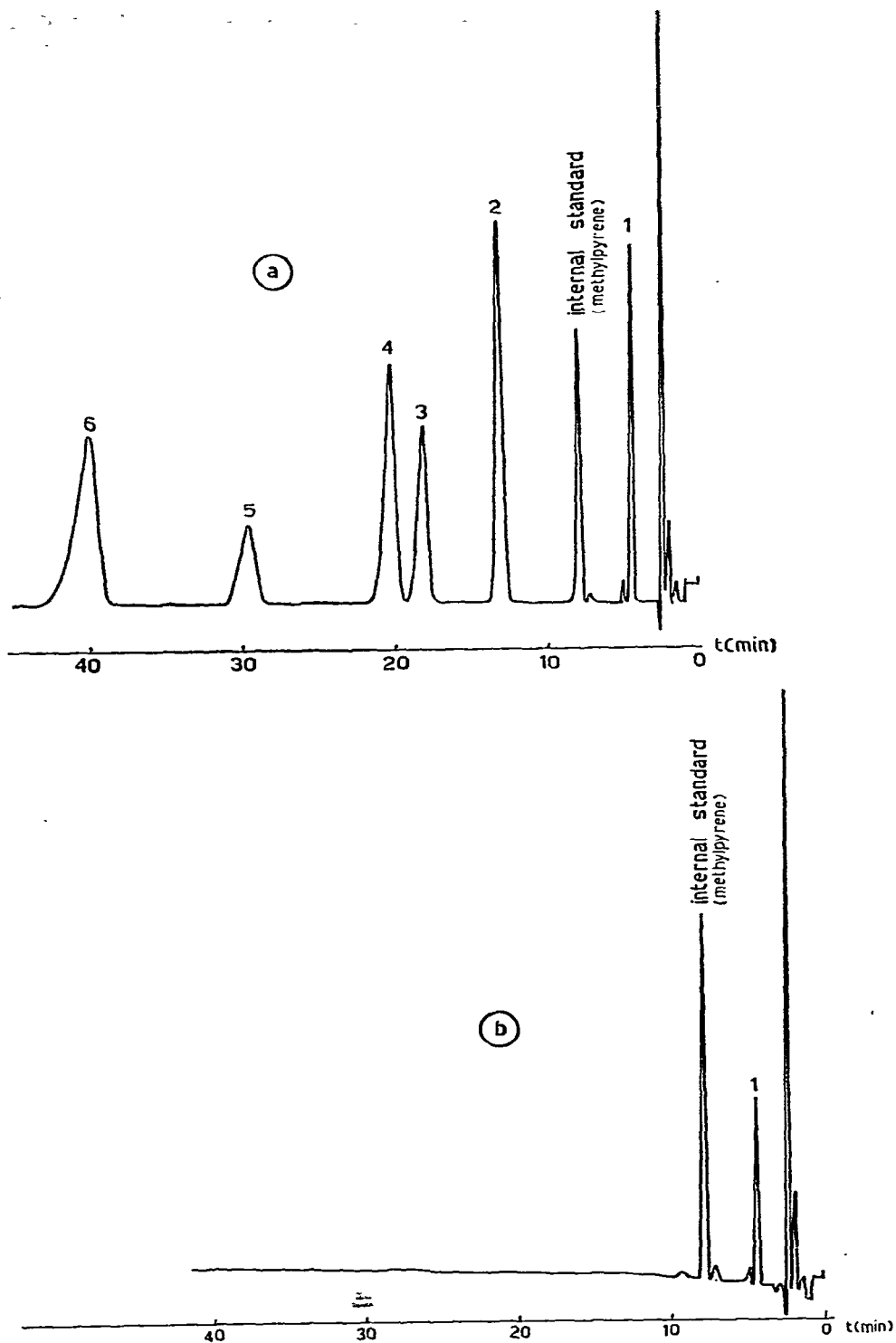


Fig. 1. Chromatograms of PAHs: (a) before passage through adsorbent column (100 mg of GCB); (b) after passage of drinking water (2.5 l) containing all PAHs ($5 \mu\text{g/l}$ of each compound) at a flow-rate of 4 ml/min. Numbers as in Table I.

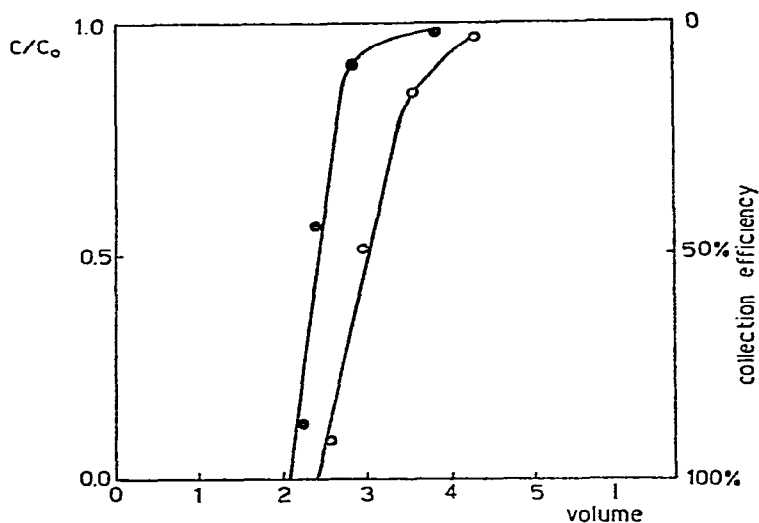


Fig. 2. Breakthrough curves on GCB column (100 mg): ● fluoranthene (5 $\mu\text{g/l}$) in river water; ○ fluoranthene (5 $\mu\text{g/l}$) in drinking water.

The compounds were extracted from water by GCB according to their partition coefficients for the adsorbent-water system. When water containing the organic compounds passes through the concentration column packed with GCB, the chromatographic process can be compared with frontal chromatography. After the passage of a certain volume of the contaminated water a reverse breakthrough occurs and the water emerging from the column contains the organic compounds at continuously increasing concentrations.

In order to recover all the PAHs completely and to measure their amounts correctly, the liquid volume passed through the column must be less than the breakthrough volume of the polycyclic compound showing the smallest retention volume.

Fig. 1 shows that fluoranthene has the smallest retention volume. We can optimize the size of the concentration column using fluoranthene as a model substance in order to obtain the breakthrough curve.

This curve depends on the following factors: type of adsorbent used, structure of the compounds under investigation, composition of the aqueous solution and original concentration of the compounds in water. Fig. 2 shows a graph of the efficiency of collection of the PAHs *versus* the volume of water passed through the column packed with 100 mg of GCB for drinking and river waters. C/C_0 is the concentration of PAH in the effluent divided by the PAH concentration in the influent.

It can be seen from Fig. 2 that fluoranthene has a specific retention volume of 29 l/g and a breakthrough volume of 2.4 l for drinking water, whereas for river water, characterized by the methylene blue anionic surfactants 0.5 mg/l, COD 15 mg/l and pH 6.7, the specific retention volume is 23 l/g and the breakthrough volume is 2.1 l.

It is noteworthy that the differences observed in Fig. 2 had to be ascribed to the effect of the composition of the solution examined. In river water a decrease in the specific retention volume and in the breakthrough volume has to be attributed to dissolved compounds that can change the distribution ratio and consequently increase the solubility of fluoranthene in water.

CONCLUSIONS

The results show that GCB can be used successfully for the recovery of PAHs from aqueous samples. However, it is necessary to bear in mind the composition of the water, as is demonstrated by shifts in the breakthrough curves. The recovery of organic compounds from GCB depends on their molecular structure, but satisfactory results can be achieved by using toluene-benzene-acetonitrile (5:2:3).

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REFERENCES

- 1 *Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants*, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, April 1977.
- 2 *International Standards for Drinking Water*, World Health Organization, Geneva, 3rd ed., 1971 p. 37.
- 3 B. Cathrone and M. Fielding, *Proc. Anal. Div. Chem. Soc.*, 15 (1978) 155.
- 4 R. Harrison, R. Perry and R. Wellings, *Environ. Sci. Technol.*, 10 (1976) 1151.
- 5 R. Harrison, R. Perry and R. Wellings, *Environ. Sci. Technol.*, 10 (1976) 1156.
- 6 K. Grob, K. Grob, Jr. and G. Grob, *J. Chromatogr.*, 106 (1975) 299.
- 7 G. Jungclaus, L. Games and R. Hites, *Anal. Chem.*, 48 (1976) 1894.
- 8 W. May, S. Chesler, S. Cram, B. Gump, H. Herts, D. Enagonio and S. Dyserel, *J. Chromatogr. Sci.*, 13 (1975) 535.
- 9 H. Herts, W. May, S. Chesler and B. Gump, *Environ. Sci. Technol.*, 10 (1976) 900.
- 10 L. H. Suffet, S. Friant, C. Marcinkiewicz, M. J. McGuire and D. T. L. Wong, *J. Water Pollut. Contr. Fed.*, 47 (1975) 1169.
- 11 V. Leoni, G. Puccetti and A. Grella, *J. Chromatogr.*, 106 (1975) 119.
- 12 G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745.
- 13 A. K. Burnham, G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec and R. Willis, *Anal. Chem.*, 44 (1972) 139.
- 14 G. A. Junk, J. J. Richard, H. J. Svec and J. S. Fritz, *J. Amer. Water Works Assoc.*, 68 (1976) 218.
- 15 J. Navratil, R. E. Sieverks and H. F. Walton, *Anal. Chem.*, 49 (1977) 2260.
- 16 D. K. Basu and J. Saxena, *Environ. Sci. Technol.*, 7 (1978) 791.
- 17 K. Ogan, E. Katz and W. Slavin, *J. Chromatogr. Sci.*, 16 (1978) 517.
- 18 F. Eisenbeiss, H. Hein, R. Joester and G. Naundorf, *Chromatogr. Newsl.*, 6 (1978) 8.
- 19 A. R. Oyler, D. L. Bodenner, K. J. Weich, R. J. Liukkonen, R. M. Carison, H. L. Kopperman and R. Capic, *Anal. Chem.*, 50 (1978) 837.
- 20 H. Kunte and J. Borneff, *Z. Wasser Abwasser Forsch.*, 9 (1976) 35.
- 21 H. Wordich, W. Pfannhauser, G. Blaicher and K. Tiefenbacher, *Mitteilungsbl. GDCh-Fachgruppe Lebensmittelchem. Gerichtl. Chem.*, 30 (1976) 141.
- 22 D. Kasiske, K. D. Klinkmüller and M. Sonneborn, *J. Chromatogr.*, 149 (1978) 703.
- 23 M. A. Fox and S. W. Staley, *Anal. Chem.*, 48 (1976) 992.
- 24 B. S. Das and G. H. Thomas, *Anal. Chem.*, 50 (1978) 967.
- 25 K. Ogan, E. Katz and W. Slavin, *Anal. Chem.*, 51 (1979) 1315.
- 26 W. Giger and C. Schaffner, *Anal. Chem.*, 50 (1978) 243.
- 27 A. Bjorseth and G. Eklund, *J. High Resolut. Chromatogr. Commun.*, 2 (1979) 22.
- 28 R. C. Lao, R. S. Thomas and J. L. Honkman, *J. Chromatogr.*, 112 (1975) 681.
- 29 W. Bertsch, E. Anderson and G. Holzer, *J. Chromatogr.*, 112 (1975) 701.
- 30 M. Lee, M. Novotny and K. Bartle, *Anal. Chem.*, 48 (1976) 405.
- 31 A. Bacaloni, G. Goretti, A. Laganà, B. M. Petronio and M. Rotatori, *Anal. Chem.*, in press.
- 32 A. C. Zettlemayer, *J. Colloid Interface Sci.*, 28 (1968) 343.