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New polymeric sorbent for the solid-phase extraction of chlorophenols from water samples followed by gas chromatography–electron-capture detection

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Abstract

A polymeric material, polyaniline, was employed as a new sorbent for solid-phase extraction (SPE) of some environmental pollutants from water samples. Chlorophenols were extracted from aqueous samples by SPE using 120 mg polyaniline and determined by gas chromatography with electron-capture detection. The acetate esters of these phenols were formed by the direct addition of acetic anhydride to the organic extractant in the presence of K_2CO_3 . Different conditions were applied to obtain higher retaining capacity and breakthrough volumes. The results compared with those obtained by other groups. The RSD for a river water sample spiked at sub-ppb level was lower than 10% ($n=3$) and detection limits were between 3 and 110 $ng\ l^{-1}$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Environmental analysis; Solid-phase extraction; Polyaniline sorbents; Chlorophenols; Phenols

1. Introduction

Phenolic compounds enter the environment in various ways: directly, as industrial effluents, and indirectly, as conversion products from natural and synthetic chemicals, including pesticides. The US Environmental Protection Agency [1] has drawn up a list of eleven phenolic compounds considered major pollutants. Chlorophenols are among the most toxic and carcinogenic of these.

Many analytical approaches have been used for the trace-level analysis of phenols, mainly using

high-performance liquid chromatography (HPLC) [2–4] or capillary gas chromatography (GC). Although HPLC methods are frequently applied for analysis of phenols, GC is often preferred, offering unrivalled high resolution and easy coupling with sensitive and selective detectors. Actually, HPLC detection was reported to be prone to interferences from matrix compounds such as humic substances naturally occurring in environmental samples [5].

In general, phenols are amenable to GC without derivatization [6–8]. But at lower concentration, peak tailing and discrimination in the injector of capillary column might occur [8,9], especially when environmental samples are analyzed. To overcome these problems, phenols have to be derivatized with a suitable derivatizing reagent [10–13]. Among the wide variety of derivatizing reagents used for this

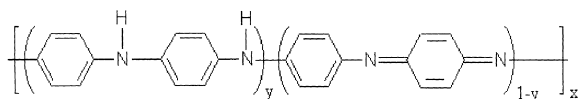
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purpose, acetylating agents have been employed to the greatest extent [6,14–16].

Because of the low concentrations of microorganic pollutants in water samples, it is necessary to apply a preconcentration step prior to the chromatographic analysis. Nowadays, solid-phase extraction (SPE) is the most common technique for sample enrichment, because of its advantages over liquid–liquid extraction [17]. A large number of procedures for the determination of chlorophenolics in water using SPE have been tested [2,3,16–18]. Various types of solid-phase sorbents have been used, including C_{18} [19,20], polystyrene–divinylbenzene–based polymers [20,21], and various forms of carbon [16,18]. A number of these sorbents show relatively low recovery for some chlorophenols [2,3,6,22,23].

Conductive polymers are organic materials that generally possess an extended conjugated π -electron system along a polymer backbone [24–26]. Polyanilines are a class of conducting polymers the base form of which has the general formula



containing y reduced and $(1-y)$ oxidized repeat units. These polymers have wide field of applications in daily life, i.e. electronics, industry, agriculture and architecture. One of the most studied polymers, polyaniline “aniline black” was first prepared in the last century [27], but current interest in such materials began in the 1970s, polyaniline can be produced by chemical or electrochemical oxidation [28–30]. Although electrochemically synthesized polyaniline arouses great interest, chemical methods have some potential advantages, such as mass production and short reaction time. In the present paper, for the first time, a conductive polymer i.e. polyaniline was used as a packing material for SPE of organic micro-pollutants. Polyaniline was synthesized with chemical oxidation of the monomer. The polymer capability was tested for preconcentration of chlorophenols from environmental water samples. Different conditions have been studied in order to obtain higher retention and breakthrough volumes; results from the polyaniline are compared with those other commercial sorbents.

2. Experimental

2.1. Reagent

2-Chlorophenol (2CP), 4-chlorophenol (4CP), 2,4-dichlorophenol (24CP), 2,4,6-trichlorophenol (246TCP) and pentachlorophenol (PCP) were obtained from Merck (Darmstadt, Germany). Standard solutions (200 mg l^{-1}) from each compound were prepared in methanol and stored in the refrigerator. A mixture of these phenolic compounds was prepared weekly by diluting the standard solution with methanol, and more diluted working solutions were prepared daily by diluting this solution with triple distilled water or river water. The concentrations in the mixture to be analyzed by GC–electron-capture detection (ECD) were 155.0, 146.3, 37.50, 11.80 and 10.10 mg l^{-1} for 2CP, 4CP, 24CP, 246TCP and PCP, respectively. For the determination by GC–flame ionization direction (FID), the concentrations in the mixture were in the range $100\text{--}200 \text{ mg l}^{-1}$.

HPLC-grade methanol and hexane (Merck) were used as eluting and extracting solvent. The pH of water samples was adjusted with sulfuric acid (Fluka, Buchs, Switzerland) or citrate buffer. Aniline, ammonium peroxodisulfate, tetrahydrofuran (THF), 1-methyl-2-pyrrolidinone (NMP) and hydrochloric acid, supplied by Merck, were used in the synthetic procedure. Anhydrous sodium sulfate was obtained from Riedel-de Haen (Seelze, Germany) and was heated at 300°C for 4 h before use. Acetic anhydride and other reagents were of the maximum purity available and obtained from Merck (Darmstadt, Germany). Naphtalene and 1, 3, 5 trichlorobenzene were used as internal standards for flame ionization (FID) and electron capture detection (ECD), respectively.

2.2. Apparatus

A Perkin–Elmer liquid chromatograph model 601 equipped with two reservoirs was modified for preconcentration and elution of the SPE precolumn. SPE was carried out on a $70 \text{ mm} \times 3 \text{ mm}$ I.D., stainless steel precolumn packed with 120 mg polyaniline. A gas chromatograph model Chrompack CP 9001 equipped with a flame ionization detector, an electron-capture detector and a split/splitless injector

was used. Separations of chlorophenols were carried out using a capillary column CP-Sil 5 CB low bleed MS, (25 m×0.25 mm I.D.) with 0.25 μm film thickness. The injector and detector temperatures were set at 250°C and 280°C, respectively. Helium and nitrogen (99.999%) were used as carrier and make-up gas, respectively. The flow-rate of carrier gas was adjusted at 1 ml min⁻¹.

The oven temperature was programmed as follows: 55°C during 3 min, at 6°C min⁻¹ to 230°C, 5 min hold at 230°C. An aliquot of 2 μl from each sample was injected.

2.3. Synthetic procedures

Details of polymer synthesis were previously described [30–32]. The polymer was prepared by oxidation of 0.08 M aniline solutions in 1.0 M H₂SO₄ with ammonium peroxodisulfate at ca. -15°C. A 1:1 molar ratio of peroxodisulfate to monomer was used. After 16 h, greenish precipitate was filtered through a buchner filter funnel connected to a water aspirator. The precipitate was washed with water and then placed in a solution of 0.1 M NH₄OH and stirred for several hours. The polymer was dried under the vacuum. The product was subsequently extracted in a soxhlet extractor with THF and then NMP until the extracted solvent was colorless. After extraction, the synthesized polymer was washed with methanol and water and dried under vacuum and following grinding. Polymer particles sized 125–180 μm were collected and used. The specific area was determined according to the BET method [33] and found to be 48 m² g⁻¹.

2.4. Sample preparation and derivitization process

Prior to the preconcentration step, the pH of sample was adjusted to 2 with sulfuric acid. A known volume of distilled or river water was spiked with chlorophenol standards and was subsequently passed through a preconditioned SPE column at a flow-rate of 2–6 ml min⁻¹. When the sample had passed through, the cartridge was eluted with 2 ml of methanol at the flow-rate of 0.2 ml min⁻¹. The cartridge was preconditioned by washing with 5 ml of methanol and activated with 5 ml of distilled water at pH 2. For those experiments where the pH

effects were studied, citrate buffer (pH 2–5) was used for the adjustment. The derivatization procedure used was based on previous report by Rodríguez et al. [16]. A volume of 2 ml of a methanol solution containing chlorophenols was mixed with 1 ml of 5% K₂CO₃ and 2 ml of *n*-hexane containing 200 μl of acetic anhydride and internal standard. The mixture was shaken for 1 min and the organic phase was allowed to be separate. The aqueous phase was then extracted with a further 1 ml of *n*-hexane containing only internal standard. The two *n*-hexane portions were collected, mixed and dried over anhydrous sodium sulfate and injected into the GC system. To access lower detection limits in the sample solution at sub-ppb concentrations, the final extract was concentrated to 0.5 ml under a gentle stream of nitrogen.

3. Results and discussion

3.1. Evaluation of sorbent

To evaluate the capability of polyaniline for the preconcentration of chlorophenols from water samples, 2CP, 4CP, 24DCP, 246TCP and PCP were used as model compounds. Effects of different parameters such as the sample pH, the sample volume, the volume of eluting solvent, the capacity of the new sorbent and the linearity of recovery were evaluated using this new polymeric sorbent.

Sample pH is an important factor, which may affect on the recovery of phenols from water. To increase the extraction recovery of chlorophenols by non-polar sorbents, it is necessary to acidify the sample [3,34]. At low pH, the acid–base equilibrium for the chlorophenols shifts significantly toward the neutral forms, which have greater affinities toward the sorbent, and the extraction efficiencies are, therefore, increased. In the other hand, in acidic media, depending on pH of the solution, polyaniline can be protonated up to 50% [35]. The proton addition to polyaniline removes electrons from the π -system [30,35,36] and this change in the polymer's electronic system may affect the sorption properties of the polymer. To study the effect of sample pH on the recovery of phenols from water samples, 100 ml samples with same concentration in

Table 1

The extraction recoveries obtained for the studied chlorophenols at various pH of sample solutions^a

Compound	pH							
	2.0		3.0		4.0		5.0	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
2CP	72.5	3.2	55.0	4.3	32.2	5.2	22.3	5.0
4CP	79.1	4.5	61.7	3.8	35.6	2.9	25.7	4.1
24DCP	100.2	6.3	85.3	5.1	42.3	4.6	37.7	3.7
246TCP	103.2	4.1	87.2	3.8	48.3	3.9	40.2	4.5
PCP	101.6	7.6	92.1	5.7	59.1	8.1	48.9	6.1

^a Values are means of three determinations.

the range 0.2–3.1 $\mu\text{g l}^{-1}$ at different pH values between 2 and 5 were preconcentrated using poly-aniline as the sorbent. Table 1 shows the recovery obtained at each pH and clearly, the maximum recovery is obtained at pH 2.

In order to determine the volume of the sample that can be concentrated with acceptable recoveries of all the compounds studied, it was necessary to obtain the breakthrough volumes. Different volumes (75, 100, and 200 ml) of distilled water, at pH 2, were spiked with a solution containing five phenolic compounds at the 0.2–3.1 $\mu\text{g l}^{-1}$ level. Following the preconcentration step, the trapped analytes on the precolumn were eluted with 2 ml of methanol. After derivatization and extraction with a total of 3 ml of *n*-hexane, an aliquot of 2 μl was injected into the GC system. The recovery of phenolic compounds and the repeatability for the different volumes are given in Table 2. Good recoveries were obtained for all compounds studied using 75-ml sample volumes. Of course, when samples of 100 ml were precon-

trated, the recoveries were still acceptable. Further experiments revealed that, for less polar compounds, i.e. 246TCP and PCP, breakthrough volumes higher than 250 ml were obtainable. A sample volume of 75 ml was, therefore, selected as an optimized sample volume. It was also found that flow-rates up to 6 ml min^{-1} for water samples loading on the precolumn had no effect on the recovery percentage.

To find the required volume of methanol to elute all chlorophenols from the cartridge, elution volumes up to 10 ml were examined. It was found that a volume of 2 ml was sufficient to desorb the trapped pollutants from the SPE precolumn. This relatively low volume of methanol eluted all compounds from the cartridge easily and other solvents were, therefore, excluded from any further examination.

In order to study the capacity of the new sorbent and the linearity of recovery, each compound was determined using a river water sample spiked at much higher levels, i.e. 200–400 $\mu\text{g l}^{-1}$, by GC–FID. No significant differences were obtained, in-

Table 2

The extraction recoveries obtained for the studied chlorophenols at different volumes of sample solutions^a

Compound	Volume (ml)					
	75		100		200	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
2CP	103.4	3.7	68.1	5.4	45.1	4.2
4CP	109.9	4.6	77.5	6.1	55.4	5.6
24DCP	98.0	4.8	106.3	3.9	98.5	6.8
246TCP	100.4	5.6	103.1	5.1	96.2	4.8
PCP	105.3	7.5	110.0	7.1	111.6	8.6

^a Values are means of three determinations.

dicating that its capacity is sufficiently high. It also demonstrates that even the preconcentration of water samples spiked with such levels of concentrations has no negative influence on the recovery results.

3.2. Comparison studies

From the results obtained, the new sorbent seems to be suitable for determining phenolic compounds. In comparison with other reports, it appears that, these recoveries, at least for some, are better than those which obtained using some commercial sorbents such as C_{18} [3,6,22,23], Cyclohexyl [23] and monofunctional C_{18} (C_{18}/OH) [3]. In a report [22], 250 mg Amberchrom CG-161 was used for the preconcentration of 100 ml of water and recoveries lower than 75% for these chlorophenols were obtained. Also, in another work [6] SPE of 250 ml of water sample by 250 mg C_{18} , led to low recoveries, specially for 2CP and PCP that were 40 and 48%, respectively. At the same time, another group [23] used cartridges of 500 mg of C_{18} , Cyclohexyl and PLRP-S, a styrene-divinyl benzene-based copolymer, for the preconcentration of phenols. Acceptable recoveries were obtained with these sorbents using different volumes of solution with and/or without use of ion-pair reagent for extraction of all compounds studied except 246TCP and PCP which had recoveries lower than 70% for all conditions applied. While some authors [3] have demonstrated that PLRP-S provides the best recoveries even for 246TCP and PCP as compared to other sorbents, in the previously described work [23] recoveries were reported to be lower than 70% for TCP and PCP. Generally, styrene-divinylbenzene-based polymers especially LiChrolut EN [37,38] because of its high surface area of $1200 \text{ m}^2 \text{ g}^{-1}$, has shown satisfactory results.

Other new copolymers, such as divinylbenzene-*n*-vinylpyrrolidone (Oasis HLB), have been used for the SPE of a variety of organic pollutants including chlorophenolic compounds [39]. Although Oasis HLB was demonstrated to be an effective and universal sorbent, preconcentration based on polyaniline led to improved recovery results for those chlorophenols having higher numbers of chlorine atoms.

Other sorbents such as Carbo-pack B and ENVI

Chrom P were used by Pocerull et al. [2] for extraction of phenols from water sample with and without ion-pair reagent (tetrabutylammonium bromide). Recoveries higher than 90% were obtained for all compounds except pentachlorophenol which had a recovery value of about 75%. Comparing these related results using some common sorbents with the present work demonstrates that polyaniline has an enhanced performance for the extraction of chlorophenols, especially TCP and PCP.

3.3. Real sample

In order to study the effects of sample matrix on the performance of the sorbent, the recovery results were examined using real-life sample spiked at two different concentration levels. A water sample from the Zayandeh-rood river (Isfahan, Iran) was spiked with $0.2\text{--}3.1 \mu\text{g l}^{-1}$ of five chlorophenols. After the SPE and the derivatization step, an aliquot of final extractant was injected into the GC-ECD system. Fig. 1 shows the gas chromatogram of the Zayandeh-rood river water sample and the same sample spiked with a standard solution of chlorophenols. As previously described, employing samples spiked with higher concentrations, i.e. $200\text{--}400 \mu\text{g l}^{-1}$, led to similar recovery results.

The limits of detection using 75 ml of water were calculated based on a signal-to-noise ratio of 3 and were in the range of $3\text{--}110 \text{ ng l}^{-1}$.

4. Conclusion

As far as we know, this is the first time that a conductive polymer has been used as a packing material for the SPE of microorganic pollutants from aquatic media. The recovery of SPE using polyaniline was compared with other commercial sorbents and the polymer showed acceptable capability to extract chlorophenols from water samples. The performance of the new sorbent is comparable with that of some other currently used sorbents, considering its relatively small specific area. The pH of sample solutions is rather important, because of its effect on both the electronic properties of the polymer and the acid-base forms of chlorophenols. The lower pH was more suited for extraction, especially

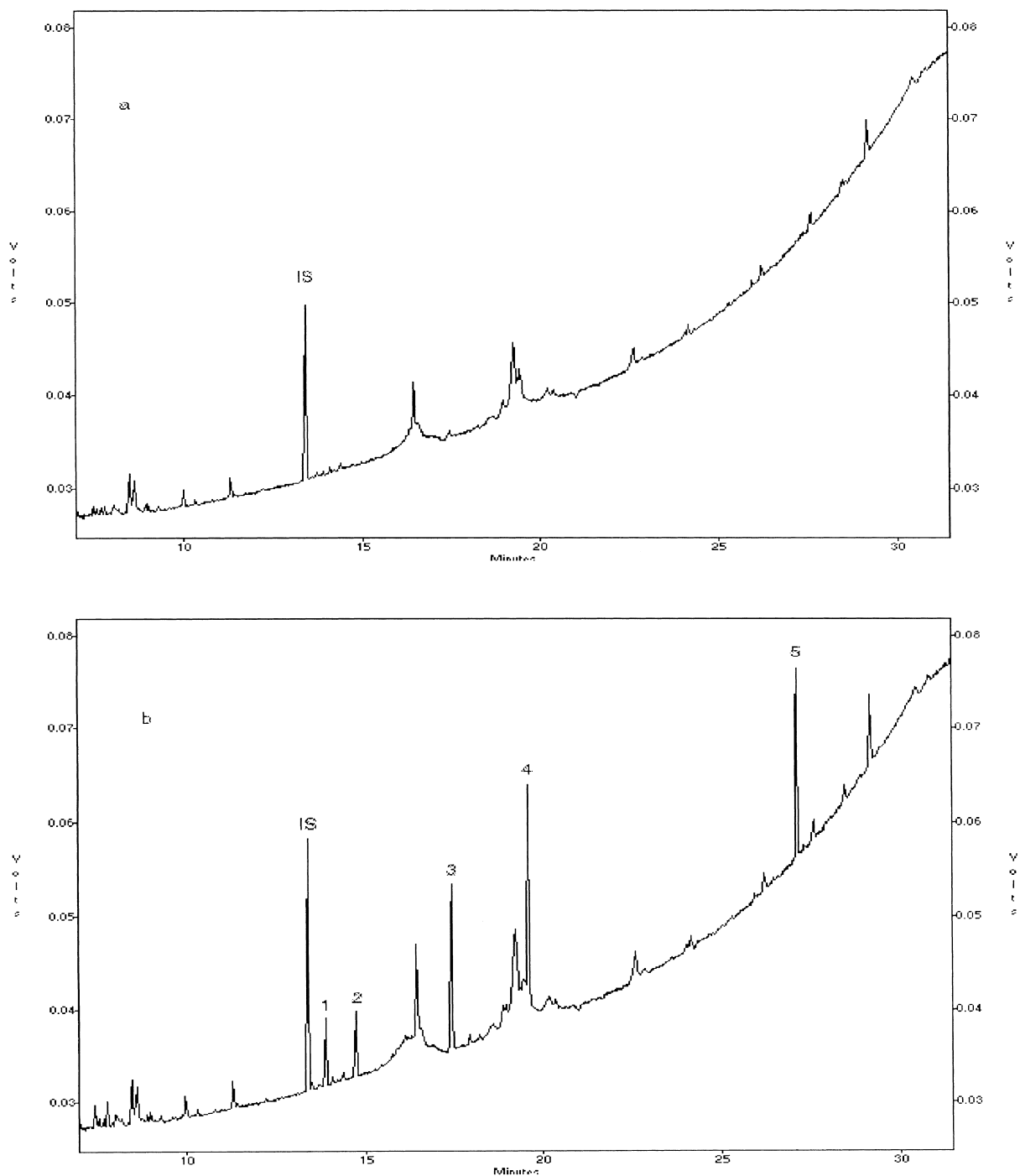


Fig. 1. Gas chromatograms obtained after SPE of: (a) 100 ml Zayandeh-rood river water and (b) 100 ml Zayandeh-rood river water spiked with 0.2–3.1 $\mu\text{g l}^{-1}$ of chlorophenols. I.S.: Internal standard, 1: 2CP, 2: 4CP, 3: 24DCP, 4: 246TCP, 5: PCP.

for PCP and TCP. One clear advantage of the polyaniline sorbent is that it can be reused after being dried out. Efforts to obtain this polymeric compound with a high specific area along with the applications of some other conductive polymers for the extraction of phenolic compounds and some other microorganic pollutants are under current investigation.

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