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Use of porous polymers in off-line preconcentration of nitrobenzenes and their reduction products from water

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Abstract

Porous polymers with different functional groups were tested as sorbents for off-line preconcentration of nitrobenzenes together with their reduction products from water. In addition to 1,4-di(methacryloyloxy-methyl)naphthalene–divinylbenzene porous copolymer, previously used for the solid-phase extraction of aromatic amines, three other porous polymers were used. The additional solid-phase minicolumns were packed with methacrylic ester of *p,p'*-dihydroxydiphenylpropane diglycidyl ether–divinylbenzene, 4,4'-bismaleimidodiphenylmethane–styrene and non-polar styrene–divinylbenzene. In order to study the sorption properties of these polymeric materials, the recoveries and breakthrough volumes of *m*-phenylenediamine, *o*-phenylenediamine, aniline, *m*-nitroaniline, *o*-nitroaniline, *p*-nitroaniline, nitrobenzene, *m*-dinitrobenzene, *o*-dinitrobenzene and 1,3,5-trinitrobenzene were determined.

Keywords: Polymer sorbents, porous; Sorbents; Water analysis; Sample pretreatment; Nitrobenzenes; Amines, aromatic; Trinitrotoluene; Nitroanilines

1. Introduction

Different nitroaromatic compounds and their reduction products, i.e., aromatic amines, are formed as by-products in the manufacture of the explosive 2,4,6-trinitrotoluene (TNT).

Nitrobenzene isomers and different nitroanilines are frequently detected in waste water discharged from TNT production facilities and also at open-burn and open-detonation grounds and neighbouring areas [1]. According to Jenkins and co-workers [2,3], nitroaromatics occur in waste water or in soil at sub-ppb concentrations. Aromatic amines usually occur at a lower con-

centration level. The latter are extremely toxic and may have mutagenic impact even at very low concentrations [4–6]. Similar properties are displayed by dinitroanilines, dinitrobenzenes and 1,3,5-trinitrobenzene. It has been proved that they are mutagenic to *Salmonella typhimurium* and toxic to various animal species and microorganisms [7]. Reduction of the nitro group of dinitrobenzene isomers and trinitrobenzene to the corresponding nitroanilines by isolated hepatocytes and by *Nocardia* species cells or phenol adapted bacteria from sewage sludge has been reported [8].

Direct determination of these compounds in water is difficult because of their low concentrations and sensitivity to pH changes. In order

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to measure the concentration of these compounds in water, preconcentration methods must be used before the analysis. A highly promising approach is to enrich the compounds of interest on suitable sorbents, prior to their separation and detection by means of a chromatographic techniques [9–11].

In trace enrichment of non-polar and moderately polar solutes from the aqueous samples, alkyl-bonded silica, carbon-based sorbents and porous polymers are widely applied. For preconcentration of highly polar aromatic amines, resin-based cation exchangers are particularly effective.

The different chemical characteristics of nitroaromatic compounds and their reduction products (aromatic amines) require the use of the appropriate sorbent for their preconcentration. In this work, different polymeric sorbents for off-line preconcentration of nitroaromatics together with their reduction products (aromatic amines) from water were investigated.

2. Experimental

2.1. Chemicals

Aniline, *p*-nitroaniline and *o*-dinitrobenzene were obtained from POCh (Gliwice, Poland), nitrobenzene, *m*-phenylenediamine and *o*-phenylenediamine from Fluka (Buchs, Switzerland) and *m*-nitroaniline, *o*-nitroaniline, *m*-dinitrobenzene and 1,3,5-trinitrobenzene from Merck (Darmstadt, Germany). Methanol (HPLC grade) was purchased from Lab-Scan (Dublin, Ireland). Doubly distilled water was used for the preparation of mobile phases and solutions for the recovery studies. Disodium hydrogenphosphate and potassium dihydrogenphosphate used for buffer preparation were of reagent grade from POCh.

Besides 1,4-di(methacryloyloxymethyl)naphthalene-divinylbenzene (1,4-DMN-DVB) porous copolymer, whose properties were described in previous papers [12,13], three other porous polymers were used: methacrylic ester of *p,p'*-

dihydroxydiphenylpropane diglycidyl ether-divinylbenzene (MEDDE-DVB), which contains ester and hydroxyl functional groups [14], 4,4'-bismaleimidodiphenylmethane-styrene (BM-ST) with imide groups [15] and non-polar Amberlite XAD-4 [styrene-divinylbenzene (ST-DVB) type] from Rohm and Haas (Philadelphia, PA, USA). The surface area of the sorbents was determined by the BET method from nitrogen adsorption data using a Sorptomatic Model 1800 (Carlo Erba, Milan, Italy).

Properties of the copolymers studied are presented in Table 1.

2.2. Apparatus

For establishing the optimum separation conditions, a Hewlett-Packard HP-1050 liquid chromatograph equipped with a UV diode-array detector, a Rheodyne Model 7125 injection valve with a sample loop of 20 μ l and a 7- μ m LiChrosorb RP-18 column (250 mm \times 4 mm I.D.) were used. Methanol-phosphate buffer (pH 7) (25:75, v/v) was used as the mobile phase at a flow-rate of 1 ml/min. Buffer solution was prepared by adding disodium hydrogenphosphate (0.500 g) and potassium dihydrogenphosphate (0.301 g) to doubly distilled water and diluting to 1 l.

Recovery studies were made on a Liquochrom Model 2010 liquid chromatograph (Labor, Budapest, Hungary) equipped with the same column and a variable-wavelength UV-Vis detector working at 228 nm. Quantification of the chromatograms was based on peak heights using calibration graphs.

Table 1
Properties of the sorbents used for preconcentration

Sorbent	Particle size (μ m)	Specific surface area (m^2/g)
1,4-DMN-DVB	40–50	187
MEDDE-DVB	40–45	71
BM-ST	40–45	73
Amberlite XAD-4	40–50	600

2.3. Recovery studies

For the preconcentration of nitrobenzenes and their reduction products from water, laboratory cartridges and a simple vacuum manifold, described previously, were used [12,13]. The mass of the sorbents was 200 mg. The dimensions of the sorbent beds in the dry state were ca. 10 mm × 9 mm I.D.

Stock standard solutions were prepared by weighing the compounds and dissolving them in methanol. A standard methanolic solution contained 20 µg/ml of each compound. This solution was stored not only in a freezer but also in dark glass bottles to prevent decomposition of the amines (the peak of *o*-phenylenediamine stored in the light decreased continuously).

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 standard solution containing 20 µg/ml of each compound by dilution to 0.4 µg/ml with doubly distilled water. Different volumes of these water samples were sucked through the minicolumn immersed in the sample and connected by PTFE tubing (Chrompack, Middelburg, Netherlands) to the water aspirator. After the sample had passed through the minicolumn, the vacuum was maintained for 5 min in order to dry the sorbent bed. The analyte compounds were then eluted with three 500-µl aliquots of methanol. After all the sorbates had eluted from the column, each sample was diluted with methanol to 2 ml or to a multiple of this volume. Sorbent regeneration was carried out using 10 ml of methanol.

In order to determine the recoveries of nitrobenzenes and their reduction products, 20 µl of preconcentrated solutions were injected into the liquid chromatograph. The same volume of standard solution of nitrobenzenes and amines (20 µg/ml) was also injected into the chromatograph under the same conditions.

The percentage recovery of nitrobenzenes and their reduction products was calculated directly

from a comparison of peak heights. Recoveries were calculated as mean values of three analyses.

3. Results and discussion

Porous polymers are widely applied as sorbents for the separation and preconcentration of various organic compounds from water. The ST-DVB polymers Amberlite XAD-2 and -4 are commonly used in solid-phase extraction.

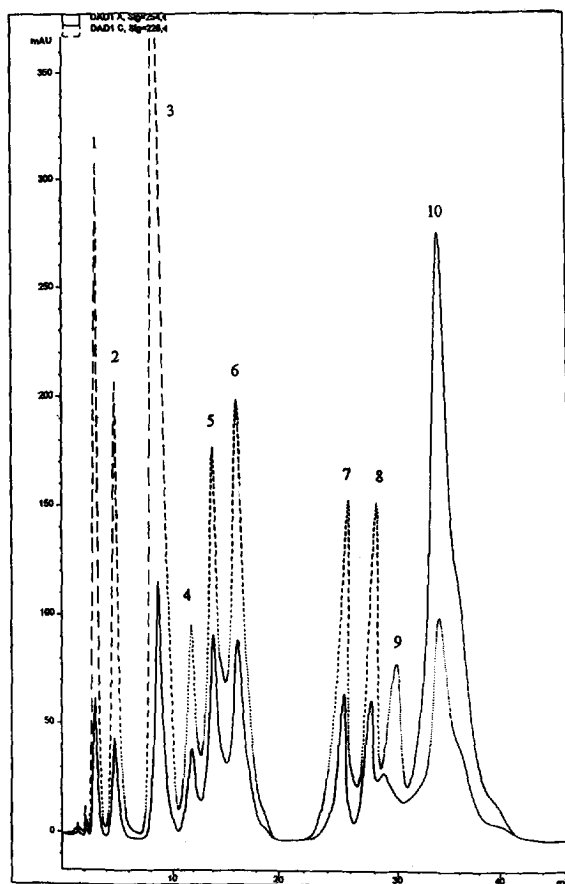


Fig. 1. Chromatogram of a standard mixture of nitrobenzenes and their reduction products. Eluent, methanol-phosphate buffer (pH 7) (25:75, v/v); detection at 228 nm. Peaks: 1 = *m*-phenylenediamine; 2 = *o*-phenylenediamine; 3 = aniline; 4 = *p*-nitroaniline; 5 = *m*-nitroaniline; 6 = 1,3,5-trinitrobenzene; 7 = *o*-nitroaniline; 8 = *m*-dinitrobenzene; 9 = *o*-dinitrobenzene; 10 = nitrobenzene.

To separate and preconcentrate the nitroaromatics together with their reduction products, not only a suitable sorbent but also an appropriate chromatographic system should be used. Recovery studies require complete separation of the peaks of the standard compounds and large peak areas to minimize errors. The work by Reddy et al. [1] suggested that for the separation and quantification of nitrobenzenes together with their reduction products, methanol–0.1% triethylamine in the water mobile phase should be used at 254 nm. Data from the diode-array detector indicated the highest and comparable peak heights of the studied compounds were obtained at a wavelength of 228 nm. Therefore, in the recovery studies detection was effected at this wavelength. A comparison of two chromatograms obtained at 254 and 228 nm is presented in Fig. 1.

As the weakly polar 1,4-DMN–DVB porous copolymer, previously studied in the preconcentration of aromatic amines, turned out to be very effective in the off-line preconcentration of *p*-nitroaniline, it was chosen as a sorbent for the solid-phase extraction of nitrobenzenes and their reduction products, aromatic amines.

In Table 2, the recoveries of the compounds studied from 100 ml of aqueous solution obtained on the minicolumn packed with 1,4-DMN–DVB copolymer are presented. As these

recoveries are poor for phenylenediamines, copolymers with different selectivities were also tested. They differed in chemical characteristics: MEDDE–DVB containing ester and hydroxyl groups and BM–ST with imide functional groups were more polar than 1,4-DMN–DVB porous copolymer, but Amberlite XAD-4 (ST–DVB type) without any groups is considered to be a non-polar sorbent. The data in Table 2 shows that the recoveries of phenylenediamines are nearly complete only on the BM–ST sorbent. On the MEDDE–DVB porous polymer not only are the recoveries of phenylenediamines very low but also aniline gives a poor recovery. When Amberlite XAD-4 is used, the recovery of aniline is higher than on MEDDE–DVB but the recoveries of phenylenediamines are the poorest.

In order to determine the sorption capacities, the breakthrough volumes for the studied compounds were measured. Figs. 2–5 show the relationships between the recovery and sample volume for nitrobenzenes and aromatic amines solution containing 0.4 µg/ml of each compound. Among the copolymers studied, the largest breakthrough volumes are obtained on BM–ST and the smallest on MEDDE–DVB. Except for BM–ST, the breakthrough for aromatic amines (phenylenediamines and aniline) occurs at very small volumes. For nitro compounds these values are very different, e.g., 1500 ml for 1,3,5-trinitro-

Table 2

Comparison of recoveries of nitrobenzenes and their reduction products on the investigated sorbents for 100-ml samples of fortified water

Compound	Recovery (%)			
	1,4-DMN–DVB	MEDDE–DVB	BM–ST	Amberlite XAD-4
<i>m</i> -Phenylenediamine	27.8	21.4	98.2	8.5
<i>o</i> -Phenylenediamine	62.7	12.8	96.7	6.2
Aniline	100.0	48.0	102.7	76.5
<i>p</i> -Nitroaniline	102.2	98.0	101.0	100.0
<i>m</i> -Nitroaniline	101.5	99.2	100.4	101.9
1,3,5-Trinitrobenzene	98.2	101.4	97.8	98.4
<i>o</i> -Nitroaniline	101.0	101.7	99.7	98.9
<i>m</i> -Dinitrobenzene	98.6	100.1	98.7	94.2
<i>o</i> -Dinitrobenzene	100.8	100.5	98.8	100.0
Nitrobenzene	99.7	102.0	100.2	101.1

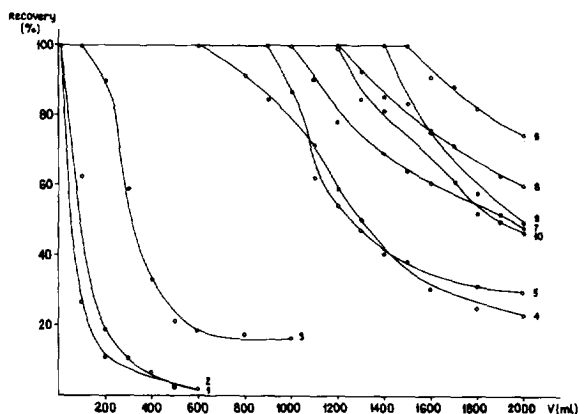


Fig. 2. Recovery of (1) *m*-phenylenediamine, (2) *o*-phenylenediamine, (3) aniline, (4) *p*-nitroaniline, (5) *m*-nitroaniline, (6) 1,3,5-trinitrobenzene, (7) *o*-nitroaniline, (8) *m*-dinitrobenzene, (9) *o*-dinitrobenzene and (10) nitrobenzene as a function of a sample volume. Conditions; minicolumn with 1,4-DMN-DVB porous copolymer; sampling rate, ca. 20 ml/min; concentration of each compound, 0.4 $\mu\text{g}/\text{ml}$ in water.

benzene on 1,4-DMN-DVB but only 300 ml on MEDDE-DVB.

The order of obtaining the breakthrough vol-

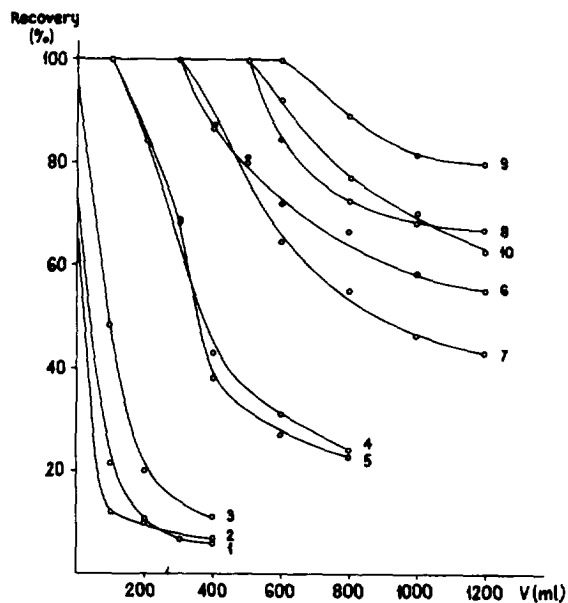


Fig. 3. Recovery of nitrobenzenes and their reduction products as a function of the sample volume for the MEDDE-DVB minicolumn. Conditions and numbering as in Fig. 2.

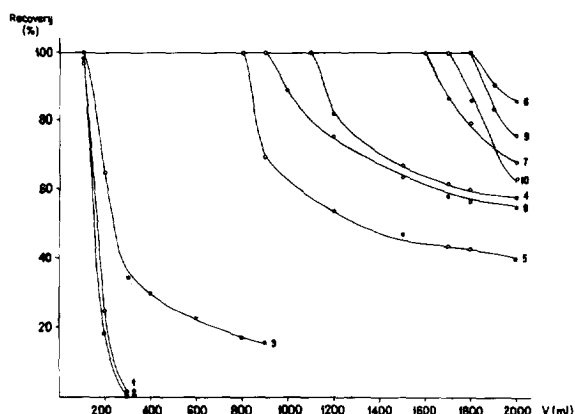


Fig. 4. Recovery of nitrobenzenes and their reduction products as a function of the sample volume for the BM-ST minicolumn. Conditions and numbering as in Fig. 2.

ume by the sorbate indicates the character of interactions with the sorbent bed. All the pre-concentrated compounds show a greater affinity for BM-ST containing imide groups. The nitro compounds interact strongly with 1,4-DMN-DVB, whereas the compounds of amine character are poorly retained on this sorbent. With non-polar Amberlite XAD-4 these interactions are even weaker. The least interactions with the studied compounds are shown by the most polar polymer, MEDDE-DVB.

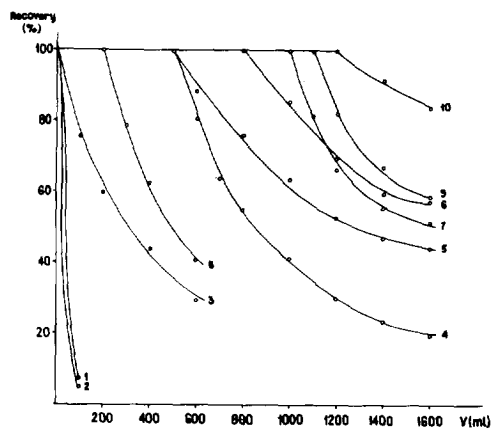


Fig. 5. Recovery of nitrobenzenes and their reduction products as a function of the sample volume for the minicolumn packed with Amberlite XAD-4. Conditions and numbering as in Fig. 2.

The above results suggest that the BM–ST porous copolymer may be used as an effective sorbent for the off-line preconcentration of nitrobenzenes with their reduction products from water.

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