Journal of Chromatography, 509 (1990) 135–140
Elsevier Science Publishers B.V., Amsterdam

CHROM. 22 204

Use of polymeric sorbents for the off-line preconcentration of priority pollutant phenols from water for high-performance liquid chromatographic analysis

B. GAWDZIK*, J. GAWDZIK and U. CZERWIŃSKA-BIL
Institute of Chemistry, Maria Curie-Skłodowska University, 20031 Lublin (Poland)

ABSTRACT

The use of porous polymeric minicolumns for the determination of phenols from the U.S. Environmental Priority Pollutant List was studied. For the off-line preconcentration of priority pollutant phenols from water by solid-phase extraction, minicolumns packed with 1,4-di(methacryloyloxymethyl)naphthalene–divinylbenzene copolymer and Amberlite XAD-4 were used. In order to compare the sorption properties of these polymeric sorbents, the recoveries and breakthrough volumes of phenol, *p*-nitrophenol, 2,4-dinitrophenol, *o*-chlorophenol, *o*-nitrophenol, 2,4-dimethylphenol, 4-chloro-*m*-cresol, 4,6-dinitro-*o*-cresol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol were studied.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) lists eleven substituted phenols as "priority pollutants"[1]. The impact of priority pollutant phenols on the aquatic environment is subject to increasing attention. These compounds are important industrial chemicals of widespread usage. Phenols often observed in waste water are released into the environment by various industrial plants. These chemicals are generated by a number of processes, including the petroleum industry, the pulp and paper industry and in the syntheses of plastics and drugs[2–4].

Chlorinated phenols are formed in drinking water as a result of treatment. In aqueous solutions they occur in ppm concentrations in waste water to sub-ppb levels in drinking water[5,6]. Even at low concentrations, phenols have an adverse effect on the taste and odour of drinking water[7].

Owing to their high toxicity, effective methods for the determination of trace amounts of priority pollutant phenols in drinking and waste waters are needed. In order to measure low levels of phenols in water, preconcentration methods must be used before the analysis. Preconcentration can be performed by solvent extraction or by sorption on solids.

Coutts *et al.*[8] formed the acetate esters of six phenols before extraction with dichloromethane from water and gas chromatographic (GC) analysis. Hajslova *et al.*[9]

0021-9673/90/$03.50

also applied solvent extraction of chlorinated phenols before their determination in the form of different derivatives. Realini[10] determined priority pollutant phenols using high-performance liquid chromatography (HPLC). Preconcentration was based on ion-pair extraction. Bigley and Grob[11] applied solid-phase extraction to preconcentrate ten priority pollutant phenols. The detection of phenols was carried out using HPLC and post-column reaction with 4-aminoantipyrine and potassium hexacyanoferrate (III). Good recoveries of priority pollutant phenols from water solutions were obtained by Chladek and Marano[12] using bonded silica cartridges for preconcentration. HPLC analysis accompanied by on-line preconcentration of priority pollutant phenols was used by Baldwin and Debowski[13]. Tateda and Fritz[14] designed an Amberlite XAD-4 minicolumn for the preconcentration of some phenols, while Werkhoven-Goewie *et al.*[15,16] proposed styrene–divinylbenzene copolymers as an effective sorbents for this purpose.

In a previous paper, a porous copolymer of 1,4-di(methacryloyloxymethyl)-naphthalene (1,4-DMN) and divinylbenzene (DVB) was investigated as a sorbent for off-line preconcentration of chlorophenols[17]. As a continuation of studies on different applications of 1,4-DMN–DVB copolymer, this sorbent was used for the preconcentration of priority pollutant phenols from water. Amberlite XAD-4 was used for comparison purposes.

EXPERIMENTAL

Apparatus

A Liquochrom Model 2010 liquid chromatograph (Labor, Budapest, Hungary) equipped with an injection valve with a sample loop of 20 μl, a variable-wavelength UV detector and a 250 mm × 4 mm I.D. LiChrosorb RP-18 (10 μm) column was used. For the determination of ten of the priority pollutant phenols acetonitrile–10^{-3} *M* phosphoric acid (30:70, v/v) was used as the mobile phase, but for pentachlorophenol acetonitrile–10^{-3} *M* phosphoric acid (80:20, v/v) was used. A flow-rate of 1 ml/min was used throughout the analyses. Detection was performed at 220 nm. Quantitation of the chromatograms was based on peak heights using calibration graphs.

Chemicals

Analytical-reagent grade chemicals were used. *o*-Chlorophenol, 2,4-dinitrophenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 4-chloro-*m*-cresol, 4,6-dinitro-*o*-cresol and 2,4,6-trichlorophenol were purchased from Merck (Darmstadt, F.R.G.), phenol, *o*-nitrophenol, *p*-nitrophenol, methanol, anhydrous phosphorus pentoxide and 85% phosphoric acid from POCh (Gliwice, Poland) and pentachlorophenol from Koch-Light (Colnbrook, U.K.). Owing to the small transmission of acetonitrile (Laborchemie, Apolda, G.D.R.) at 220 nm it was preliminary distilled from over anhydrous phosphorus pentoxide. Doubly distilled water was used for the preparation of mobile phases and solutions for the recovery studies.

The sample of 1,4-DMN–DVB copolymer (0.04–0.05 mm) whose properties were described in a previous paper[17] was used. Amberlite XAD-4 (Rohm and Haas, Philadelphia, PA, U.S.A.) was ground and sieved to 0.04–0.05 mm and purified according to the procedure described by Junk *et al.*[18].

Recovery studies

For the preconcentration of priority pollutant phenols from water, laboratory-made cartridges and a simple vacuum manifold, as described previously[17,19], were used. The weight of both sorbents (1,4-DMN–DVB and Amberlite XAD-4) was 200 mg. The dimensions of the sorbent beds in the dry state were length 10 mm and I.D. 9 mm. The volumes of the bed were about 1 ml. The Amberlite XAD-4 bed swelled to about 1.5 ml in methanol during the regeneration and elution steps. The volume of the 1,4-DMN–DVB bed did not change significantly.

Before sampling, each minicolumn was conditioned with 10 ml of methanol using a vacuum manifold and water aspirator, then 5 ml of doubly distilled water were added to prepare the surface of the sorbent for adsorption.

Water samples were prepared from a methanolic stock solution containing 20 μg/ml of each phenol by dilution with doubly distilled water to 0.4 μg/ml. Different volumes of these water samples were sucked through the minicolumn immersed in the sample and connected by PTFE tubing to the water aspirator. After the sample had passed through the minicolumn, the latter was installed in the vacuum manifold and 1 ml of doubly distilled water was flushed through it. The vacuum was maintained for 5 min in order to dry the sorbent bed. Priority pollutant phenols were then eluted into a collection tube with three 500-μl aliquots of methanol. After all the sorbates had eluted from the minicolumn, each sample was diluted with methanol to 2 ml or to a multiple of this volume.

The eluate in the collection tube was analysed directly or capped and stored in a freezer. Volumes of 20 μl of preconcentrated samples were injected into the liquid chromatograph. A standard phenol solution (20 μg/ml) was also injected into the chromatograph under the same conditions.

The percentage recovery of priority pollutant phenols was calculated directly from a comparison of peak heights. Recoveries were calculated as mean values of three analyses.

Preconcentration of pentachlorophenol was performed separately by the same procedure.

RESULTS AND DISCUSSION

The problem of the determination of priority pollutant phenols has been a subject of several papers[10,11,20,21]. Recovery studies require complete separation of the peaks of the standard compounds and large peak areas to minimize errors. Complete separation of ten priority pollutant phenols with the exception of pentachlorophenol was achieved using acetonitrile–10^{-3} *M* phosphoric acid (30:70, v/v) as the mobile phase as proposed by Realini[10]. The addition of phosphoric acid to the mobile phase was necessary to prevent peak tailing due to ionized phenols. Comparable peak heights of phenols were attained at a wavelength of 220 nm. The separation of ten priority pollutant phenols is shown in Fig. 1.

In order to preconcentrate priority pollutant phenols from water solutions, minicolumns packed with 1,4-DMN–DVB copolymer or the commonly used Amberlite XAD-4 were applied. 1,4-DMN–DVB porous polymer proved to be an effective sorbent for the preconcentration of various chlorophenols[17].

Table I gives the recoveries of priority pollutant phenols on these materials from

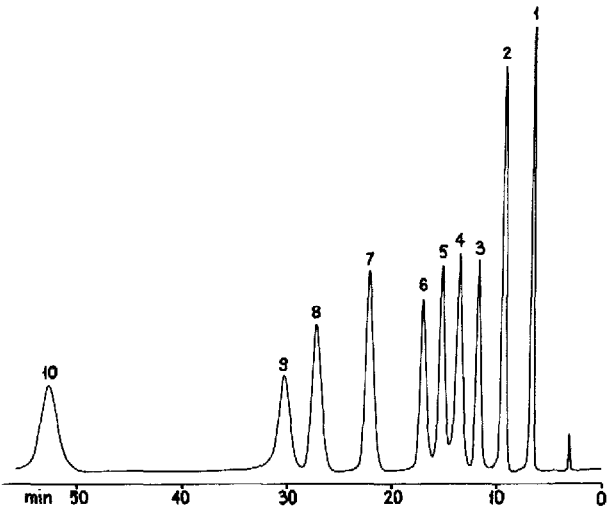

Fig. 1. Chromatogram of a standard mixture of ten priority pollutant phenols. Eluent, acetonitrile–10^{-3} *M* phosphoric acid (30:70, v/v); detection, 220 nm at 0.1 a.u.f.s. Peaks: 1 = phenol; 2 = *p*-nitrophenol; 3 = *o*-chlorophenol; 4 = 2,4-dinitrophenol; 5 = *o*-nitrophenol; 6 = 2,4-dimethylphenol; 7 = 4-chloro-*m*-cresol; 8 = 2,4-dichlorophenol; 9 = 4,6-dinitro-*o*-cresol; 10 = 2,4,6-trichlorophenol.

100 ml of aqueous solutions containing 0.4 μg/ml of each compound. It can be seen that with the exception of 2,4-dinitrophenol, the 1,4-DMN–DVB copolymer gives yields of about 100%. With Amberlite XAD-4, the recoveries of 2,4-dinitrophenol and 4,6-dinitro-*o*-cresol are not quantitative. For other compounds, recoveries with a sample volume of 100 ml are almost identical with the Amberlite XAD-4 and 1,4-DMN–DVB copolymer columns.

TABLE I

COMPARISON OF RECOVERIES OF PRIORITY POLLUTANT PHENOLS ON THE INVESTIGATED SORBENTS FOR 100-ml SAMPLES OF FORTIFIED WATER, AND BREAKTHROUGH VOLUMES

Phenol	*Recovery (%)*		*Breakthrough volume (ml)*	
	1,4-DMN–DVB	*Amberlite XAD-4*	*1,4-DMN–DVB*	*Amberlite XAD-4*
Phenol	100.4	100.6	200	200
2,4-Dinitrophenol	67.2	79.8	50	< 100
o-Chlorophenol	99.6	103.8	600	600
p-Nitrophenol	102.2	102.7	600	500
o-Nitrophenol	102.8	99.2	600	1200
2,4-Dimethylphenol	100.4	101.8	600	1200
4,6-Dinitro-*o*-cresol	102.5	92.1	800	1200
4-Chloro-*m*-cresol	101.0	102.6	800	1800
2,4-Dichlorophenol	99.2	98.3	1300	2000
2,4,6-Trichlorophenol	99.4	99.0	1300	2000
Pentachlorophenol	102.1	101.3	2000	2600

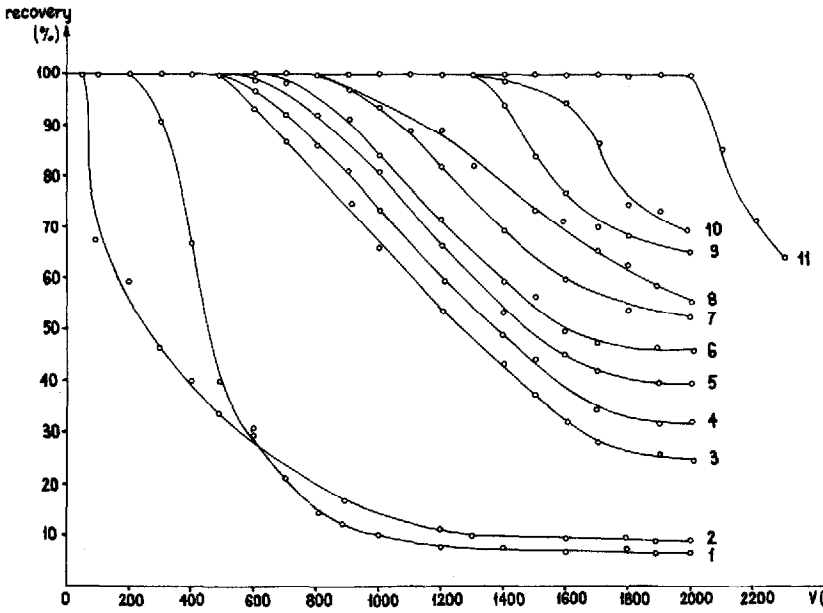

Fig. 2. Recovery (%) of (1) phenol, (2) 2,4-dinitrophenol, (3) *o*-chlorophenol, (4) *p*-nitrophenol, (5) *o*-nitrophenol, (6) 2,4-dimethylphenol, (7) 4,6-dinitro-*o*-cresol, (8) 4-chloro-*m*-cresol, (9) 2,4-dichlorophenol, (10) 2,4,6-trichlorophenol and (11) pentachlorophenol as a function of the sample volume (V). Conditions: minicolumn with 1.4-DMN–DVB porous copolymer; sampling rate, *ca.* 20 ml/min; concentration of phenols 0.4 μg/ml in water.

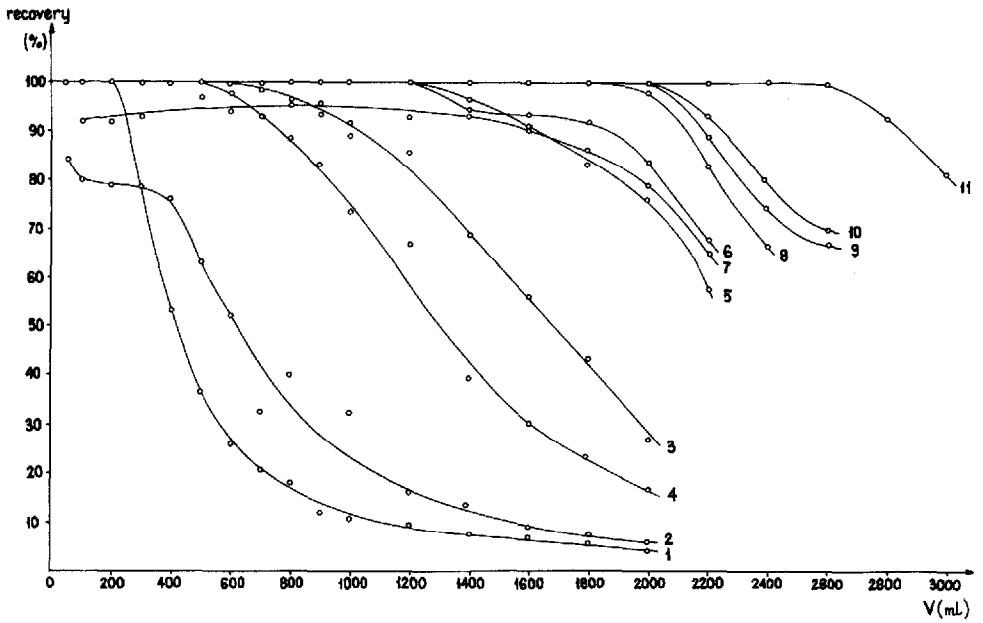

Fig. 3. Recovery (%) of phenols as a function of the sample volume (V) for Amberlite XAD-4 minicolumn. Conditions as in Fig. 2.

In order to check the applicability of porous polymers for the preconcentration of priority pollutant phenols from water solutions the breakthrough volumes were determined. Figs. 2 and 3 show the relationships between recovery and sample volume for priority pollutant phenols solutions contaning 0.4 μg/ml of each compound. It can be seen that for some phenols the same volumes can be applied before breakthrough occurs. For both porous polymers the breakthrough volume for phenol is 200 ml and for *o*-chlorophenol and *p*-nitrophenol about 500–600 ml.

For highly substituted phenols the breakthrough volumes on Amberlite XAD-4 are generally greater than those on 1,4-DMN–DVB copolymer. This phenomenon is especially visible for 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol. Probably the substituted chlorophenols show a greater affinity for Amberlite XAD-4 than for 1,4-DMN-DVB copolymer. Additionally, the specific surface area of Amberlite XAD-4 is about three times larger than that of 1,4-DMN–DVB and its sorption properties should be better. On the other hand, 1,4-DMN–DVB copolymer has a weakly polar character owing to the presence of ester groups in its skeleton and it probably interacts more strongly than Amberlite XAD-4 with polar compounds.

The above results suggest that in spite of the greater breakthrough volumes for highly substituted chlorophenols obtained on Amberlite XAD-4, the retention characteristics of the two polymers are similar. However, 1,4-DMN–DVB copolymer has the advantage over Amberlite XAD-4 that it does not shrink or swell with changes in the nature of the eluent because of its high degree of cross-linking.

REFERENCES

1 *Toxic Substance Control Act*, U.S. Environmental Protection Agency, Washington, DC, 1979.
2 K. Tsuji, *J. Chromatogr.*, 158 (1978) 337.
3 K. Abrahamsson and T. M. Xie, *J. Chromatogr.*, 279 (1983) 199.
4 P. G. Nielsen, *Chromatographia*, 18 (1984) 323.
5 D. E. Weishaar, D. E. Talman and J. L. Anderson, *Anal. Chem.*, 53 (1980) 1809.
6 E. M. Lores, J. R. Edgerton and R. F. Moseman, *J. Chromatogr. Sci.*, 19 (1981) 466.
7 C. D. Chriswell, R. C. Chang and J. S. Fritz, *Anal. Chem.*, 47 (1975) 1325.
8 R. T. Coutts, E. E. Hargesheimer and F. M. Psautto, *J. Chromatogr.*, 179 (1979) 291.
9 J. Hajslova V. Kocourek, I. Zemanova, F. Pudil and J. Davidek, *J. Chromatogr.*, 439 (1988) 307.
10 P. A. Realini, *J. Chromatogr. Sci.*, 19 (1981) 124.
11 F. P. Bigley and R. L. Grob, *J. Chromatogr.*, 350 (1985) 407.
12 E. Chladek and R. S. Marano, *J. Chromatogr. Sci.*, 22 (1984) 313.
13 D. A. Baldwin and J. K. Debowski, *Chromatographia*, 26 (1988) 186.
14 A. Tateda and J. S. Fritz, *J. Chromatogr.*, 152 (1978) 329.
15 C. E. Werkhoven-Goewie, W. M. Boon, A. J. J. Prot, R. W. Frei, U. A. T. Brinkman and C. J. Little, *Chromatographia*, 16 (1982) 53.
16 C. E. Goewie, *Ph.D. Thesis*, Free University, Amsterdam, 1983.
17 J. Gawdzik, B. Gawdzik and U. Czerwińska-Bil, *Chromatographia*, 25 (1988) 504.
18 G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arquello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745.
19 J. Gawdzik, *Chem. Anal. (Warsaw)*, 33 (1988) 445.
20 H. A. McLeod and G. Laver, *J. Chromatogr.*, 244 (1982) 385.
21 H. K. Lee, S. F. Y. Li and Y. H. Tay, *J. Chromatogr.*, 438 (1988) 429.