

CHROM. 20 741

PERFORMANCE OF GRAPHITIZED CARBON BLACK CARTRIDGES IN THE EXTRACTION OF SOME ORGANIC PRIORITY POLLUTANTS FROM WATER

F. MANGANI, G. CRESCENTINI, P. PALMA and F. BRUNER*

Istituto di Scienze Chimiche, Università di Urbino, Piazza Rinascimento 6, 61029 Urbino (Italy)

SUMMARY

The use of graphitized carbon black (GCB) cartridges for the extraction of organic pollutants (pesticides, phthalates, herbicides and polynuclear aromatic hydrocarbons) from water is discussed. Recovery tests carried out by spiking either the adsorbent or the water showed that nearly 100% recoveries can be obtained in most instances with 1 ml of a suitable eluent using 50 mg of GCB (Carbopack B). Examples of analyses of actual samples by gas chromatography–mass spectrometry are also shown. Levels as low as 10 ppt can be determined.

INTRODUCTION

Sample preparation and preconcentration prior to gas chromatography and/or gas chromatographic–mass spectrometric (GC–MS) analysis of organic pollutants in water traditionally relies on liquid–liquid extraction methods. However, solid-phase extraction is becoming an emerging technique in this field, because of substantial advantages over liquid–liquid extraction: (i) the use of much smaller volumes of expensive or hazardous solvents; (ii) a shorter time and simpler facilities (very little glassware is needed); and (iii) fewer steps during sample preparation. Therefore, the risk of sample loss and introduction of artefacts is considerably reduced. In addition, the commercial availability of disposable cartridges packed with a variety of adsorbents makes the use of solid-phase extraction more attractive than in the past. XAD resins^{1,2}, porous polyurethane foams^{3,4}, Tenax^{5,6}, porous polymer beads⁷, graphitized carbon black^{8–14} and C₁₈ bonded phase^{15–18} have been studied as adsorbents for the extraction of several classes of organic pollutants from water.

In this work a small diameter cartridge packed with Carbopack B was studied for the recovery of some important priority pollutants such as pesticides, herbicides, phthalates and polynuclear aromatic hydrocarbons (PAHs). Carbopack B is the commercial name for a non-specific and non-porous graphitized carbon black with a surface area of about 90 m²/g. Because of the peculiar homogeneity of its surface it has been extensively used in gas–liquid–solid chromatography^{19–23}, where the surface properties are modified according to the performance needed, by adding a suitable amount of a liquid phase. Carbopack B has been already used for the sample enrichment of some organic compounds from water, air and biological fluids^{9,12,24–26}.

EXPERIMENTAL

Reagents

Pesticide-grade acetone, light petroleum (b.p. 40–60°C) and toluene from Carlo Erba (Milan, Italy) were used for sample extraction and the preparation of standards. Standard kits of pesticides, herbicides, PAHs and phthalates, 2 mm I.D. C₁₈ cartridges (Supelclean LC-18, 40 µm, 3 ml) and Carbo-pack B (60–80 mesh) were purchased from Supelco (Bellefonte, PA, U.S.A.). Porapak P (50–80 mesh) and Tenax TA (35–60 mesh) were obtained from Chrompack (Middelburg, The Netherlands). All capillary columns were obtained from Supelco.

Instrumentation and analysis

A Carlo Erba MRGC 5160 Mega gas chromatograph equipped with a flame ionization detector and on-column injector and a Dani 6500 gas chromatograph (Dani, Monza, Italy) equipped with an electron-capture detector and programmed-temperature vaporizer injector were used for GC analysis when recovery tests were performed.

A Hewlett-Packard 5270 quadrupole mass spectrometer (Hewlett-Packard, Avondale, PA, U.S.A.) coupled with a Hewlett-Packard 5990 gas chromatograph equipped with a split/splitless injector was used for the analysis of actual samples. The GC analysis of phthalates and PAHs was performed on an SPB5 capillary column (30 m × 0.32 mm I.D.) with a 0.25-µm film thickness and temperature programming from 90 to 120°C at 40°C/min then up to 270°C at 12°C/min. The same column was used for the analysis of herbicides but the temperature programme was 2 min at 130°C and then 4°C/min up to 230°C. The GC analysis of pesticides was carried out on an SPB 608 capillary column (30 m × 0.25 mm I.D.) with a 0.25-µm film thickness and a temperature programme of 4 min at 150°C and then 8°C/min up to a final temperature of 290°C.

The GC-MS analysis of actual samples was carried out on the SPB5 column described above using the following temperature programmes: 2 min at 100°C and then 6°C/min up to 300°C for the analysis of herbicides and phthalates and 1 min at 50°C and 10°C/min up to 300°C for the analysis of pesticides and PAHs. The mass spectrometer was used in the selected ion monitoring mode (SIM). The most intense and structurally significant ions in the mass spectra of the single compounds were monitored in this instance. Two different SIM programmes were used for pesticides, phthalates and herbicides and for PAHs. Helium was used as the carrier gas.

Apparatus and procedure

The graphitized carbon black cartridges were made of glass-lined stainless-steel tubing (6 cm × 0.3 cm I.D.) packed with 50 mg of Carbo-pack B (60–80 mesh), kept in place by two plugs of silanized glass-wool. Both the Carbo-pack B and the silanized glass-wool were previously extracted in a Soxhlet apparatus for 6 h using light petroleum-toluene (1:1).

Cartridges containing materials other than Carbo-pack B were prepared following the same procedure and using the same amount of adsorbent (50 mg) with the exception of the C₁₈ cartridges, which were used as received.

The apparatus used for the recovery tests and extraction of actual samples is shown in Fig. 1. The upper part of the cartridge is connected through a stainless-steel

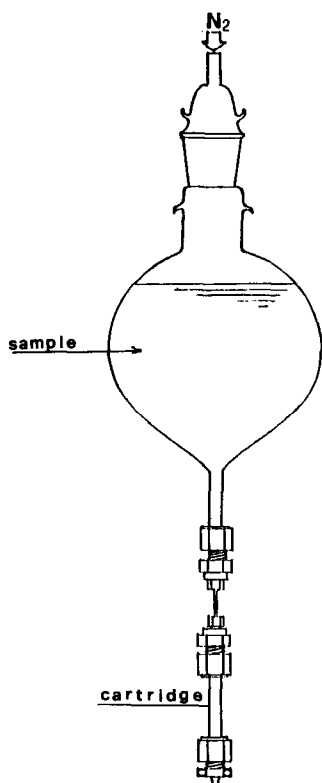


Fig. 1. Extraction apparatus.

union to a glass reservoir containing the water. A water flow-rate of 15 ml/min was ensured by applying a slight nitrogen pressure.

Recovery tests were carried out by following two different procedures. In the first, 100 μl of a standard solution in acetone containing 0.20–20 ng/ μl of the compounds of interest were placed on the top of the cartridge and the solvent was evaporated under a flow of nitrogen. A 10-ml volume of water was allowed through the cartridge, which was then dried again under a flow of nitrogen. The compounds were eluted with 1 ml of light petroleum–toluene (1:1). The choice of the elution mixture was based on previous studies carried out in this laboratory⁹. In the second procedure, 1 l of organic-free potable water was allowed through the trap, after having been spiked with 100 μl of the same standard solution according to a technique already described⁹. Also, in this instance the cartridge was dried under a flow of nitrogen and the compounds were eluted using the same solution as employed in the first procedure. The recoveries were calculated by comparing the chromatograms obtained after injection of the standard solutions and injection of the eluate from the cartridge. The recovery data are averages of three replicates and the relative standard deviation, calculated for some selected compounds with eight replicates, was 3%.

Before use, all glassware was washed with a detergent (Extran Ma 02 neutral) and thoroughly rinsed with doubly distilled water and acetone. A blank analysis with

TABLE I
RECOVERIES OF SOME CHLORINATED PESTICIDES FROM DIFFERENT ADSORBENTS

Pesticide	Recovery (%)				
	Carbopack B	Tenax	Porapak P	C ₁₈ *	C ₁₈ **
α -BHC	93	81	55	95	94
β -BHC	100	81	60	93	94
γ -BHC	100	77	51	93	—
Heptachlor	97	94	70	96	77
δ -BHC	97	94	50	96	93
Aldrin	96	88	71	88	87
Heptachlor epoxide	95	100	63	99	—
4,4'-DDE	100	87	77	93	—
Dieldrin	100	95	80	95	94
Endrin	99	89	75	94	—
4,4'-DDD	100	83	63	92	—
4,4'-DDT	100	86	55	95	83

* This work.

** Ref. 15.

the whole apparatus using 1 l of organic-free water showed no significant presence of the compounds of interest.

Thermal desorption was not tested thoroughly, but a few experiments showed that the recovery is poor in most instances and that thermal decomposition may occur with some compounds.

RESULTS AND DISCUSSION

In Table I the recoveries of twelve chlorinated pesticides from cartridges packed with five different adsorbents using only 1 ml of the extraction mixture are shown. A 50-mg amount of adsorbent was used in all instances and the recovery tests were carried out following the first procedure, *i.e.*, by placing on the top of the cartridge 100 μ l of a standard solution containing 0.50 ng/ μ l of each pesticide.

The recoveries are very low for Porapak P. Tenax TA shows a better performance, although some problems seem to exist with the elution of the benzene hexachlorides (BHCs) in general and of γ -BHC in particular. Some results obtained with Tenax GC have recently been reported⁶ using the adsorption-thermal desorption technique. Although only four compounds were tested, and a comparison is possible only for dieldrin and *p,p'*-DDE, the data are similar to those shown in Table I. Carbopack B shows the best overall recoveries with values near to 100% in most instances. Lower but still good recoveries are obtained with C₁₈. It should be noted that a double amount of adsorbent was used in this instance. The different recoveries obtained with Carbopack B and C₁₈ cannot be ascribed to the choice of the elution solvent. In fact, the data from ref. 15 show that similar values are obtained when ethyl acetate, selected after a detailed investigation, was used. The cartridge used in that work contained 200 mg of the adsorbent and 1.5 ml of ethyl acetate were used.

If organic pollutants have to be determined at trace levels it is important to

TABLE II
RECOVERIES FROM CARBOPACK B FOR DIFFERENT AMOUNTS OF PESTICIDES

Pesticide	Recovery (%)			
	50 ng	20 ng	10 ng	5 ng
α -BHC	93	93	92	92
β -BHC	100	100	100	100
γ -BHC	100	100	98	85
Heptachlor	97	98	98	96
δ -BHC	97	98	97	75
Aldrin	96	96	92	91
Heptachlor epoxide	95	95	95	93
4,4'-DDE	100	100	100	100
Dieldrin	100	100	100	100
Endrin	99	99	96	95
4,4'-DDD	100	100	86	86
4,4'-DDT	100	100	100	100

establish when irreversible adsorption becomes relevant. Table II shows the data obtained when different amounts of pesticides were placed on the top of the Carbo-pack B cartridge and 100 μ l of solutions containing 0.50, 0.20, 0.10 and 0.05 ng/ μ l of the single compounds were used with 1 ml of light petroleum-toluene (1:1) as eluent. It can be seen that a slight but consistent decrease in the recovery is observed when 5 ng of pesticides are desorbed. Moreover, this concerns only two compounds (γ - and δ -BHC), so that it can be safely stated that irreversible adsorption or the effect of decomposition is significant below the 5-ng level. Consequently, the use of a 50-mg Carbo-pack B cartridge in the extraction step allows the determination of very low levels of pesticides (5 ppt in 1 l of water).

Table III shows the recovery data for pesticides and the other classes of compounds studied, by spiking the adsorbent directly and by spiking the water. In the first instance 50 ng of pesticides and herbicides and 500 ng of phthalates and PAHs were used to spike the adsorbent. In the second, 1 l of water was spiked with the same amounts of pollutants so that the concentrations were 5 ppt for pesticides and herbicides and 50 ppt for phthalates and PAHs.

When the adsorbent was spiked, the recoveries for herbicides, phthalates and PAHs were similar to those obtained for pesticides, except for the heavier PAHs. This problem may be solved by extracting with toluene at 100°C²⁷ or by using a Carbo-pack with a smaller surface area. The small difference in the recoveries when the water was spiked is probably due to adsorption on the glass wall of the reservoir^{1,9,19}. The larger differences observed for di-*n*-octyl phthalate and some PAHs can be explained by the poor solubility of these compounds in water. In fact, if the cartridge was extracted with several portions of 1 ml of the eluent no appreciable amount of the compounds of interest was found after the first 1-ml fraction.

A 1-l volume of mineral water was extracted by the method described and analysed by capillary GC with flame ionization detection after storage in a plastic

* Throughout this article, the American billion (10^9) and trillion (10^{12}) are meant.

TABLE III

RECOVERIES OF PESTICIDES, HERBICIDES, PHTHALATES AND PAHs OBTAINED BY SPIKING THE ADSORBENT (A) AND BY SPIKING THE WATER (B)

2,4-DME = 2,4-dichlorophenoxy acetic acid methyl ester, 2,4,5-TME = 2,4,5-trichlorophenoxy acetic acid methyl ester, DCPA = 2,3,5,6-tetrachloroterephthalic acid dimethyl ester.

Compound type	Recovery (%)		
	Compound	A	B
Pesticides	α -BHC	93	94
	β -BHC	100	96
	γ -BHC	100	95
	Heptachlor	98	87
	δ -BHC	98	94
	Aldrin	96	90
	Heptachlor epoxide	95	97
	4,4'-DDE	100	92
	Dieldrin	100	97
	Endrin	99	99
	4,4'-DDD	100	94
	4,4'-DDT	100	95
Herbicides	2,4-DME	97	92
	Trifluralin	98	92
	Simazine	100	97
	Atrazine	96	93
	Propazine	100	97
	2,4,5-TME	96	92
	DCPA	99	98
Phthalates	Di- <i>n</i> -Butylphthalate	100	100
	Butylbenzylphthalate	100	100
	Bis(2-Ethylhexyl) phthalate	100	100
	Di- <i>n</i> -octyl phthalate	100	50
PAHs	Acenaphthene	99	87
	Acenaphthylene	100	88
	Fluorene	89	89
	Phenanthrene	99	88
	Anthracene	100	87
	Fluoranthene	69	57
	Pyrene	65	48

bottle for 6 months. The presence of ethylhexyl phthalate was detected at a level of 0.6 ppb. The column and chromatographic conditions were as described under Experimental.

Water from a river near Urbino (Metauro) was analysed by GC-MS and the reconstructed ion chromatograms are shown in Fig. 2. In Fig. 2a the SIM programme was selected to detect the pesticides, phthalates and herbicides of interest. PAHs were detected in Fig. 2b by injecting another aliquot of the same sample with a suitable SIM programme. Pesticides were absent, as expected, but atrazine, phthalates and PAHs are present at ppb and ppt levels. The presence of atrazine is probably due to leaching from the nearby fields by rain water. A number of unknown peaks were detected that give a response to the m/z values in the programmes.

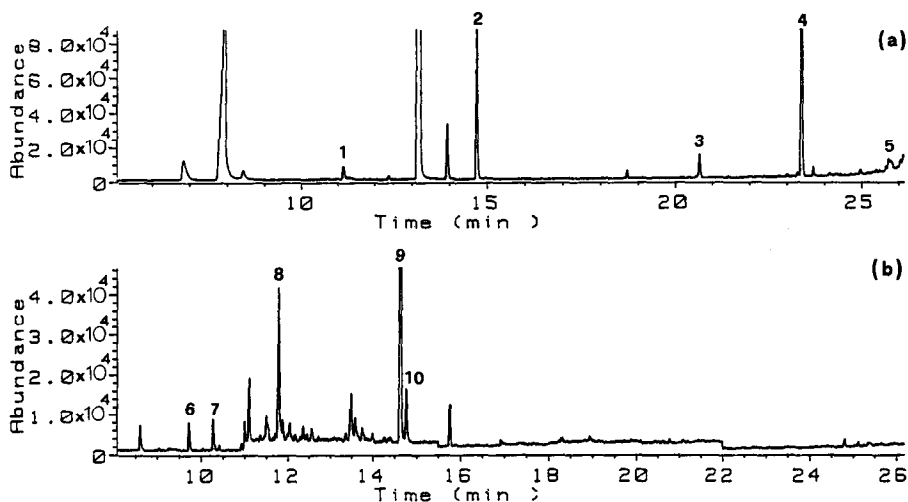


Fig. 2. Reconstructed ion chromatograms of 1 l of river water from near Urbino obtained by two injections of 2 μ l of the same light petroleum-toluene extract (1 ml) from a Carboxpack B cartridge. Chromatographic conditions: see text. (a) Pesticides, herbicides and phthalates; (b) PAHs. Concentrations (μ g/l): (1) atrazine, 0.60; (2) di-*n*-butyl phthalate, 1.40; (3) butylbenzyl phthalate, 0.60; (4) bis(2-ethylhexyl) phthalate, 4.30; (5) di-*n*-octyl phthalate, 0.30; (6) acenaphthylene, 0.01; (7) acenaphthene, 0.01; (8) fluorene, 0.05; (9) phenanthrene, 0.02; (10) anthracene, 0.02.

CONCLUSION

The extraction method presented here is very fast and allows quantitative recoveries (nearly 100%) of the compounds of interest. As a very low volume of eluent mixture is used, a high preconcentration ratio is reached (1:1000). Further, light petroleum can be eliminated in few minutes by flushing with nitrogen, so that the ratio can be as high as 1:2000. The cartridge can be reused and a large number of extractions per time unit can be carried out by a single operator. If GC-MS analysis with a quadrupole mass spectrometer is used, 10 ppt of the compounds of interest can be determined in water.

The limitations concerning the elution of the heavier PAHs can be overcome by using a graphitized carbon black with a much smaller surface area. This problem is currently under study in this laboratory.

ACKNOWLEDGEMENT

The authors thank E. Sisti for technical assistance.

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