

Conductive polymers as new media for solid-phase extraction: Isolation of chlorophenols from water sample

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Abstract

Three different conductive polymers, poly-*N*-methylaniline (PNMA), polyaniline and polydiphenylamine were synthesised and used as sorbents for the solid-phase extraction of some phenolic compounds from water. The separation and determination was, subsequently, performed by gas chromatography–electron-capture and flame ionization detection. Among these easy-made polymers, PNMA gave better recovery for the extraction of the studied analytes. The capability of the PNMA to extract other non-polar compounds such as chloro- and methylbenzene, decane, decanol, cyclohexane and cyclohexanol was also studied. The polymer showed some sort of selectivity towards aromatic compounds than aliphatic. Preconcentration of sample volumes up to 1 l at pH 2 using 120 mg of PNMA led to acceptable recoveries for phenolic compounds, except for phenol. Recovery of phenol for 100 ml of water was 72%. Limits of detection for chlorophenols when 250 ml river water was preconcentrated were between 1 and 40 ng l⁻¹, analyzed by GC–electron-capture detection. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solid-phase extraction (SPE) is a well established and an effective procedure in the field of separation science. It is used for the preconcentration and clean up of analytical samples and more than 50 companies, currently, deal with its products and accessories [1–4]. SPE is usually performed using a small column or cartridge containing an appropriate sorbent. The sorbents may be of mineral or organic

origin. The most commonly used mineral materials for this, is chemically bonded silica, usually with a C₈ or C₁₈ organic group. On the other side, most commonly used organic sorbents in SPE are porous polystyrene. During the last few years a series of different packing materials either polymer-based or bonded silicas have been developed. In general, silica based materials exhibit some problems such as pH instability or inconsistent results due to the presence of free silanol groups in amounts that can not be controlled or reproduced. For these reasons, a trend to use more stable organic polymer sorbents such as PLRPS, Hysphere-1, Isolute ENV+, LiChrolut EN and Porapak RDX is observed.

Among different organic pollutants in water, the most problematic compounds to extract are the polar

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ones, having low breakthrough volumes on most of the sorbents mentioned. Of the polar compounds, which are of environmental interest, phenolic compounds are a very significant group. Since phenol, nitro- and 2-chlorophenol display the lowest breakthrough volumes, they represent practical limits and can be used to evaluate the efficiency of a given sorbent for phenol trapping.

New functionalized polymeric sorbents and highly cross-linked polymers have appeared as alternatives to the typical SPE sorbents for the trace enrichment of these polar analytes. Resulting materials still retain the high capacities to trap less polar phenols, but, in addition, the hydrophilic character of the introduced functional group, improves their wetting characteristics and, consequently aids mass transfer of most polar phenols from the water solution to the sorbent. A number of common groups such as acetyl [5], hydroxymethyl [6], benzoyl [7], *o*-carboxybenzoyl [8], carboxylic [9] and sulphonic acid [10] have been used to modify polymeric sorbents.

The new generation of polymers, i.e. Oasis from Waters; Absolute from Varian, are designed to extract extensive spectrum of analytes. They are capable to extract acidic, basic and neutral compounds whether polar or non-polar [11]. The increase in retention of polar analytes in these sorbents, is due to both the polymeric skeleton (reversed-phase mechanism and π - π interactions), and the occurrence of the functional groups.

Conductive polymers are organic materials that generally possess an extended conjugated π -electron system along a polymer backbone [12–14]. They are versatile materials in which molecular/analyte recognition can be achieved in different ways, including: (1) the incorporation of counter ions that introduce selective interaction of counter ions; (2) utilizing the inherent and unusual multifunctionality (hydrophobic, acid–base and π - π interactions, polar functional groups, ion-exchange, hydrogen bonding, electroactivity, etc.) of the polymers; (3) the introduction of functional groups to the monomers. These materials can be easily synthesized in both aqueous and non-aqueous medium, chemically and electrochemically; there are varieties in type of dopant and additives during their synthesis. All these conditions and varieties affect on the chemical, mechanical, morphological and electronic properties of the polymers.

These polymers could be synthesized from a wide range of commercial monomers, which could lead to many polymers having different properties.

Among the many conducting polymers, polyaniline (PANI) and its derivatives have become one of the most widely used since the 1980s up to now. They have been applied in the many fields of applications such as electronic industries, sensors, corrosion and agriculture sciences [15–19]. Recently, we used polyaniline as a SPE packing material for extraction of chlorophenols from water samples [20]. Also, Pawliszyn and co-workers have applied polypyrrole and poly *N*-phenylpyrrols as a coating material for solid-phase microextraction of some inorganic anions and organic compounds [21–23].

The aim of this work was to investigate the efficiency of some aniline-based conductive polymers as SPE materials for the preconcentration of different organic compounds from aqueous solutions. Following the previous work [20], three types of aniline-based polymers, i.e. PANI, poly-*N*-methylaniline (PNMA) and polydiphenylamine (PDPA), were easily synthesized with chemical oxidation of the monomer in aqueous acidic solutions. All of these polymers have benzene ring and nitrogen atom on their structures. In PDPA, coupling occurs through the para positions of the phenyl groups to yield a C–C coupled polymer [24]. NMA and ANI polymerizes head-to-tail [13,24]. PANI and PDPA have rather the same structure but PNMA has a methyl group on nitrogen atom. Each nitrogen atom in the oxidized polymer bears a slightly positive charge in the acidic media. The degree of oxidation depends on parameters such as, type of polymer, pH of the solution and synthesis condition.

Capabilities of these easy-made polymers as SPE sorbent for extraction of phenols from water samples were evaluated and compared with some commercial packing materials.

2. Experimental

2.1. Reagent

The phenolic compounds phenol (Ph), 2,4-dimethylphenol (24DMP), 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 (2000 mg l^{-1}) from each individual compound were prepared in methanol. A mixture of these phenolic compounds, applied to different detection systems, was prepared weekly by diluting the standard solutions with methanol, and more diluted working solutions were prepared daily by diluting these solutions with triple distilled water or river water. The concentration of mixture to be analyzed by GC–electron-capture detection (ECD) was made at a range of $10\text{--}150 \text{ mg l}^{-1}$ for 2CP, 4CP, 24CP, 246TCP and PCP. For the GC–flame ionization detection (FID) determination, the concentration of mixture of all the phenolic compounds was in the range $100\text{--}200 \text{ mg l}^{-1}$.

The compounds toluene, *p*-xylene, 1,3,5-trimethylbenzene, chlorobenzene, 1,4-dichlorobenzene, 1,3,5-trichlorobenzene, cyclohexanol, cyclohexane, decane, 1-decanol and anthracene were supplied by Merck. Lindane was obtained from Riedel-de Haën (Seelze, Germany). A stock solution of these compounds was prepared in methanol at a concentration of 100 mg l^{-1} . The spiking solution was made by dilution of the stock solution in water samples at the concentration of $100 \text{ } \mu\text{g l}^{-1}$.

HPLC-grade methanol and hexane (Merck, Darmstadt, Germany) were used as eluting and extracting solvent. The pH of water samples was adjusted at 2 with sulfuric acid (Fluka, Buchs, Switzerland). Anhydrous sodium sulfate was obtained from Riedel-de Haën and was heated at $300 \text{ }^\circ\text{C}$ for 4 h before use. Acetic anhydride and other reagents were of the maximum purity available and obtained from Merck. Naphthalene and 1,3,5-trichlorobenzene were used as internal standards for FID and ECD, respectively. The commercial cartridges used were C_{18} (200 mg) from IST (Cambridge, UK); LiChrolut EN (200 mg) from Merck and Oasis HLB (60 mg) from Waters (Milford, MA, USA).

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 $70 \times 3 \text{ mm I.D.}$, stainless steel precolumn packed with 120 mg polymer.

A gas chromatograph model Chrompack CP 9001 equipped with flame ionization detector, electron-capture detector and a split/splitless injector was used. Separation of phenols were carried out using a capillary column CP-Sil 5 CB low bleed MS, ($25 \text{ m} \times 0.25 \text{ } \mu\text{m I.D.}$) with 0.25 mm film thickness. The injector and detector temperatures were set at 250 and $280 \text{ }^\circ\text{C}$, 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: $55 \text{ }^\circ\text{C}$ for 3 min, at $4 \text{ }^\circ\text{C min}^{-1}$ to $230 \text{ }^\circ\text{C}$, 5 min hold at $230 \text{ }^\circ\text{C}$. An aliquot of $2 \text{ } \mu\text{l}$ from each sample was introduced into the GC as splitless injection.

2.3. Polymer preparation

Details of PANI synthesis were previously described [12–14,20]. A modified version of previously described procedure was followed for the polymerizations [20]. Monomer (0.045 mmole) and concentrated HCl (24 g.) were dissolved in water to give a monomer solution (100 ml) and then chilled to $-25 \text{ }^\circ\text{C}$. Another solution (100 ml) was made by dissolving concentrated HCl (24 g) and ammonium peroxodisulfate (8.0 g) in water. The later solution was also chilled to $-25 \text{ }^\circ\text{C}$ and was then slowly added to the monomer solution, followed by stirring at $-25 \text{ }^\circ\text{C}$. The prepared polymer was, then, filtered through a buchner filter funnel connected to a water aspirator. The precipitate was washed with water and then placed in a solution of $0.1 \text{ M NH}_4\text{OH}$ and stirred for several hours. The polymer was dried under the vacuum. The product was subsequently extracted in a Soxhlet with methanol, tetrahydrofuran (THF) and then 1-methyl-2-pyrrolidone until the extracted solvent was colorless. After extraction, the synthesized polymer was washed with methanol and water and dried under vacuum and followed by grinding. Polymer particles sized $75\text{--}106 \text{ } \mu\text{m}$ were collected and used. The structures of the polymers are shown in Fig. 1. The specific surface area was determined according to the BET method [25]. Mercury porosimetry was used to determine the pore volume and the pore size distribution (Carlo Erba 800).

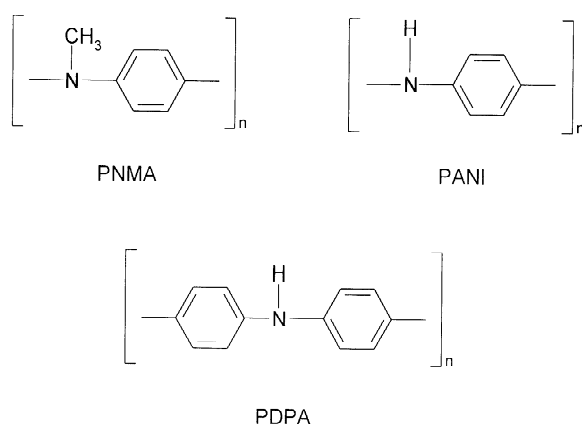


Fig. 1. Simple chemical structure of three polymers studied.

2.4. Sample preparation and derivatization process

A known volume of distilled or river water was spiked with phenol standards and was subsequently passed through a preconditioned SPE column at a flow-rate of 6 ml min^{-1} . When the sample had passed through, the cartridge was eluted with 2 ml of methanol at the flow-rate of 0.4 ml min^{-1} . The cartridge was preconditioned by washing with 5 ml of methanol and activated with 5 ml of distilled water. The derivatization procedure used was based on previous report by Rodríguez et al. [26]. A volume of 2 ml of a methanol solution containing phenols was mixed with 1 ml of 5% K_2CO_3 and 2 ml of *n*-hexane containing 200 ml of acetic anhydride and internal standard. The mixture was shaken for 1 min and the organic phase was allowed to 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 limit in the sample solution at sub-part per billion (ppb) concentration, final extract was

concentrated to 0.5 ml under a gentle stream of nitrogen.

In the case study of other compounds used for evaluating the selectivity of the polymer, the extraction was performed with 2 ml of methanol and an aliquot of $2 \mu\text{l}$ was injected into the GC system with FID detection.

3. Results and discussion

3.1. Evaluation of sorbents

Table 1 gives the physical features of three synthesized polymers. Both GC–FID and GC–ECD were used for evaluation of retention and elution efficiency of these SPE materials. Since phenols are environmentally important to be monitored in water samples, they were chosen as model compounds in this study. It has been known the acidic condition leads to higher extraction recoveries for acidic compounds, e.g. chlorophenols, on non-polar sorbents [27]. Our previous work using polyaniline also showed that, maximum recoveries for chlorophenols were obtained for sample solutions having low pH [20]. To compare the new sorbents, 200 ml standard solutions containing $50 \mu\text{g l}^{-1}$ from each phenol, acidified with sulfuric acid at pH 2, were preconcentrated on the cartridges containing these polymers. The results of this study are shown in Table 2. High recoveries for all analytes except phenol were found when PNMA was used. The recovery value for the most polar compound, phenol was 32% with PNMA, while it was not concentrated on PANI and PDPA. PANI and PDPA showed relatively good recoveries for all compounds except phenol. Both sorbents gave similar recoveries, between 55 and 72% for 2CP, 4CP and 24DMP and more than 86% for 246TCP and PCP. These results clearly demonstrate that

Table 1
Physical features of studied polymers

| Polymer | Pore volume (ml g^{-1}) | Average pore radius (nm) | Specific surface area ($\text{m}^2 \text{g}^{-1}$) | Particle size (μm) |
|---------|---------------------------------------|-----------------------------|---|------------------------------------|
| PNMA | 0.79 | 5 | 38 | 75–106 |
| PANI | 0.75 | 6 | 33 | 75–106 |
| PDPA | 0.15 | 5.9 | 32 | 75–106 |

Table 2
Recoveries of extraction of phenols from 200 ml water sample spiked at $50 \mu\text{g l}^{-1}$ with the three sorbents^a

| Compound | % Recovery | | |
|----------|------------|------|------|
| | PNMA | PDAD | PANI |
| Ph | 32 | nd | nd |
| 2CP | 101 | 65 | 53 |
| 4CP | 106 | 72 | 62 |
| 24DMP | 98 | 67 | 53 |
| 24DCP | 101 | 98 | 102 |
| 246TCP | 104 | 102 | 99 |
| PCP | 111 | 86 | 108 |

^a The relative standard deviations (RSD) are between 3 and 10% ($n=3$).

breakthrough volume of phenol using PNMA polymer is higher than the ones obtained with other two polymers. PNMA was, therefore, selected for further studies.

In order to determine the volume of the sample that can be concentrated with the acceptable levels of recoveries and also the effect of sample pH, different volumes (75, 100, 250, 500 and 1000 ml) of distilled water, at pH 2 and 6 (distilled water without additive) were spiked with a solution containing phenolic compounds at the $20\text{--}100 \mu\text{g l}^{-1}$ level. The trapped compounds on the precolumn were, then, eluted with 2 ml of methanol; followed by derivatization and extraction with a total of 3 ml of *n*-hexane and gentle evaporation to 1 ml, an aliquot of $2 \mu\text{l}$ was injected into the GC system. The recoveries of phenolic compounds for the different volumes are given in Table 3. Preconcentration of up

to 1000 ml of water sample at pH 2, led to more than 63% recovery for all of the analytes, whereas only 8% of the phenol was recovered. In order to determine and quantify phenol, the most difficult species, a sample volume not more than 100 ml should be employed. Of course, when the determination of phenol is excluded, the preconcentration of large volumes of samples, up to 1 l, leads to rather satisfactory results for others.

Comparing the recoveries values obtained at two different sample pH (Table 3), it is found that there is no great difference between the results of the method for the preconcentration of volumes up to 1 l of water sample; of course PCP is an exception. But all recovery values at neutral pH are slightly lower than acidic pH. In neutral solution, PCP is not trapped on PNMA even if 50 ml of sample is pumped through the sorbent. With respect to $\text{p}K_{\text{a}}$ of PCP ($\text{p}K_{\text{a}}=4.93$), one can find that the ratio of ionized to uncharged form of PCP is between 12 and 37 at pH 6–6.5. This shows that the ionized form of PCP is the dominant species at this pH. Because of high solubility of the ionized form, sorption of PCP would not take place.

To have a better overview on the efficiency of these polymers, a comparison study was carried out using C_{18} , Oasis HLB and LiChrolut EN. C_{18} is a well-known and widely used commercial sorbent and the other two polymers are relatively new and more efficient sorbents. Spiked distilled water samples with phenols were passed through the cartridges. After elution and derivatization, an aliquot of $2 \mu\text{l}$ was injected onto the GC. As Table 4 demonstrates, the recoveries of all compounds except 24DCP and

Table 3
The extraction recoveries obtained for the studied phenols at different volume (ml) of sample solution spiked in the range between 20 and $100 \mu\text{g l}^{-1}$ using PNMA^a

| Compound | % Recovery | | | | | | | | | |
|----------|------------|-----|-----|-----|------|------|-----|-----|-----|------|
| | pH 2 | | | | | pH 6 | | | | |
| | 75 | 100 | 250 | 500 | 1000 | 75 | 100 | 250 | 500 | 1000 |
| Ph | 93 | 73 | 36 | 14 | 8 | 69 | 68 | 38 | 15 | <7 |
| 2CP | 90 | 95 | 101 | 102 | 65 | 101 | 92 | 66 | 69 | 56 |
| 4CP | 88 | 100 | 106 | 85 | 70 | 92 | 94 | 71 | 86 | 65 |
| 24DMP | 93 | 98 | 108 | 92 | 63 | 110 | 102 | 82 | 106 | 53 |
| 24DCP | 96 | 103 | 95 | 89 | 84 | 93 | 99 | 86 | 95 | 83 |
| 246TCP | 98 | 95 | 92 | 97 | 93 | 106 | 97 | 97 | 98 | 89 |
| PCP | 109 | 114 | 107 | 101 | 96 | Nd | nd | nd | nd | nd |

^a The relative standard deviations (RSD) are between 5 and 12% ($n=3$).

Table 4

The extraction recoveries obtained for the studied phenols at different volume (ml) of sample solution spiked in the range between 20 and 50 $\mu\text{g l}^{-1}$ using C_{18} ^a

| Compound | % Recovery | | |
|----------|------------|-----|-----|
| | 50 | 100 | 250 |
| Ph | 40 | 11 | <5 |
| 2CP | 47 | 24 | 18 |
| 4CP | 80 | 50 | 30 |
| 24DMP | 94 | 55 | 38 |
| 24DCP | 78 | 56 | 46 |
| 246TCP | 86 | 82 | 71 |
| PCP | 97 | 90 | 82 |

^a The relative standard deviations (RSD) are between 4 and 11% ($n=3$).

PCP are less than 46% using 250 ml of water samples when C_{18} was used. There are many published data regarding the preconcentration of phenols using C_{18} [27–31]. As Table 3 demonstrates, PNMA shows a clear advantage, over C_{18} , on the recoveries of phenols under similar circumstances. Moreover, Oasis HLB and LiChrolut EN showed excellent recoveries for all compounds, which are listed in Table 5. The results obtained from PNMA are comparable with those listed in Table 5 except phenol. Apparently PNMA, in the present synthesized form, suffers from the lack of high specific surface area and traps phenol not as efficiently as Oasis and LiChrolut EN.

Table 5

The extraction recoveries obtained for the studied phenols at different volume (ml) of sample solution spiked in the range between 20 and 50 $\mu\text{g l}^{-1}$ using Oasis and LiChrolut EN^a

| Compound | % Recovery | | | |
|----------|------------|-----|--------------|-----|
| | Oasis HLB | | LiChrolut EN | |
| | 250 | 500 | 250 | 500 |
| Ph | 82 | 72 | 95 | 91 |
| 2CP | 89 | 78 | 94 | 89 |
| 4CP | 95 | 87 | 97 | 95 |
| 24DMP | 93 | 89 | 95 | 101 |
| 24DCP | 98 | 95 | 93 | 95 |
| 246TCP | 94 | 93 | 93 | 96 |
| PCP | 93 | 91 | 98 | 94 |

^a The relative standard deviations (RSD) are between 2 and 10% ($n=3$).

3.2. Real samples

The sensitivity of the method with FID would not meet the demands of today's environmental analysis. ECD was, therefore, employed to achieve lower detection limits. Five chlorophenols were selected for this part of study. Different volumes (250, 500 and 1000 ml) of the sample solution, at pH 2, spiked with these chlorophenols at levels between 0.1 and 1.5 $\mu\text{g l}^{-1}$ passed through the PNMA cartridge. After extraction and derivatization an aliquot of 2 μl of hexane solution was injected into GC. Results are shown in Table 6. Recoveries of 85% and more for sample volumes up to 1 l are obtained. The results are slightly better than those obtained at higher spiked level (Table 3).

To check the linearity of the method with GC–ECD, the PNMA sorbent was loaded with 500 ml of the sample solution spiked with 0.02–0.31 and 0.4–6.2 $\mu\text{g l}^{-1}$ of five studied analytes. No significant differences between the recovery results based on the RSD of the method were observed.

The performance of the sorbent was tested using a 250 ml water sample from the Karoun river (Ahwaz, Iran), spiked with 0.04–0.62 $\mu\text{g l}^{-1}$ of standard solutions of five chlorophenols. After the extraction and derivatization step, an aliquot of final extractant was injected into the GC system. The recoveries obtained for real sample were similar to those obtained when distilled water was used. Fig. 2 shows the gas chromatograms of the Karoun river water sample and the same sample spiked with a standard solution of chlorophenols. The chromatogram of

Table 6

The extraction recoveries obtained for the studied phenols at different volume of sample solution spiked at 0.1–1.5 $\mu\text{g l}^{-1}$ using PNMA and ECD detection^a

| Compound | % Recovery | | |
|----------|------------|-----|------|
| | 250 | 500 | 1000 |
| 2CP | 101 | 102 | 85 |
| 4CP | 106 | 95 | 93 |
| 24DCP | 95 | 93 | 99 |
| 246TCP | 92 | 97 | 102 |
| PCP | 88 | 101 | 94 |

^a The relative standard deviations (RSD) are between 3 and 8% ($n=3$).

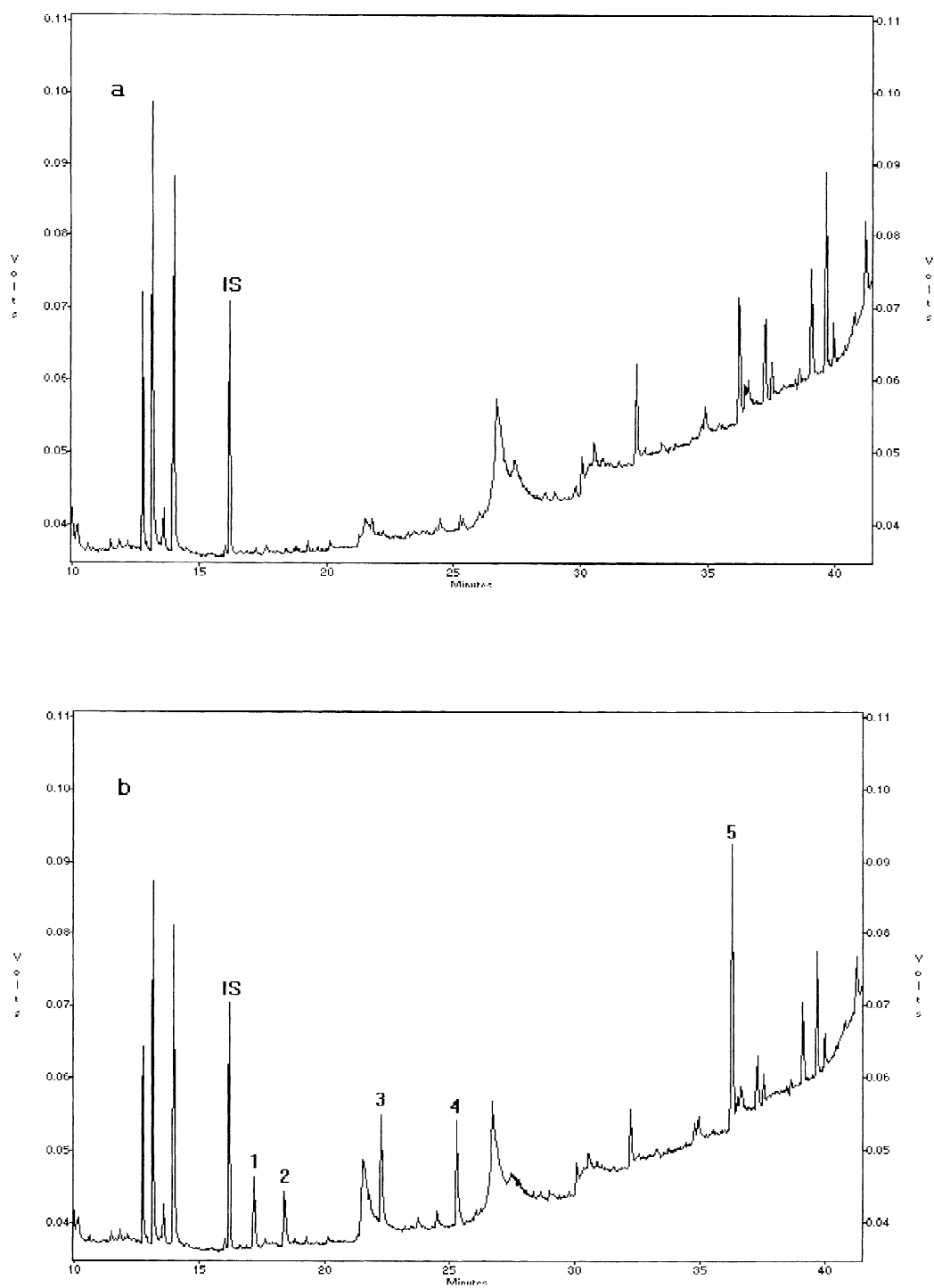


Fig. 2. Gas chromatograms obtained after SPE of (a) 250 ml Karoun river water and (b) 250 ml Karoun river water spiked with 0.04–0.62 $\mu\text{g l}^{-1}$ of chlorophenols. I.S., internal standard, 1: 2CP, 2: 4CP, 3: 24DCP, 4: 246TCP, 5: PCP.

unspiked river water shows a peak at retention time due to the presence of PCP, which would correspond to concentration of 24 ng l^{-1} . The limits of detection, using 250 ml of water, were calculated with S/N of 3 based on peak-to-peak noise and were in the range of $1\text{--}40 \text{ ng l}^{-1}$ for chlorophenols.

3.3. SPE of other compounds

In order to have a better understanding of the nature of interactions between analyte and sorbent, a number of other compounds of different classes were also studied. In Table 7 the recovery of these compounds on PNMA using a sample volume of 250 ml water spiked at a concentration of about $50 \mu\text{g l}^{-1}$ at different pH's is listed.

It is known that the polymer has polar functional groups and carries a slightly positive charge in its structure. This makes the polymer suitable to have tendency towards sorption of negatively charged species [21]. But, as we previously discussed, anionic form of PCP cannot be retained on polymer. Nevertheless, it is possible that the polar sites share hydrogen bonding with hydroxyl group of phenols and sorption may occur due to this phenomenon.

Another possibility in the retention mechanism is hydrophobic interaction. The polymer network consists benzene rings with an extensive conjugated π

system. In Table 7 the extraction recoveries for all aromatic compounds are more than 75% at both pHs. On the other hand, surprisingly, for aliphatic compounds decane, 1-decanol, cyclohexane and cyclohexanol, the recoveries obtained are poor and less than 20%. All of these compounds are known as non-polar compounds. This indicates that compounds with aromatic zones are more capable than aliphatic ones to be trapped on the polymer. It shows that probably sorption of analyte on PNMA mainly occurs as a result of $\pi\text{--}\pi$ interaction between the aromatic structure of the sorbent and π -electrons of the analyte. On the other hand, the very low recovery for aliphatic compounds demonstrated that the polymer has low tendency toward sorption of saturated compounds.

With respect to recoveries results achieved at two pHs, it is also found that, recovery values at pH 2 are slightly lower than those obtained at acidic pH. Unlike phenols, the compounds studied in Table 7 are not ionizable under effect of sample pH, and any effect on the recovery of the compounds with changing the pH of the solution will be, therefore, assigned to changes in electronic structure and population of π -system of the polymer. Although, this effect is negligible, extraction of organic compounds under acidic condition is preferred.

4. Conclusion

New types of sorbents, originally classified as conductive polymers, have been introduced and evaluated for extraction of organic pollutants from water samples. The capability of these sorbents to extract phenols has been compared with commercial C_{18} and PNMA, with a relatively small specific surface area, showed higher breakthrough volumes for the studied compounds. Using PNMA as a SPE sorbent, led to quantitative results for preconcentration of chlorophenols from 1 l water sample. Considering the existence of efficient sorbents such as LiChrolut EN and Oasis HLB, octadecyl-bounded silica has remained the most used sorbent for off-line procedures. However, these laboratory-made polymers with the ease of preparation show better performance than C_{18} , at least in some field of applications.

Table 7

Recoveries of extraction of organic compounds with different characteristics from a 250 ml water sample spiked at $50 \mu\text{g l}^{-1}$ using PNMA at two different pH^a

| Compound | % Recovery | |
|------------------------|------------|------|
| | pH 2 | pH 6 |
| Cyclohexane | <7 | <7 |
| Toluene | 79 | 76 |
| Chlorobenzene | 95 | 86 |
| <i>p</i> -Xylene | 87 | 80 |
| Cyclohexanol | 12 | 13 |
| 1,3,5-Trimethylbenzene | 92 | 90 |
| Decane | 19 | 13 |
| 1,4-Dichlorobenzene | 99 | 86 |
| 1,3,5-Trichlorobenzene | 87 | 79 |
| Lindane | 104 | 90 |
| Anthracene | 75 | 73 |
| 1-Decanol | <10 | <10 |

^a The relative standard deviations (RSD) are between 3 and 11% ($n=3$).

The existence of functional groups in polymer backbone, also, affects the performance of polymer for sorption of organic analytes. Our observations indicate that these laboratory-made polymers can be used frequently even after being dried out. It can be added that conductive polymers have shown to have potential to be employed as packing material for the SPE purposes. Clearly, enlarging the specific surface area by changing the synthesis conditions could lead to much more efficient sorbents.

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