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# Efficient solid-phase extraction procedures for trace enrichment of priority phenols from industrial effluents with high total organic carbon content<sup>☆</sup>

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## Abstract

Polymeric solid-phase extraction (SPE) cartridges and Speedisks were used to extract 17 phenols from HPLC-grade water, tap water, river water and industrial effluents. With SPE cartridges, recoveries between 60 and 120% were obtained for waters with a total organic carbon (TOC) content below 20 mg C/l. However, when extracting industrial effluent waters with higher TOC values (75 mg C/l), only the polar phenols were recovered from the water fraction. Nonpolar compounds (di-, tri- and tetrachlorophenols) remained attached to the particulate matter and were recovered from the 0.45- $\mu$ m filter membrane disks by Soxhlet extraction. Speedisks offered a high efficiency and permitted one to extract phenols without a prior filtration step. Acceptable recoveries were obtained when processing heavily charged industrial effluents with a TOC of 505 mg C/l. Liquid chromatography with electrochemical detection was used for the routine determination of 17 priority phenols. © 1999 Published by Elsevier Science B.V. All rights reserved.

**Keywords:** Solid-phase extraction; Total organic carbon; Water analysis; Industrial effluents; Phenols

## 1. Introduction

Phenol and substituted phenols such as chlorophenols and methylphenols are well known because they are frequently found in surface and tap waters. Effluent discharges of industries (paper, pulp, pesticide industries, etc.) are the main sources of these compounds [1]. Due to their toxicity and adverse effects upon biota [2,3] and humans [4], the Euro-

pean Union (EU) [4], the World Health Organization (WHO) [5], and the US Environmental Protection Agency (EPA) [6,7] have determined maximum permissible levels of phenols in surface, ground and drinking waters and have listed the more toxic and persistent compounds. A recent review summarizes the actual regulations [8]. Moreover, a new Directive has appeared in 1996 [9] indicating the need to monitor industrial effluents, which represent a far more complex matrix than surface or groundwater samples. Industrial effluent waters are characterized, among other attributes, by their high total organic carbon (TOC) (from 20 up to 1000 mg C/l or more, compared to levels of 1 to 10 in surface waters) and by containing a high amount of particles. This means

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that the extraction procedures developed for surface and ground waters may not necessarily work for industrial effluent waters since filtration and extraction will be influenced by the TOC, humic and fulvic material and the particle content of the water matrix. Scott et al. [10] reported that changes in the type of water could lead to considerable variations in the breakthrough volumes and detection limits. Liquid–liquid extraction (LLE) [6,7] has been used to extract phenols from water, but recent studies are directed to the use of solid-phase extraction (SPE) either on-line [11–14] or off-line [15,16]. Regarding SPE,  $C_{18}$  and polymeric sorbents have been tested [11–21], the latter being the most effective for trapping phenolic compounds [22]. Modern detection techniques use liquid chromatography (LC) with diode array detection (DAD) [11,16], electrochemical detection (ED) [23,24], coulometric detection [25,26], mass spectrometry [27] and enzyme-linked immunosorbent assays (ELISAs) [28]. Capillary zone electrophoresis has also been used for a quick and selective separation [29].

In this study, 17 phenolic compounds, which included phenol, methylphenol and chlorophenols, were extracted from HPLC-grade water, tap water, river water and industrial effluents using polymeric SPE cartridges (Oasis 60 mg) and Speedisks. The effect of the TOC and particle content upon recovery was tested in order to determine whether phenols were extracted from the water or particulate fraction of the sample. LC–ED was used because it provides both selectivity and sensitivity [23,24].

## 2. Experimental

### 2.1. Chemicals and reagents

Pure standards (98–99%) phenol, 3-methylphenol, 2-chlorophenol, 4-chlorophenol, 3-chlorophenol, 2,4-dimethylphenol, 2,6-dichlorophenol, 2,5-dichlorophenol, 2,4-dichlorophenol, 2,3,6-trichlorophenol, 2,3,4-trichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol and 2,3,5-trichlorophenol were from Sigma–Aldrich (France). 3,4,5-Trichlorophenol, 2,3,5,6-tetrachlorophenol and 2,3,4,6-tetrachlorophenol were purchased from Dr. Ehrenstorfer (Ehrenstorfer Labs., Augsburg, Germany). Acetonitrile was a gift from Baker (Deventer, The Nether-

lands) and dichloromethane was purchased from SDS (Peypin, France). Pure HPLC-grade water was generated with a Maxima Ultra Pure Water (Elga, France). SPE cartridges were Oasis 60 mg from Waters (USA). SPE Speedisks packed with styrene–divinylbenzene were from Baker (Deventer, The Netherlands). Normapur chloridric acid and Normapur acetic acid were from Prolabo (France). Sodium acetate was purchased from Merck (Darmstadt, Germany).

### 2.2. Sample collection and preparation

Four types of water were tested: HPLC-grade, tap, river and industrial effluents. Four liters of each water sample was collected in Pyrex borosilicate glass bottles. River water was collected from the Rhône, on its way through the city of Lyon. The TOC content was 5 mg C/l, which is characteristic for surface water samples, where, in general, TOC values are between 1 and 10 mg C/l. Three different industrial effluents were tested, with a TOC of 20 mg C/l, 75 mg C/l, and a charged water with a TOC of 505 mg C/l. Upon reception, samples were immediately stored at 5°C and the TOC content was determined. All the samples used in this study did not contain any traces of phenols. Within 24 h, samples were acidified with 2 M HCl to a pH of 2 and spiked at a level of 1 to 3 ng/ml. HPLC-grade water and tap water were never filtered. Prior to SPE with Oasis 60 mg cartridges, river water and industrial effluents with a TOC of 20 mg C/l were filtered through a 0.45- $\mu$ m porous nylon membrane filter of 47 mm diameter (Whatman, UK) to remove all the particles which would obstruct the cartridge. Industrial effluents with a TOC above 20 mg C/l needed a prior filtration through 1.2- $\mu$ m glass fiber filters of 47 mm diameter (Whatman). These membrane filtration disks were Soxhlet extracted to check whether phenols had been retained in the particulate matter of the sample. Speedisks incorporate a membrane which retains the particles and filtration was not needed.

### 2.3. Solid-phase extraction

#### 2.3.1. Extraction with cartridges

Samples were extracted using the automated system ASPEC XL (Gilson, Villiers-le-Bel, France).

Oasis 60 mg cartridges were rinsed with 3 ml of dichloromethane. Conditioning was performed with 3 ml of acetonitrile and 3 ml of water at a flow-rate of 6 ml/min, letting the solvent soak the cartridge for 1 min before allowing it go through the cartridge. Cartridges were never allowed to dry. A 200-ml sample was applied at a flow-rate of 5 ml/min. After the preconcentration step, cartridges were rinsed with 1 ml of water at a flow-rate of 30 ml/min, to remove matrix impurities. Afterwards, the cartridges were dried, under nitrogen, during 20 min. Elution for these type of cartridges was performed with 2.5 ml of acetonitrile at a flow-rate of 1 ml/min, followed by a second elution with 2.5 ml of acetonitrile–dichloromethane (1:1). The extract was evaporated under a gentle stream of nitrogen to an approximate volume of 500–1000  $\mu$ l. The extract was weighed and the exact volume was corrected by density. In all cases, 10  $\mu$ l of the extract was analyzed by LC–ED. Triplicate extractions were performed with each type of matrix.

Breakthrough volumes for this type of cartridges were measured by percolating 50, 100, 250 and 500 ml of unfiltered tap water samples spiked at a level of 1 ng/ml using the method described above. No breakthrough was observed by percolating 500 ml of water, so 200 ml was used for SPE with cartridges since it provided enough sensitivity.

### 2.3.2. Soxhlet extraction of membrane filtration disks

An industrial effluent with a TOC of 75 mg C/l was spiked with the 17 phenols at a level of 3 ng/l. Prior to SPE with cartridges, this sample was filtered through 1.2- $\mu$ m glass fiber filters and afterwards through 0.45- $\mu$ m nylon membrane disks. For each 200 ml, one glass fiber filter disk and two nylon filter disks were used. These membrane filtration disks were wrapped in aluminum foil and were kept at  $-20^{\circ}\text{C}$  until analysis.

Each set of disks were Soxhlet extracted during 6 h using 200 ml of dichloromethane. Afterwards, the extract was rotaevaporated under 780 bar, at  $35^{\circ}\text{C}$  just to dryness. The extract was transferred to vials and the solvent was changed from dichloromethane to acetonitrile by successive evaporations under a gentle stream of nitrogen, to a final volume of approx. 4 ml. The vials were weighed before and after transferring the sample, and the exact volume

was corrected by density. A 10- $\mu$ l volume of this extract was analyzed by LC–ED.

Furthermore, the HPLC-grade water spiked at 3 ng/ml was also extracted, and both the water and the membrane filtration disks were analyzed using the same procedure as described above. This procedure was used to discard adsorption of phenols on the membrane filtration disks.

### 2.3.3. Extraction with Speedisks

An expanded extraction six-port processing system (Baker) was used. Speedisks were of styrene–divinylbenzene and contained a mesh on top of the sorbent which acted as a filter. HPLC-grade, tap, river and industrial effluent waters were spiked with 17 phenols at a level of 1 ng/ml. Five hundred ml of water was extracted at a flow-rate of 100 ml/min without any prior filtration. Only 250 ml of the spiked industrial effluent was preconcentrated due to the high TOC (505 mg C/l) and a high particle content. Prior to extraction, the disks were rinsed by soaking them with 20 ml of dichloromethane during 1 min and afterwards the solvent was removed under vacuum. Conditioning was performed with 20 ml of acetonitrile followed by 20 ml of HPLC-grade water, without allowing the disk to dry. Immediately after, the water sample was dispensed from the containers to the disk via a remote sample adapter (Baker). Afterwards, the disks were rinsed with 5 ml of HPLC-grade water and were dried under vacuum during 30 min. Elution was carried out in two steps: (i) with 10 ml of acetonitrile, allowing it to stay for 2 min, and letting it pass through the disk drop to drop before applying the vacuum to remove all the solvent and (ii) using the same protocol with 10 ml of acetonitrile–dichloromethane (1:1, v/v). The extracts were evaporated under a gentle stream of nitrogen to a final volume of approx. 3 ml. These vials were weighed and the volume was corrected by solvent density (acetonitrile). A 10- $\mu$ l volume was analyzed by LC–ED. By using this extraction procedure, a concentration factor between 150 and 200 was achieved. Triplicate extractions were performed with each type of matrix.

### 2.4. Liquid chromatography–electrochemical detection

A HP 1050 isocratic pump was connected to a HP

1049 programmable electrochemical detector (Hewlett-Packard, Waldbronn, Germany). A column oven Model CTO-10A from Shimadzu (Tokyo, Japan) was set at 40°C. Data acquisition was performed with a HP B.02.06 Chemstation. An Alltech (USA) on-line degassing system was used to degas the mobile phase. The chromatographic separation was performed with a Hewlett-Packard Hypersil BDS C<sub>18</sub> stainless steel column (250×4 mm I.D.) with a particle size of 5 µm. The mobile phase consisted of a 20 mM sodium acetate–acetic acid solution (pH 4.5) which was mixed with a proportion of 60% of buffer, 30% of acetonitrile and 10% methanol. The flow-rate was set at 1.5 ml/min. The potential used in ED was 1 V. A potential of 1.2 V increased the noise, and therefore it was discarded. The electrochemical detector was set to amperometric mode and worked with a glassy carbon electrode. An Ag/AgCl reference electrode was used. Since most of the samples were from industrial effluents, the working electrode had to be polished at least once a week and every time the system was started. A proper electrode had to give a current below 50 nA.

Quantification was performed by external standard comparison. Calibration was performed by injecting a standard mixture of the phenols over a concentration range of 20 to 600 ng/ml.

### 3. Results and discussion

#### 3.1. Detection and quantification by LC–ED

LC–ED is a suitable procedure to detect phenolic compounds at µg/l levels [23,24]. Under isocratic conditions it was possible to separate 17 phenols in 30 min. Good linearity was observed between 20 and 600 ng/ml ( $r^2 > 0.99$ ). The limit of detection (LOD) was calculated from the chromatogram obtained at a concentration of 20 ng/ml. By taking three-times the signal-to-noise ratio, the LOD varied from 2 to 10 ng/ml for phenol, 3-methylphenol, monochlorophenols and dichlorophenols and from 20 to 60 ng/ml, for the other compounds due to some peak broadening under isocratic conditions. The reproducibility of the technique was tested by injecting a calibration solution containing the 17 phenols at a concentration of 300 ng/ml every time the system

was started. Because LC–ED is very sensitive to changes in the mobile phase composition and the electrode condition, the buffer was carefully prepared to avoid pH shifts, and the working electrode was polished at the beginning of each experiment. Even under these conditions, the reproducibility was up to 40% ( $n=5$ ). This is one of the main drawbacks of using LC–ED for environmental water analysis since its robustness is limited due to the fact that the electrochemical cell maintenance and calibration have to be performed frequently. The repeatability of the LC–ED procedure was 4% ( $n=3$ ).

#### 3.2. Effect of TOC on SPE using Oasis 60 cartridges

The analysis of environmental water samples poses a problem because such samples often contain a high particle and TOC content. The phenolic compounds tested have different physico-chemical properties. Water-soluble and polar compounds, such as phenol, have a tendency to migrate to the water phase. In contrast, nonpolar compounds can adsorb to the particulate material and humic and fulvic acids present in the water. As reported by Liska et al. [30], adsorption of organic pollutants onto humic substances results in a decrease of the breakthrough volumes and recoveries, since only the dissolved fraction is enriched. Table 1 reports the recoveries obtained after the preconcentration of 200 ml of HPLC-grade, tap and river waters and an industrial effluent with a TOC of 20 mg C/l. Most phenolic compounds were recovered at levels of 60 to 120%. The high recovery of 2,5-dichlorophenol from tap water was attributed to a matrix interference. Lowest relative standard deviations (RSDs) correspond to HPLC-grade water, since there is no matrix effect. RSDs below 12% were obtained when analyzing industrial effluents which had a TOC 4–5-times higher than that of surface waters.

Table 2 shows the recovery of phenols from an industrial effluent with a TOC of 75 mg C/l. Recoveries refer to the water fraction (extracted with Oasis cartridges) and the particulate matter (filtration membrane disks, Soxhlet extracted). The most polar compounds were extracted from the water fraction while tri- and tetrachlorophenols were recovered from the filtration membranes. For intermediate

Table 1

Recovery data in percentage (% *R*) and relative standard deviation (RSD) of the studied phenols after pre-concentration of 200 ml of HPLC-grade, tap and river waters (TOC of 5 mg C/l) and an industrial effluent (TOC of 20 mg C/l) spiked at a level of 1 ng/ml (*n*=3)<sup>a</sup>

Compound	HPLC-grade water		Tap water		River water		Industrial effluent	
	% <i>R</i>	RSD	% <i>R</i>	RSD	% <i>R</i>	RSD	% <i>R</i>	RSD
Phenol	89	9.0	83	1.5	108	2.9	145	1.9
3-Methylphenol	64	10.1	83	1.4	86	8.3	88	11.6
2-Chlorophenol	91	1.7	91	8.4	95	2.1	105	2.0
4-Chlorophenol	98	2.2	91	8.4	90	6.5	85	2.4
3-Chlorophenol	87	2.5	74	6.7	94	2.8	96	8.5
2,4-Dimethylphenol	93	3.6	75	7.0	113	1.9	153	5.7
2,6-Dichlorophenol	95	2.7	90	5.4	99	1.6	89	2.8
2,5-Dichlorophenol	96	3.4	147	1.1	118	3.1	90	1.4
2,4-Dichlorophenol	97	2.3	97	3.9	95	1.8	99	2.8
2,3,6-Trichlorophenol	94	0.6	103	9.1	97	6.8	96	8.7
2,3,4-Trichlorophenol	94	6.4	110	6.9	97	5.2	96	7.5
2,4,6-Trichlorophenol	96	7.6	101	7.5	108	8.9	105	11.7
2,4,5-Trichlorophenol	99	4.7	80	5.3	89	6.5	99	7.0
2,3,5-Trichlorophenol	93	3.7	84	3.0	91	7.2	81	6.5
3,4,5-Trichlorophenol	117	2.5	85	5.8	87	5.3	81	3.5
2,3,5,6-Tetrachlorophenol	100	4.8	107	14.3	107	4.2	117	1.9
2,3,4,6-Tetrachlorophenol	115	7.2	61	1.8	79	9.1	51	8.7

<sup>a</sup> Extraction was carried out using Oasis 60 mg cartridges and detection by LC–ED.

Table 2

Mean percentage recovery (% *R*) and relative standard deviation (RSD, *n*=3) of phenols from a spiked industrial effluent (TOC of 75 mg C/l) after off-line SPE with Oasis 60 mg cartridges and percentage recovery of phenols from the particulate fraction of the same sample (% *R*<sub>sox</sub>) (*n*=1) after Soxhlet extraction of membrane filtration disks<sup>a</sup>

Compound	% <i>R</i>	RSD	% <i>R</i> <sub>sox</sub>
Phenol	126	3.1	int. <sup>b</sup>
3-Methylphenol	116	18.7	15
2-Chlorophenol	7	4.2	0
4-Chlorophenol	58	11.5	0
3-Chlorophenol	165	19.4	0
2,4-Dimethylphenol	125	20.3	28
2,6-Dichlorophenol	74	5.9	18
2,5-Dichlorophenol	82	8.9	30
2,4-Dichlorophenol	72	35.1	29
2,3,6-Trichlorophenol	48	4.8	55
2,3,4-Trichlorophenol	0	0	92
2,4,6-Trichlorophenol	49	2.3	74
2,4,5-Trichlorophenol	0	0	81
2,3,5-Trichlorophenol	0	0	98
3,4,5-Trichlorophenol	0	0	99
2,3,5,6-Tetrachlorophenol	0	0	140
2,3,4,6-Tetrachlorophenol	0	0	77

<sup>a</sup> Determination by LC–ED.

<sup>b</sup> int.=Interference.

polarities, the low recovery from water was compensated by a high recovery from the filtration membranes. Fig. 1A shows the chromatogram of a standard solution at 40 ng/ml. Fig. 1B and C present results after SPE with cartridges of an industrial effluent spiked at 3 ng/l and its blank. Fig. 1D and E represent the particulate fraction of the same spiked and blank industrial effluent, respectively. Comparison of chromatograms B and D, shows that phenol, 3-methylphenol, monochlorophenols and dichlorophenols were mainly recovered from the water fraction, indicating that these compounds have a higher affinity for the water phase than for the particulate matrix. The other compounds were predominantly present in the Soxhlet-extracted particulate fraction. Blank analyses of the water and particulate fractions of the industrial effluents give an idea of the matrix contribution of each fraction, which appears during the first 5 min of elution. The high recoveries of phenol, 3-methylphenol and 3-chlorophenol from water were attributed to matrix interferences due to their early elution times (see Fig. 1). 3-Methylphenol was recovered in 15% from the Soxhlet-extracted filtration disks, which added to the amount recovered from water, gave a recovery of 130%. As can be seen from Table 2, the recovery of

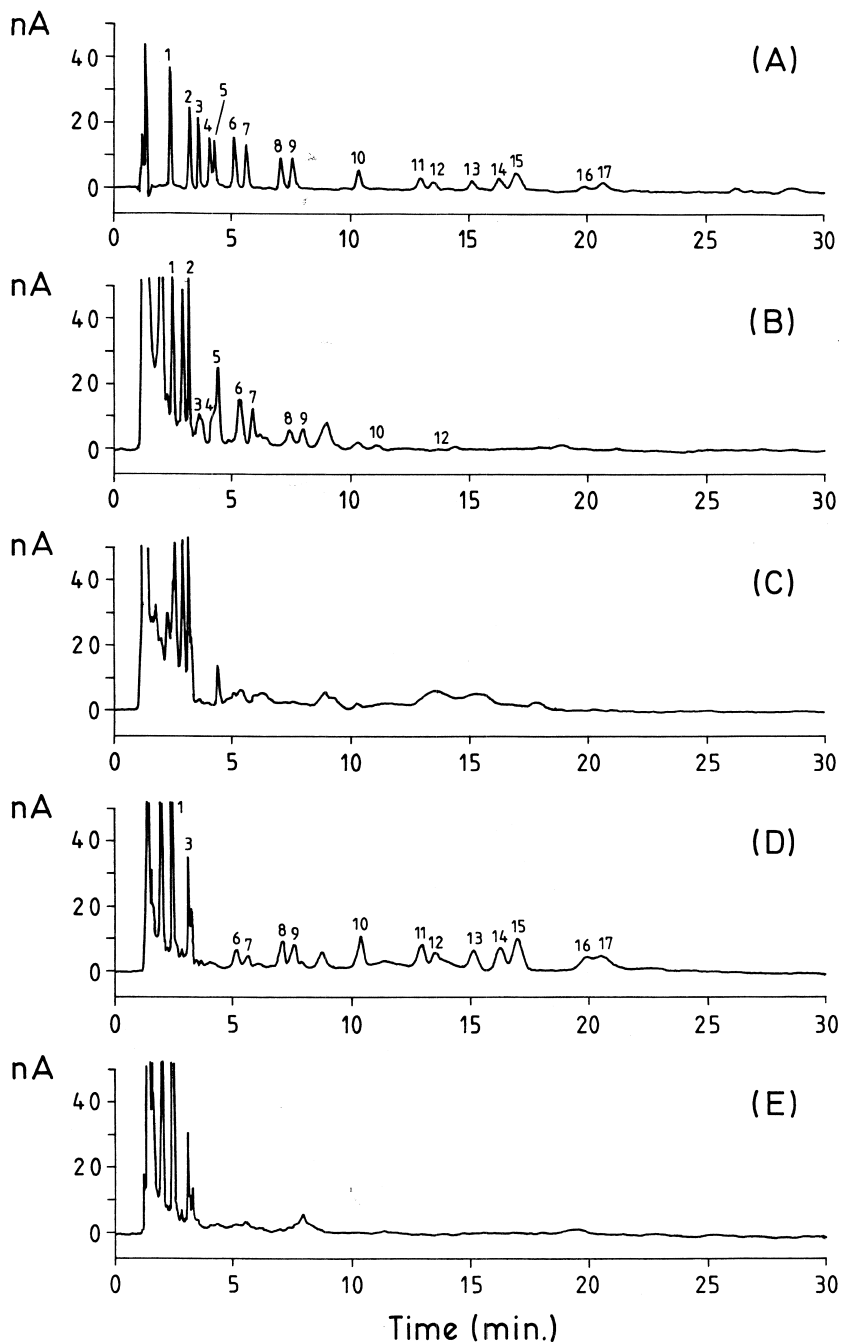


Fig. 1. LC-ED chromatograms which correspond to (A) standard at 40 pg/μl; (B) industrial effluent water extract (75 mg C/l TOC) spiked at a level of 3 ng/l extracted with Oasis 60 mg cartridges; (C) corresponding blank industrial effluent water extract; (D) Soxhlet extracted filtration membranes corresponding to the industrial effluent particulate matter; (E) Soxhlet extracted filtration membranes corresponding to a blank industrial effluent particulate matter. Peaks: 1=phenol; 2=3-methylphenol; 3=2-chlorophenol; 4=4-chlorophenol; 5=3-chlorophenol; 6=2,4-dimethylphenol; 7=2,6-dichlorophenol; 8=2,5-dichlorophenol; 9=2,4-dichlorophenol; 10=2,3,6-trichlorophenol; 11=2,3,4-trichlorophenol; 12=2,4,6-trichlorophenol; 13=2,4,5-trichlorophenol; 14=2,3,5-trichlorophenol; 15=3,4,5-trichlorophenol; 16=2,3,5,6-tetrachlorophenol; 17=2,3,4,6-tetrachlorophenol.

2-chlorophenol was poor. This compound has been reported to volatilize during preconcentration of neutral or acidic eluates, humic and fulvic acids being responsible for these losses, although the mechanism is not well understood [19]. Moreover, it was noticed that the evaporation time needed to concentrate the industrial effluent extract was longer than that for HPLC-grade or tap water extracts so that volatilization of 2-chlorophenol could be enhanced.

2,4-Dimethylphenol and dichlorophenols were extracted from the filtration membranes at levels between 18 and 30%. These compounds have an intermediate polarity, calculated by the octanol–water coefficient [31], and have a tendency to remain in the water fraction, although a migration to the particulate fraction of the sample is not discarded. In most cases, if we add the amount of each compound recovered from water and the one recovered from the filtration disk, the overall recovery is close to 100%, indicating that part of these compounds remained attached to the particles and humic and fulvic material. Moreover, under acidic conditions the hydrophobic character of humic and fulvic material is increased, which leads to an increased adsorption of phenolic compounds. The effect is more pronounced for more apolar compounds. 2,3,6- and 2,4,6-trichlorophenols were recovered at levels of 50% in the water extracts. Their recovery from the membrane filter disks was 55 and 74%, respectively, which complements the amount found in water. However, the other tri- and tetrachlorophenols were attached to the sample matrix and were only detected on the Soxhlet-extracted membrane filter disks. These compounds, with a high octanol–water partition coefficient ( $\log K_{ow}$  of 3.72 for 2,4,6-trichlorophenol [31]), have a strong affinity for the particulate and humic material present in the sample, especially under acidic conditions. Therefore, in order to determine all phenolic compounds in industrial effluents, both the water and the particulate fraction of the sample should be analyzed.

In spiked HPLC-grade water that was filtered and extracted exactly as the industrial effluent all phenols were recovered from the water fraction (80–110%).

### 3.3. Effect of TOC on SPE using Speedisks

Speedisks represent a good alternative to off-line

SPE with cartridges since there is no need for prior filtration. Speedisks embody a filtration membrane on top of the active SPE sorbent so that the sample can be directly applied and filtration and adsorption take place simultaneously. The main advantages of Speedisks are their high capacity, so that high volumes of water can be processed, and the high sample flow, which can be as high as 200 ml/min, allowing the extraction of 500 ml in 3 min. These characteristics make them suitable for extracting very loaded industrial effluents. In this study, extraction was performed with styrene–divinylbenzene disks using spiked HPLC-grade, tap and river waters (TOC of 5 mg C/l) and a very charged industrial effluent (TOC of 505 mg C/l). Table 3 lists the recoveries obtained for each type of water and Fig. 2 shows the corresponding LC–ED chromatograms. In general, recoveries in the order of 80 to 120% were obtained in HPLC-grade water, tap and river water, irrespective of the type of water. 3-Methylphenol and 2,4-dimethylphenol were lost during the concentration of the extract, since 20 ml of solvent were evaporated to a final 3 ml. To avoid losses of the most volatile compounds, some authors suggest a basification of the extract to produce phenolate ions which are non-volatile [19,22]. By preconcentrating 500 ml of water, breakthrough of phenol occurred. Higher recoveries could be obtained by lowering the water volume preconcentrated. Similar to what was found after preconcentration of tap water with the Oasis cartridges, an interference coeluted with 2,5-dichlorophenol and produced a higher recovery than expected.

For the spiked industrial effluent with a TOC of 505 mg C/l, only 250 ml of raw water sample was percolated to avoid obstructing the disks with the high amount of particles present in the sample. In this case, percolation of the sample was slower even though the vacuum was set at the maximum speed. With the method used, acceptable recoveries were obtained for most of the compounds (Table 3). This indicates that: (i) although the disk was filled with particles, it did not prevent the adsorption of the analytes onto the sorbent and (ii) since the filtration membrane is set on top of the solid-phase sorbent, elution with acetonitrile and dichloromethane desorbed the analytes retained both in the filter and the sorbent. As a result, most phenolic compounds could

Table 3

Percentage of recovery of phenols after SPE with Speedisks corresponding to the preconcentration of 500 ml of HPLC-grade, tap, river and industrial effluent (250 ml) waters spiked at a level of 1 ng/ml

Compound	HPLC-grade water		Tap water		River water		Industrial effluent	
	% R	RSD	% R	RSD	% R	RSD	% R	RSD
Phenol	74	3.0	64	5.5	118	9.7	int.	–
3-Methylphenol	46	7.4	9	53.4	int. <sup>a</sup>	–	int.	–
2-Chlorophenol	72	3.0	61	5.9	78	7.4	int.	–
3-Chlorophenol	89	0.6	79	7.2	81	5.9	100	4.8
4-Chlorophenol	77	4.0	65	3.5	75	3.9	77	6.8
2,4-Dimethylphenol	24	14.8	0	0	9	100.3	0	0
2,6-Dichlorophenol	76	4.7	60	13.0	76	8.1	48	7.0
2,5-Dichlorophenol	80	6.3	143	5.6	88	7.0	85	7.1
2,4-Dichlorophenol	86	2.4	77	6.1	83	3.8	90	3.2
2,3,6-Trichlorophenol	88	7.0	77	3.8	77	9.0	int.	–
2,3,4-Trichlorophenol	88	3.5	103	2.8	83	11.9	93	2.4
2,4,6-Trichlorophenol	102	9.5	81	7.7	78	13.4	109	2.7
2,4,5-Trichlorophenol	91	6.6	78	4.0	82	6.7	125	4.4
2,3,5-Trichlorophenol	89	9.4	76	10.6	77	9.2	93	3.4
3,4,5-Trichlorophenol	87	4.8	81	5.8	88	4.5	94	14.7
2,3,5,6-Tetrachlorophenol	119	7.1	70	9.8	86	13.4	121	3.0
2,3,4,6-Tetrachlorophenol	61	7.9	46	6.0	60	8.7	29	89.1

<sup>a</sup> int.=Interference, not determined.

be recovered from industrial effluents in a single step, in contrast to SPE cartridges, for which the water and particles have to be extracted separately. Taking into account the type of matrix, RSDs below 10% indicate excellent performance, even though the method is not automated. The most polar analytes, e.g., phenol and monochlorophenols, were not determined due to the large amount of interferences present at this part of the chromatogram (Fig. 2C and D). With ED it is impossible to discern the interferences from the analyte of interest. Further work includes the use of more selective detection techniques, such as mass spectrometry, to overcome this problem.

#### 4. Conclusions

Nowadays efforts are directed towards the development of analytical techniques which permit a rapid and accurate measurement of organic pollutants in environmental waters. However, surface waters differ substantially in their TOC, humic and fulvic acid content and amount of particulate material. The water type affects the analytical performance, and it should be optimized in order to achieve good

recoveries and limits of detection at the low ppb level. By off-line SPE with Oasis 60 mg cartridges, it was possible to recover 17 priority phenolic compounds (including phenol and methylphenols) in waters with a TOC below 20 mg C/l. However, when using SPE with cartridges, it was necessary to filter the sample before extraction. The filtration step produced retention of nonpolar compounds (tri- and tetrachlorophenols) in the particulate matter and humic and fulvic material present in an industrial effluent with a TOC of 75 mg C/l. These compounds were only recovered from the Soxhlet-extracted 1.2- and 0.45- $\mu$ m filter membrane disks used before SPE. Speedisks are an alternative to SPE with cartridges. They have the advantage that no filtration is needed and the sample can be applied at a flow-rate of 200 ml/min. Speedisks of styrene–divinylbenzene permitted the extraction of 17 phenols from spiked HPLC-grade, tap, river water and a charged industrial effluent (TOC 505 mg C/l). Recoveries of 100% were obtained in most cases by percolating 250 to 500 ml of water. To summarize, SPE with cartridges is recommended for the extraction of relatively “clean” water samples, since the method can be automated. However, the use of Speedisks represent an advantage over SPE with cartridges for



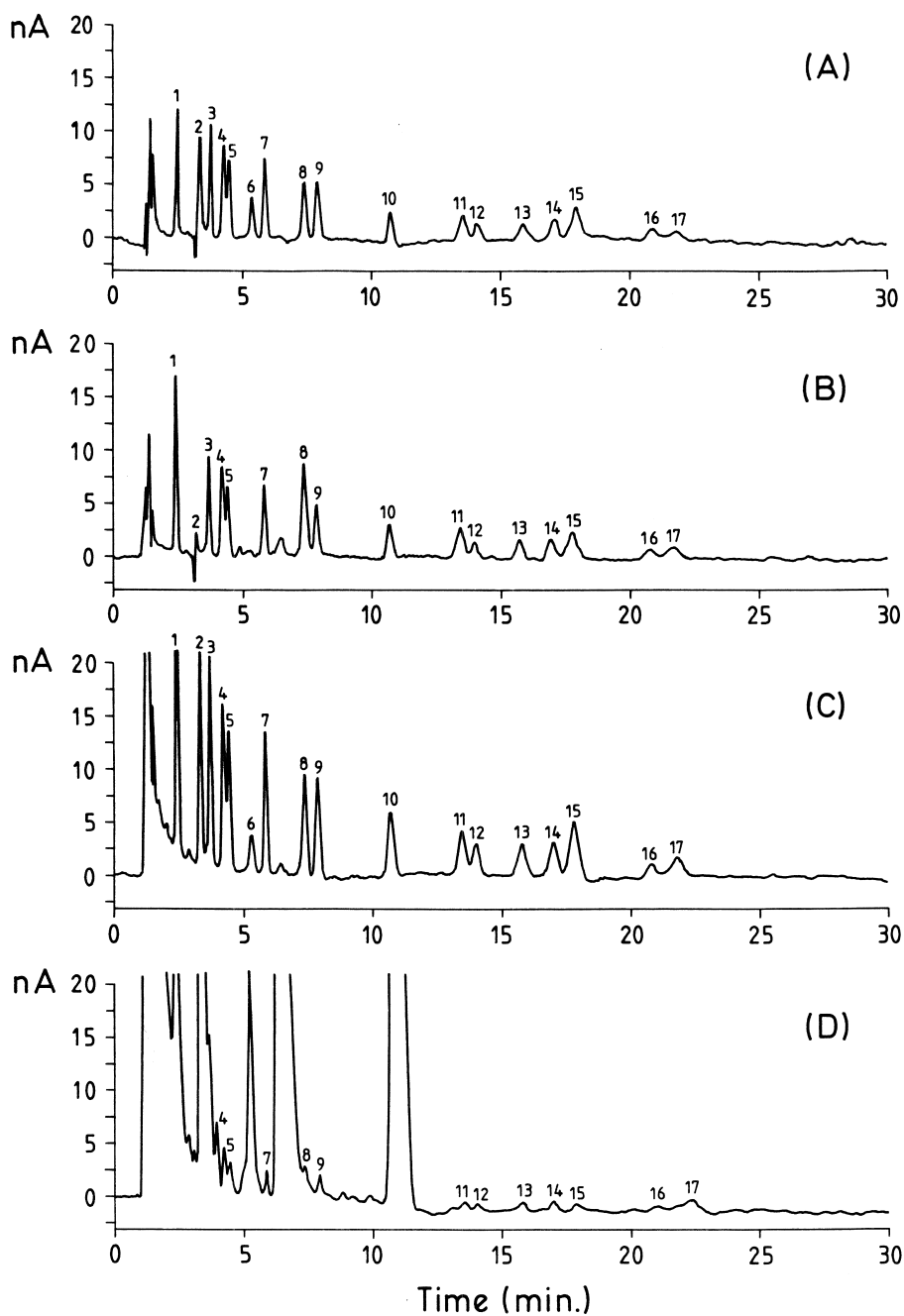


Fig. 2. LC-ED chromatograms obtained after percolation of 500 ml of water spiked at a level of 1 ng/ml through Speedisks. (A) HPLC-grade water; (B) tap water; (C) river water (5 mg C/l TOC); (D) industrial effluent (505 mg C/l TOC; 250 ml pre-concentrated). Peaks as in Fig. 1.

the analysis of phenolic compounds in charged industrial effluents since raw water can be processed directly and the speed of analysis is increased.

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