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## SAMPLE ENRICHMENT FOR GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS IN WATER AND IN ORGANIC MIXTURES

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### SUMMARY

The properties of different kinds of graphitized carbon black as traps for the extraction and preconcentration of polynuclear aromatic hydrocarbons from water and mineral oil have been investigated. The best results are obtained with Carbpack F, eluted with toluene at 100°C. Graphitized carbon black is preferred because of its thermal and chemical stability and its high purity.

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### INTRODUCTION

A very large amount of scientific and technical work has been done in the last two decades on preconcentration techniques and analytical methods for polynuclear aromatic hydrocarbons (PAHs) in environmental matrices, such as atmospheric dust and river, drinking or waste water. The amount of literature is vast; a good review has been published in recent years that covers the most important information on this topic<sup>1</sup>. The analytical methods are well developed for PAH of relatively low molecular weight; capillary gas chromatography (GC) is the method of choice for compounds up to about 250 Daltons. For heavier compounds a good attempt has been made<sup>2</sup> by high-performance liquid chromatography (HPLC) for the separation of PAH up to about 500 Daltons.

Among the extraction and preconcentration steps, Soxhlet extraction is largely used for atmospheric dust or other solid materials, while liquid-liquid extraction is the method suggested for extraction from water<sup>1</sup>. Liquid-solid extraction has been used by Navratil *et al.*<sup>3</sup> and Leoni *et al.*<sup>4</sup>. The idea of using graphitized carbon black (GCB) as an adsorbent for liquid-solid extraction and preconcentration from water and other liquid phases came to us after the success obtained with this material in the preconcentration procedure for pesticides and herbicides from water<sup>5-8</sup>.

GCB is commercially available as a solid column material for liquid-modified gas adsorption chromatography and has recently been made available for these purposes as Carbotrap (Supelco, Bellefonte, PA, U.S.A.). This material has two major advantages over Tenax, Amberlite XA-D2 and polyurethane columns; one is that, being a completely inorganic material, it does not bleed at all into the solvents used and cannot be decomposed by polar solvents or heat treatment<sup>1</sup>. The second advan-

tage is that GCB is the adsorbent of choice for retaining PAH preferentially, because of its structural similarity to condensed aromatic rings. In this respect, this material is the best available. However, problems may arise when the PAH adsorbed on the graphitic surface must be recovered with a few ml of an organic solvent. In fact, the main advantage of liquid-solid extraction is that few ml of solvent are necessary to recover the organics trapped. Benzene would work best but it has been proscribed for environmental health reasons. Toluene has been chosen, because it is the best PAH solvent and its low volatility is not important since no evaporation of the solution is required if the concentration of PAH in the original liquid phase is at the low ppb level. In this paper some results obtained with GCB of different surface areas in the recovery of PAH from water and oil are presented.

## EXPERIMENTAL

Three types of GCB, obtained from Supelco, have been tested: Carbopack B, surface area *ca.* 100 m<sup>2</sup>/g; Carbopack C, *ca.* 11 m<sup>2</sup>/g and Carbopack F, *ca.* 6 m<sup>2</sup>/g. These materials were sieved in the 60–80 mesh range and Soxhlet extracted for 24 h to remove possible residues of organic material. In fact, GCB is extremely pure, but it may adsorb various kinds of organic substances from air or moisture. The material was then stripped with helium at 350°C according to the procedure previously reported<sup>9</sup>.

The apparatus used for water extraction and sample preconcentration is illustrated in Fig. 1. The water sample, containing a known amount of PAH, is connected to the trap, and the flow-rate is controlled by means of a needle valve. The PAH solution in water was prepared by injecting a known amount of a standard solution in acetone while stirring. The use of this solvent or of methanol is recommended on the basis of the results described previously<sup>6,7</sup>. In this way, a true solution of PAH in water is obtained, provided of course that the concentration of the stock solution is such that water is not saturated. If a non-polar solvent is used, the formation of emulsions is unavoidable and the formation of microdroplets prevents the use of this method of preconcentration. The average concentration of PAH in water ranged between 1 and 0.5 ppb (10<sup>-9</sup>) w/v.

A stainless-steel tube (6 cm × 4 mm I.D.) was used as a trap and filled with about 400 mg of Carbopack F and C or with about 200 mg Carbopack B, according to the relative densities of the different materials. Glass-wool plugs kept the material stationary. Multiple traps, containing different kinds of carbon blacks, have also been used, in order to obtain increased selectivity when working with engine oil as a matrix for PAH. Carbopack F, having a smaller surface area was placed first, while Carbopack B was placed last to retain the low-molecular-weight compounds. After the water had passed through the trap at a rate of about 2.5 ml/min (regulated by slight nitrogen pressure), the trap was dried with a stream of nitrogen at room temperature.

The extraction procedure was analogous, but the solvent (toluene) was heated to 100°C by means of a heating jacket. Toluene was passed through at a rate of 0.5 ml/min and every 1-ml fraction was collected separately for analysis. When PAH were analysed in an organic matrix, such as engine oil, the oil was also passed through the GCB trap. In our experiments we have used "white oil", artificially polluted with

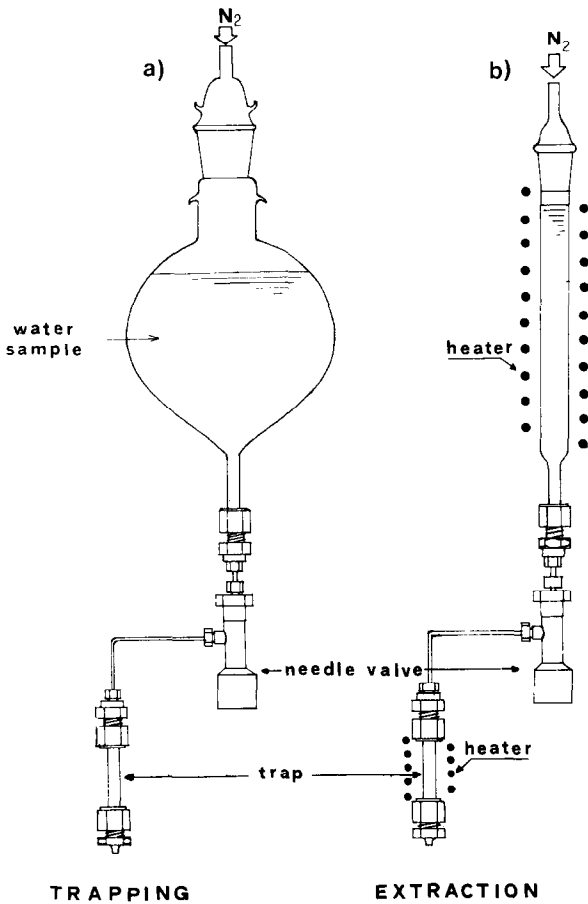


Fig. 1. Scheme of the trapping and extraction apparatus.

1 ppm of the PAH tested. The factor of  $10^3$  takes into account the difference between the concentrations of these compounds in the two matrices when real samples have to be analysed. Before passing it through the column, the oil was diluted 10–20 times in pentane to decrease its viscosity. Because of the high solubility of PAH in oil, the trap was made in a different way: 400 mg Carboxpack F were placed in a stainless-steel tube of the same dimensions as the one used for water analysis. Below this column, a similar tube, filled with 200 mg Carboxpack B, was placed to collect any material unadsorbed by the lighter adsorbent. Because the two adsorbents have different densities, the length and diameter of the second column was the same. Then, 20 ml *n*-pentane were passed through the two columns at room temperature in order to separate the non-polycyclic fraction of the oil. At this point, the same procedure was followed as for water samples. Hot toluene was passed through the columns after they were separated. The data in Table II were thus obtained. In practice, only one trap can be used, if the lower part is filled with Carboxpack B and the upper part with Carboxpack F. When eluting with toluene, the traps should be reversed for obvious reasons. Analyses were carried out with a 30-m fused-silica SE-54 bonded-

phase capillary column (Supelco) in a DANI 3600 (Monza, Italy) gas chromatograph, equipped with a programmed temperature vaporizer (PTV). Gas chromatographic-mass spectrometric (GC-MS) analyses were carried out with a VG Micromass 70-70H (Altrincham, U.K.) instrument, coupled with a DANI 3800 PTV, with the same equipment and the same capillary column.

## RESULTS AND DISCUSSION

In Table I the results obtained for some of the classical PAH are reported when various types of Carbopacks were used under different conditions. Carbopack C appears to be unsuitable for this work. Even the very light PAH, such as acenaphthene yielded an unsatisfactory recovery. The situation was improved to a large extent when Carbopack F (6.0 m<sup>2</sup>/g) was used. An acceptable recovery was obtained at room temperature for compounds containing up to four condensed rings. However, for five-ring compounds, good results were obtained only by eluting the column with toluene heated to 100°C. Under these conditions, even the two six-membered-ring compounds were recovered to a significant extent, although not completely satisfactorily. The recoveries reported refer to the first 3 ml of toluene passed through the column, with an enrichment factor of more than 300. Under these conditions, 1 ppb of benzo[*a*]pyrene yields a very good peak quite usable for quantitative analysis with a 30-m capillary column and a flame ionization detector. A mass spectrometer, used in the selected ion monitoring (SIM) mode, gave even better results. Quantitative data were obtained in a range of concentrations down to 0.1 ppb.

In Fig. 2 a graphic representation of the elution of PAH with toluene is reported. It is useful to show that the phenomenon occurring when PAHs are adsorbed

TABLE I

### RECOVERY (%) OF PAH FROM WATER BY USING DIFFERENT ADSORBENTS

The temperatures given are the toluene temperatures during extraction. Total toluene volume used: 5 ml in each case.

Compound	Recovery (%)		
	Carbopack C (25°C)	Carbopack F (25°C)	Carbopack F (100°C)
Acenaphthylene	59	97	93
Acenaphthene	56	98	95
Fluorene	55	98	99
Phenanthrene	51	98	99
Anthracene	53	96	92
Fluoranthene	62	98	94
Pyrene	62	97	93
Benzo[ <i>a</i> ]anthracene	28	74	87
Chrysene	26	75	88
Benzo[ <i>k</i> ]fluoranthene	19	24	86
Benzo[ <i>b</i> ]fluoranthene	18	23	86
Benzo[ <i>a</i> ]pyrene	16	22	81
Dibenz[ <i>a,h</i> ]anthracene	—	—	23
Benzo[ <i>g,h,i</i> ]perylene	—	—	22

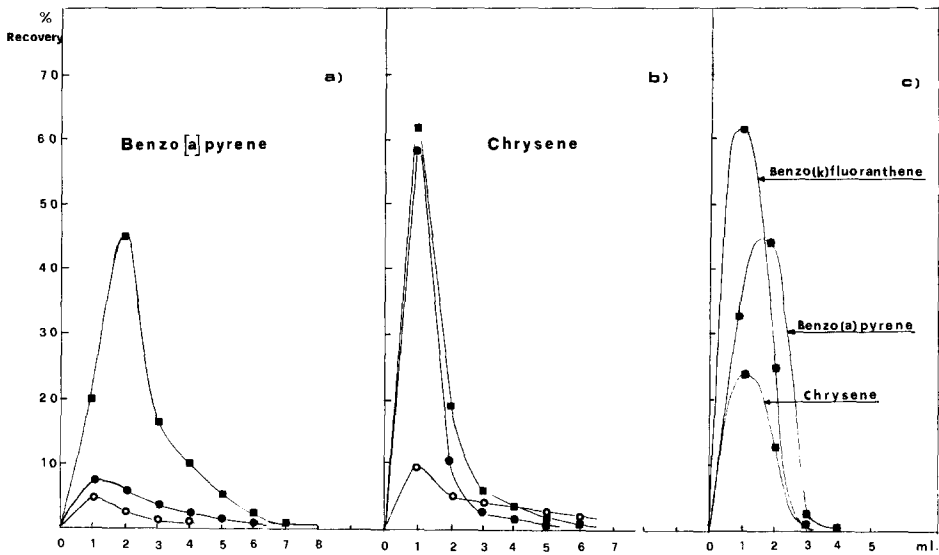


Fig. 2. Elution curves from the trap for some PAH using toluene as mobile phase. a and b; extracted from water; c, extracted from mineral oil. ■, Carbo-pack F, toluene, 100°C; ●, Carbo-pack F, toluene, 25°C; ○, Carbo-pack C, toluene, 25°C.

from water is irreversible adsorption, a different situation from the simple strong retention. It can be diminished by changing the solvent, but the only way to avoid irreversible adsorption is to operate at higher temperature, as we have done to obtain the data of Table I.

A different situation obtains when the matrix containing the PAH is of organic nature. First, these compounds are very soluble in the matrix, so that only a great

TABLE II

RECOVERY (%) OF SOME PAH FROM OIL BY USING TWO TANDEM TRAPS OF CARBO-PACK B AND F

Each trap was eluted with 3 ml toluene.

Compound	Recovery (%)		
	Carbo-pack B (100°C)	Carbo-pack F (100°C)	Total (B + F)
Phenanthrene	41	—	41
Anthracene	56	—	56
Fluoranthene	83	6	89
Pyrene	82	6	88
Chrysene	43	38	81
Benz[ <i>a</i> ]anthracene	45	39	84
Benzo[ <i>k</i> ]fluoranthene	—	88	88
Benzo[ <i>a</i> ]pyrene	—	83	83
Bibenz[ <i>a,h</i> ]anthracene	—	41	41
Benzo[ <i>g,h,i</i> ]perylene	—	45	45

affinity for the adsorbent will cause retention. In fact, no recovery at all was obtained for the very light PAH, even on Carbopack B, so that these results are not reported in Table I, but six-membered-ring compounds were recovered. The results in Table II show that the PAH are apparently less strongly retained by the GCB when contained in an organic matrix than in an aqueous matrix. This is due to two reasons: one is the higher affinity for the solid phase in comparison with the liquid phase when the latter is water. Another reason is that the high-molecular-weight components of the oil are adsorbed by the GCB and modify the graphitic surface making it less active. This is shown graphically in Fig. 2c. The elution curves obtained for some PAH desorbed with hot toluene from Carbopack F after being adsorbed from oil are practically symmetrical. A striking difference is observed in comparison with the curves obtained after adsorption of PAH from water. In our opinion, the best explanation for this behaviour is that the adsorbent is modified by the heavy components of the oil in such a manner that the number and activity of the active sites are diminished.

In conclusion, this work shows that GCB can be used with advantage to pre-concentrate trace levels of PAH in different matrices, especially because it exhibits no bleeding and has a high selectivity.

#### ACKNOWLEDGEMENTS

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