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Comparison of different sorbent materials for on-line liquid–solid extraction followed by liquid chromatographic determination of priority phenolic compounds in environmental waters

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Abstract

A comparative study of the performance of four sorbents [PLRP-S, LiChrolut EN, Isolut ENV and porous graphitic carbon (PGC)] for on-line liquid–solid extraction (LSE) followed by liquid chromatography (LC) of phenolic compounds in water was carried out. Better breakthrough volumes were obtained when working with LiChrolut EN and Isolute ENV than the other sorbent materials. Recoveries in ground water were in the range 55–105% and detection limits down to 0.1 μg/l were achieved, except for catechol and 2-amino-4-chlorophenol. A few differences were found when comparing sorbents from various suppliers, which was attributed to their different physico-chemical properties. PGC gave good results only for aminophenols. Binding phenomena among phenols and humic substances were detected, leading to interferences in the determination. The procedure was validated by participating in various inter-laboratory exercises using ground water samples distributed by Aquachek (WRC, Medmenhan, UK), containing phenols at levels ranging from 0.1 to 5 μg/l.

Keywords: Environmental analysis; Water analysis; Sorbents; Extraction methods; Sample preparation; Phenolic compounds

1. Introduction

Phenolic compounds of environmental interest come from a wide variety of industrial sources such as the plastics and dye industries and particularly from pulp processing [1]. They also occur as biodegradation products of humic substances, tannins and lignins [2]. Chloro- and nitrophenols are the main degradation products of many chlorinated phenoxy acid herbicides and organophosphorus pesticides, respectively [3,4].

Phenols, especially chlorophenols, are toxic at concentrations of a few μg/l and are also persistent. For these reasons, a number of phenolic compounds are listed in the European Community (EC) Directive 76/464/EEC concerning dangerous substances discharged into the aquatic environment [5]. The US Environmental Protection Agency (EPA) list of priority pollutants also includes eleven phenolic compounds [6–8]. EC Directive 75/440/EEC states that maximum

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levels of phenolic compounds in surface water for drinking purposes should be in the range 1–10 μg/l depending on the required treatment [9]. In this respect, it should be added that many EC countries follow the US EPA list of compounds in monitoring studies and for this reason it is of interest to develop a method for all the phenols included in both lists.

Current official analytical methods, e.g., US EPA 604 and 625 (acid-extractable section), consist of acidification of the sample, followed by dichloromethane liquid–liquid extraction (LLE), concentration and determination by gas chromatography using different detection methods such as electron capture or mass spectrometry [6–8]. Nowadays there is a tendency to change the current LLE procedures to on-line liquid–solid extraction (LSE) methods [10], thus avoiding manipulation of the samples, analyte losses in the different analytical steps and the use of toxic solvents.

In our previous work, eight different sorbents (C_{18}, C_{18}/OH, C_8, C_2, CH, CN, Ph and PLRP-S types) were compared using on-line LSE followed by LC [11]. PLRP-S (styrene–divinylbenzene copolymer) was found to be the most suitable sorbent, giving recoveries of up to 80% for most of the phenolic compounds, but problems still occur for the most polar analytes such as phenol and catechol. Moreover inter-calibration exercises organized by Aquacheck (WRC, Medmenham, UK) showed that the determination of phenol at the 0.5–5 μg/l level is still unsatisfactory.

To overcome the aforementioned problems, alternative methodologies have been published, e.g., by using electrochemical detection [12,13] or the use of extraction disks based on the use of acetyl-poly(styrene–divinylbenzene) [14]. Recently, new packing materials also based on styrene–divinylbenzene copolymer (e.g., ENVI-chrom, LiChrolut EN and Isolute ENV) have been introduced. ENVI-chrom gave higher breakthrough volumes than PLRP-S but important band broadening still occurred [15]. However, LiChrolut EN and Isolute ENV exhibit an open structure (high-porosity materials), thus allowing a higher real active surface area than PLRP-S with higher retention of analytes. Graphitized carbon black (GCB) has also been reported as a suitable sorbent for off-line trace enrichment of certain phenols [16]. Porous immobilized graphitic carbon (PGC) is more stable than GCB because in this case the graphite is in a silica structure [17], and it has been used for the on-line trace enrichment of aminophenols and catechols in water [18]. Other methods such as solid-phase microextraction (SPME) permitted the determination of phenol at 0.13 μg/l [19], always combined with GC methods.

In view of the different approaches to the determination of phenolic compounds in water, the aims of this work were (i) to carry out a comparative study of different polymeric materials (PLRP-S, LiChrolut EN and Isolute ENV) for the on-line LSE of phenolic compounds included in both EC and EPA lists at levels required by EC legislation for surface water for drinking purposes (Directive 75/440), (ii) to compare the performances of these polymeric sorbents with PGC and (iii) to validate the whole system by analysing ground water samples distributed through Europe by the Aquacheck programme, where most of the participating laboratories are using current dichloromethane LLE methods. All the aforementioned aspects should encourage the implementation of the on-line LSE method developed in this work.

2. Experimental

2.1. Materials

HPLC-grade water, methanol and acetonitrile were obtained from J.T. Baker (Deventer, Netherlands). All the solvents were passed through a 0.45-μm filter (Scharlau, Barcelona, Spain). Catechol and phenol were obtained from Sigma (St. Louis, MO, USA), 4-chloro-2-aminophenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 3,4,5-trichlorophenol, pentachlorophenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 4-methylphenol and 2,4-dimethylphenol from Merck (Darmstadt, Germany) and 3-chlorophenol, 2,3,4-trichloro-

phenol and 2,3,5-trichlorophenol from Aldrich (Milwaukee, WI, USA).

2.2. Apparatus

Experiments were performed using an automatic sample processor from Gilson (Villers-le-Bel, France). This system includes an Aspec XL automatic sample processor equipped with two Reodyne six-port valves, a Model 305 high-pressure preconcentration pump, a Model 401C low-pressure pump, and a Model 817 eight-port valve valve actuator. The HPLC system was purchased from Gilson and consisted of two Model 305 pumps, a Model 811c dynamic mixing chamber, a Model 805 manometric module and a Model 117 UV detector.

2.3. On-line liquid–solid extraction study

Stainless-steel precolumns (10 × 0.2 mm I.D.) were packed manually with a slurry system purchased from the Free University (Amsterdam, Netherlands). Isolute ENV sorbent was obtained from International Sorbent Technology (Cambridge, UK), PLRP-S from Polymer Laboratories (Church Stretton, UK) and LiChrolut EN from Merck. PGC precolumns were obtained prepacked with Hypercarb PGC from Shandon Scientific (Runcorn, UK). The on-line experimental set-up is similar to that used in previous studies [10].

Conditioning of the precolumn was carried out with 5 ml of methanol and afterwards with 1 ml of water (pH 3) at 1 ml/min. Spiked samples, acidified to pH 2.5 were passed through the precolumn at 4 ml/min. After washing the sorbent with 1.5 ml of water at 1 ml/min, analytes were directly eluted by the mobile phase to the analytical column in the backflush mode. Before the next run, the precolumn was washed with 5 ml of acetonitrile at 1 ml/min. Breakthrough curves for ground water were calculated by making successive injections of the same batch, raising the sample volume by 15 ml every time in the range from 15 to 210 ml for all the target compounds. On plotting results on $X-Y$ coordinates (volume vs. area), a linear graph for low sample volumes was obtained. When breakthrough of analytes began, the relationship of area against volume deviated from linearity. The initial linear relationship was extrapolated and it was assumed that breakthrough occurred when the ratio of the extrapolated plot to the experimental plot was 5%.

2.4. Chromatographic conditions

A Hypersil Green ENV (C_{18}) analytical column (150 × 4.6 mm I.D.) equipped with a guard column and a Hypercarb analytical column (250 × 4.6 mm I.D.), both from Shandon Scientific, were used. Gradient elution was carried out with water (containing 1% acetic acid) and methanol–acetonitrile (1:1) (containing 1% acetic acid) as organic modifier. Detection was carried out at 280 nm, except for pentachlorophenol, 4-nitrophenol and 2,4-dinitrophenol, which were quantified at 310 nm.

Quantification was performed by using external standard calibration methods. Calibration graphs were constructed over the concentration range 0.01–25 μg/l depending on the studied compound. The reproducibility varied from 3 to 9%.

3. Results and discussion

3.1. Polymeric sorbents

3.1.1. Breakthrough volumes, recoveries and detection limits

It has been reported that copolymers such as styrene–divinylbenzene are suitable for the trace enrichment of relatively polar compounds such as phenols [11,15,20,21]. Theoretically, direct coupling of these sorbents with typical reversed-phase analytical columns is not suitable because of band broadening. This effect can be minimized by using a suitable gradient which causes peak compression on the top of the analytical column and a good compromise between breakthrough volume and peak efficiency. Moreover, for the enrichment of polar compounds, where the breakthrough volume is a critical parameter,

some loss of efficiency should be accepted in order to achieve the desired detection limits.

Fig. 1 shows the chromatographic profiles obtained with the three polymeric sorbents when analysing river water spiked at 4 μg/l. Slight band broadening was observed in all cases owing to the bad elution profile of phenols when working with eluents with a high percentage of water. This was found to be strongly dependent on the physico-chemical characteristics of the sorbent and will be discussed later. PLRP-S provided the best peak shape; band broadening was observed when using LiChrolut EN and Isolute ENV owing to their higher adsorption power, which makes analyte elution difficult. Moreover, even though Isolute ENV is designed for use in an off-line approach (see Table 4, particle size), only a slight increase in band broadening was obtained, especially for the most retained analytes such as trichlorophenols and pentachlorophenol.

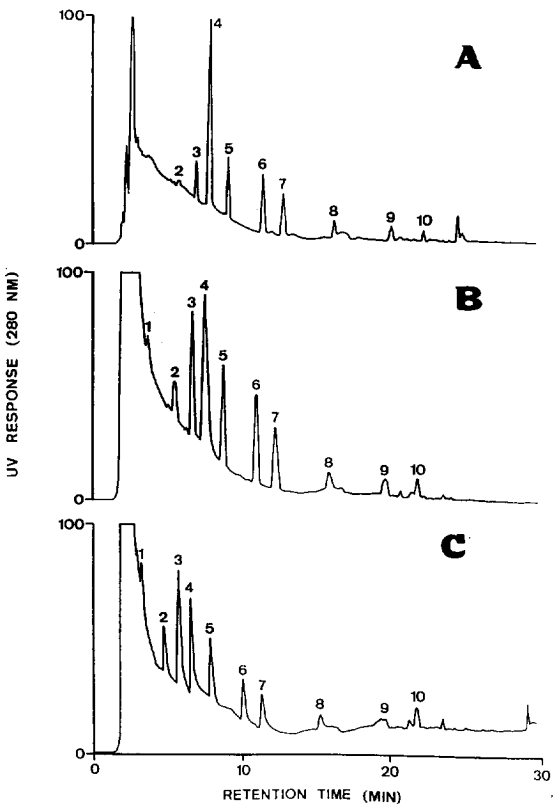

Fig. 1. LC–UV (280 nm) traces of phenolic compounds spiked in ground water after on-line LSE using a 10 × 2 mm I.D. stainless-steel precolumn with different polymeric sorbents: (A) PLRP-S; (B) LiChrolut EN; (C) Isolute ENV. Sample volume, 50 ml. Peaks: 1 = catechol; 2 = phenol; 3 = 4-nitrophenol; 4 = 2,4-dinitrophenol; 5 = 4-chlorophenol; 6 = 2,4-dimethylphenol; 7 = 4-chloro-3-methylphenol; 8 = 2,4-dichlorophenol; 9 = 2,4,6-trichlorophenol; 10 = pentachlorophenol. Concentration, 4 μg/l. For other conditions, see Experimental.

Breakthrough volumes and recoveries of phenols in ground water at the 4 μg/l level obtained using the three polymeric sorbents are shown in Tables 1 and 2, respectively. The data were found to be strongly dependent on the type and number of substituents. In general, analytes having strong positive resonance capacity substituents such as nitro groups or with a large number of electron-withdrawing substituents such as trichlorophenols and pentachlorophenol gave the highest values. For example, the breakthrough volumes for 4-nitrophenol were 45, 70 and 80 ml using PLRP-S, LiChrolut EN and Isolute ENV, respectively, whereas a value up to 200 ml was obtained for 2,4-dinitrophenol when using any of the polymeric sorbents (Table 1). Similar behaviour was observed for chlorophenols. Breakthrough volumes in the range 60–85 ml for monochlorophenols and >200 ml for trichlorophenols and pentachlorophenol were obtained when using any of the polymeric sorbents. The breakthrough volumes were in general improved when working with both LiChrolut EN and Isolute ENV sorbents compared with those obtained with PLRP-S. Especially notable was the improvement obtained for the most polar analytes such as phenol and catechol compared with PLRP-S. When working with PLRP-S, the breakthrough volumes were below 10 ml for phenol and catechol, giving recoveries below 20%, but for LiChrolut EN and Isolute ENV the breakthrough volumes and recoveries were in the ranges 25–35 ml and 55–67%, respectively.

Detection limits for target compounds in (A) ground and (B) river waters using PLRP-S, LiChrolut EN and Isolute ENV sorbents are given in Table 3. Data were recorded at 280 nm, except for 4-nitrophenol and pentachlorophenol (310 nm). The values were strongly dependent

Table 1
Breakthrough volumes (ml) of phenolic compounds in ground water using different sorbents and on-line LSE using a 10 × 2 mm I.D. stainless-steel precolumn

Compound	Sorbent			
	PLRP-S	LiChrolut EN	Isolute ENV	PGC
Catechol	<10	25	25	25
Phenol	<10	35	30	30
4-Methylphenol	50	55	60	25
2,4-Dimethylphenol	180	>200	>200	n.d.
2-Nitrophenol	60	75	70	n.d.
4-Nitrophenol	45	70	80	n.d.
2,4-Dinitrophenol	>200	>200	>200	n.d.
2-Amino-4-chlorophenol	<10	<10	<10	45
4-Chloro-3-methylphenol	100	110	100	n.d.
2-Chlorophenol	60	75	75	40
3-Chlorophenol	70	80	75	45
4-Chlorophenol	70	85	75	45
2,4-Dichlorophenol	100	120	130	n.d.
2,4,6-Trichlorophenol	>200	>200	>200	n.d.
2,3,5-Trichlorophenol	>200	>200	>200	n.d.
2,3,4-Trichlorophenol	>200	>200	>200	n.d.
3,4,5-Trichlorophenol	>200	>200	>200	n.d.
Pentachlorophenol	>200	>200	>200	n.d.

Spiking level, 4 μg/l ($n = 6$ for each phenolic). For other conditions, see Experimental.
n.d. = Not detected.

on the matrix, especially in the case of the most polar analytes that appear at low retention times, thus co-eluting with the matrix interferences. Values obtained in HPLC-grade water (not shown) were generally better 0.4 and 0.1 μg/l for phenol and 4-methylphenol, respectively. Surprisingly, better values for 2,4-dinitrophenol were obtained when working with PLRP-S. The strong adsorption of this compound to LiChrolut EN and Isolute ENV makes its elution difficult under the conditions used, leading to important band broadening and a poor detection limit.

LiChrolut EN and Isolute ENV are the most suitable sorbents when the whole range of phenolics has to be monitored, with the exception of 2-amino-4-chlorophenol. Even though Isolute ENV provides very good breakthrough volumes, the detection limits were slightly worse than those obtained with LiChrolut EN, mainly because of the higher band broadening. However, the breakthrough volumes obtained with Isolute ENV are promising and the development of a small particle size version will certainly improve these values. In general, LiChrolut EN will be the sorbent of choice when the whole range of phenols has to be monitored, and only in the case of nitro- or highly chlorinated phenols is PLRP-S to be preferred because of the lower detection limits.

3.1.2. Correlation with polymer characteristics

The differences in sorbent behaviour should be related to the different physico-chemical characteristics of the sorbent. Table 4 shows the characteristics of the three polymeric materials. The efficiency of the sorbents depends on various physico-chemical parameters such as particle size, surface area, pore diameter, pore volume, degree of cross-linking and particle size distribution.

The available surface area is the key parameter to explain the differences in the data obtained on the different sorbents. LiChrolut EN and Isolute ENV have an open structure (highly

Table 2
Mean percentage recoveries ± standard deviations of phenolic compounds in ground water using different sorbents and working with on-line LSE using a 10 × 2 mm I.D. stainless-steel precolumn

Compound	Sorbent			
	PLRP-S	LiChrolut EN	Isolute ENV	PGC
Catechol	<20	55 ± 9	57 ± 8	61 ± 7
Phenol	34 ± 5	67 ± 7	62 ± 7	54 ± 6
4-Methylphenol	69 ± 6	75 ± 6	82 ± 5	52 ± 7
2,4-Dimethylphenol	81 ± 4	98 ± 4	92 ± 4	n.d.
2-Nitrophenol	76 ± 5	88 ± 5	88 ± 5	n.d.
4-Nitrophenol	78 ± 5	84 ± 6	100 ± 4	n.d.
2,4-Dinitrophenol	100 ± 4	102 ± 5	98 ± 4	n.d.
2-Amino-4-chlorophenol	<20	<20	<20	87 ± 6
4-Chloro-3-methylphenol	85 ± 5	92 ± 6	88 ± 5	n.d.
2-Chlorophenol	76 ± 4	86 ± 6	81 ± 4	85 ± 7
3-Chlorophenol	78 ± 6	83 ± 5	79 ± 5	88 ± 6
4-Chlorophenol	85 ± 6	84 ± 5	80 ± 4	88 ± 5
2,4-Dichlorophenol	81 ± 3	94 ± 5	92 ± 3	n.d.
2,4,6-Trichlorophenol	96 ± 4	103 ± 5	99 ± 5	n.d.
2,3,5-Trichlorophenol	94 ± 5	96 ± 4	101 ± 6	n.d.
2,3,4-Trichlorophenol	95 ± 5	101 ± 4	105 ± 6	n.d.
3,4,5-Trichlorophenol	93 ± 5	99 ± 4	98 ± 4	n.d.
Pentachlorophenol	100 ± 4	100 ± 3	99 ± 5	n.d.

Spiking level, 4 μg/l ($n = 6$ for each phenolic). Sample volume, 100 ml, except for phenol, catechol and 4-chloro-2-aminophenol (50 ml). For other conditions, see Experimental.

porous materials), so a higher real active surface is available than with PLRP-S. This can be seen in Table 4, where the PLRP-S, LiChrolut EN and Isolute ENV are shown to have pore volumes of 0.62, 0.75 and 1.1 ml/g, respectively. The higher porosity of Isolute ENV can also explain why only a slight increase in band broadening was obtained over LiChrolut EN because it minimizes band dispersion. On the other hand, band broadening is also minimized when working with PLRP-S because it shows the narrowest particle size distribution (16–18 μm for PLRP-S and 8–39 μm for LiChrolut EN), thus allowing elution in a narrow profile which provides an excellent peak shape. Another parameter which can influence the performance of the sorbents is the degree of cross-linking. It was reported that π–π interactions play an important role in retention when using polystyrene stationary phases [22,23]. Here the polymer can act as an electron donor for analytes having electron-withdrawing or positive electron resonant capacity substituents. This can explain why nitrophenols have the highest breakthrough volumes, being dependent on the number of substituents. Hence the degree of cross-linking of the copolymer is also an important parameter which can explain the differences in adsorption capacity among the sorbents. LiChrolut EN and Isolute ENV have a higher degree of cross-linking than PLRP-S and favour higher breakthrough volumes. However, as these data are not usually provided by the suppliers, no definitive conclusion can be drawn in this respect.

3.1.3. pH study

The presence of interfering materials in the sample, mainly humic and fulvic acids, should be always taken into consideration because it will affect the analytical performance. It has been reported that humic matter can bind organic pollutants [24,25], thus leading to a decrease in breakthrough volumes and recoveries because only the dissolved fraction will be enriched. Since

Table 3
Detection limits (μg/l) of phenolic compounds in (A) ground and (B) river water with on-line LSE and using the three polymeric sorbents

Compound	Sorbent						
	PLRP-S		LiChrolut EN		Isolute ENV		PGC
	A	B	A	B	A	B	A
Catechol	4	14	2	9	2	n.d.	2.5
Phenol	3	11	0.7	3.5	0.8	4	1
4-Methylphenol	0.7	4	0.4	2	0.6	3	1.2
2,4-Dimethylphenol	0.05	0.8	0.03	0.5	0.05	0.6	n.d.
2-Nitrophenol	0.1	1	0.05	0.8	0.08	0.8	n.d.
4-Nitrophenol[a]	0.05	0.1	0.01	0.08	0.02	0.1	n.d.
2,4-Dinitrophenol[a]	0.01	0.08	0.09	0.3	0.09	0.2	n.d.
2-Amino-4-chlorophenol	7	n.d.	n.d.	n.d.	n.d.	n.d.	0.5
4-Chloro-3-methylphenol	0.1	1.2	0.05	1	0.1	1.2	n.d.
2-Chlorophenol	0.4	1.4	0.2	1.2	0.4	1.4	n.d.
3-Chlorophenol	0.4	1.4	0.2	1.2	0.4	1.4	n.d.
4-Chlorophenol	0.5	1.5	0.2	1.4	0.4	1.5	1
2,4-Dichlorophenol	0.4	0.9	0.1	0.8	0.2	1	n.d.
2,4,6-Trichlorophenol	0.1	0.6	0.08	0.3	0.1	0.9	n.d.
2,3,5-Trichlorophenol	0.1	0.5	0.07	0.3	0.2	1	n.d.
2,3,4-Trichlorophenol	0.1	0.5	0.08	0.3	0.1	0.9	n.d.
3,4,5-Trichlorophenol	0.1	0.4	0.08	0.3	0.1	0.9	n.d.
Pentachlorophenol[a]	<0.01	0.04	<0.01	0.02	0.01	0.05	n.d.

Sample volume, 100 ml, except for phenol, catechol and 4-chloro-2-aminophenol (50 ml). For other conditions, see Experimental.
[a] Deletion at 310 nm.

this phenomenon can be strongly dependent on the working pH, various experiments at different pH values were carried out. In general, sample acidification is normal practice in water environmental analysis, to ensure preservation of the sample and to avoid partial deprotonation of low-pK_a analytes. However, phenolic compounds have a wide range of pK_a values, e.g., 4-methylphenol 10.17 and 2,4-dinitrophenol 3.9, so the optimum pH for extraction should be checked carefully.

When analysing river water spiked at the 5 μg/l level at pH 6.6 (unbuffered) and pH 2 (acidified with 50% sulphuric acid), significant differences were obtained: up to a 50% decrease in recovery was found for 4-nitrophenol and 2,4-

Table 4
Characteristics of the three polymeric sorbents

Sorbent	Particle size (μm)	Pore size (Å)	Pore volume (ml/g)	Surface area (m^2/g)
PLRP-S	16–18	300	0.62[a]	Not available
LiChrolut EN	15–40	29	0.75	1200
Isolute ENV	40–140	850	1.1	1100

Data provided by the different manufacturers.
[a] Approximate value.

dinitrophenol but 27% for only 2-nitrophenol. However, this decrease for chlorophenols was much smaller. In the case of low-pK_a analytes such as 2,4-dinitrophenol (pK_a = 4), this can be attributed either to the binding of the analytes with the humic substances and to the partial deprotonation of the analyte at the working pH. However, the important decrease in recovery for 4-nitrophenol (pK_a = 7.15), the fact that 2-nitrophenol (pK_a = 7.17) shows only a 27% decrease although it has similar a ionization constant to 4-nitrophenol and the small decrease obtained for highly chlorinated phenols (pK_a = 5.8–4.7) indicate that adsorption of some analytes on fulvic or humic acids occurs at neutral pH. This adsorption may be related to the octanol–water partition coefficient [26]. The different behaviour of mononitrophenols indicates that not only the nature of the functional group but also steric effects should be considered. On the other hand, alkyl-substituted phenols in general showed the opposite tendency, and small decreases in recovery were obtained when working at acidic pH, thus showing that no significant binding occurs.

Acidification of the sample can help to overcome this drawback and can also prevent the deprotonation of the most acidic phenols such as 2,4-dinitrophenol and pentachlorophenol. However, in this case, adsorption of humic material to the sorbent is increased caused by an increase in the hydrophobic character and a large interfering peak appears somewhere in the chromatogram [27]. Therefore, this can result in a decrease in the breakthrough volume of analytes which lack a strong affinity for the sorbent (e.g., 2,4-dimethylphenol and cresols). This means that the optimum extraction pH is a parameter which should be optimized depending on the target phenol.

Additionally, two different kinds of water samples (ground and river water) spiked at 4 μg/l were analysed at pH 2.5 using LiChrolut EN sorbent in order to study matrix effects. Fig. 2 shows the chromatographic profiles of the matrices spiked with some phenolics at 4 μg/l and analysed using LiChrolut: (A) ground water and (B) river water. Quantification of catechol is difficult at this level because of early elution of the matrix peak in the case of ground water. For river water the matrix recoveries and detection limits were reduced owing matrix effects. These differences are less important for the most apolar analytes such as trichlorophenols and pentachlorophenol, which appear at the end of the chromatogram after the matrix peak, and also for the analytes quantified at 310 nm (see Table 3).

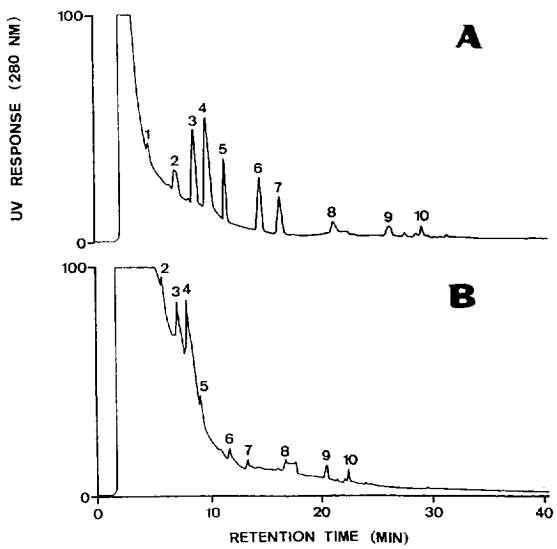

Fig. 2. LC–UV (280 nm) traces of phenolic compounds spiked in different water matrices after on-line LSE using a 10 × 2 mm I.D. stainless-steel precolumn packed with LiChrolut EN. (A) Ground water; (B) river water. Sample volume, 50 ml. Peaks: 1 = catechol; 2 = phenol; 3 = 4-nitrophenol; 4 = 2,4-dinitrophenol; 5 = 4-chlorophenol; 6 = 2,4-dimethylphenol; 7 = 4-chloro-3-methylphenol; 8 = 2,4-dichlorophenol; 9 = 2,4,6-trichlorophenol; 10 = pentachlorophenol. Concentration, 4 μg/l. For other conditions, see Experimental.

3.2. Porous graphitic carbon (PGC)

Carbon-based sorbents were tested because it has been reported that GCB was an excellent sorbent for the off-line trace enrichment of traces of medium-polarity analytes [16]. Owing to the special characteristics of this sorbent, coupling to a PGC column was necessary in order to prevent excessive band broadening [28].

PGC was considered as a pure reversed-phase sorbent because there are no uncovered polar groups (e.g., free silanols) on the surface. The retention mechanism is unclear but it is different to that with current reversed-phase packings. Substituents with large steric parameters, strong electron-withdrawing power and hydrogen donor capacity have the greatest impact on the retention, but the lipophicility of the compounds does not seem to affect the retention significantly [29]. For this reason, even though the solvents which are used are the same as in current reversed-phase LC, the retention times cannot be predicted or correlated with data obtained from these columns.

Initially the same conditions and compound mixture as used for C_{18} columns were tested. Phenolic compounds having strong positive resonance capacity substituents such as nitro groups or highly chlorinated phenols were strongly adsorbed under these conditions and appear at unsuitable retention times, in some cases (e.g., 2,4-dinitrophenol) being irreversibly adsorbed on the column. On the other hand, important tailing was observed for analytes which appear in a suitable retention time window, such as phenol, catechol and 4-chlorophenol. The mobile phase gradient was modified to start with 70% methanol. Even though some tailing was still observed, the isolation of catechol, phenol, 2-amino-4-chlorophenol, 4-methylphenol and 4-chlorophenol was then feasible, but the rest of the target compounds were still excessively adsorbed in the analytical column.

Tables 1 and 2 show the breakthrough volumes and recoveries obtained for selected phenolic compounds in ground water at the 4 μg/l level, respectively. It can be seen that the values for phenol and catechol are not really significantly different from those obtained using LiChrolut EN or Isolute ENV. A breakthrough volume of 45 ml for 2-aminophenol was obtained, thus significantly improving the data obtained with the other sorbents tested, which all gave values under 20 ml. The values for 4-chlorophenol and 4-methylphenol were worse than those obtained using polymeric materials (see Tables 1 and 2). PGC gave breakthrough volumes of 45 and 25 ml for 4-chlorophenol and 4-methylphenol and the polymeric sorbents in the range 70–85 and 50–60 ml, respectively. This shows that PGC is to be preferred only in the case of polar analytes such as aminophenols.

The most important problem encountered when working with this column is that elution is difficult using the on-line LSE approach. This can be seen in Fig. 3, showing the on-line LSE–LC profile of tap water spiked with catechol, phenol, 2-amino-4-chlorophenol, 4-methylphenol and 4-chlorophenol at 4 μg/l. The peak shape for phenol and 2-amino-4-chlorophenol was acceptable but bad elution profiles for 4-chlorophenol and 4-methylphenol were obtained. For this reason, the detection limits for the latter compounds were not as good as expected considering the breakthrough volumes, with values of 1 and 1.2 μg/l for 4-chlorophenol and 4-methylphenol, respectively. Moreover, humic substances become strongly adsorbed when working with PGC, thus giving memory effects. Regeneration of the precolumn can be carried out by washing after two–three analyses by flushing it with water–tetrahydrofuran (50:50) containing 0.1% of perchloric acid. When river water samples are analysed, precolumns should be discarded after 10–12 runs even when performing such an aggressive washing procedure. Matrix interferences become irreversibly absorbed and deterioration of the sorbent is ob-

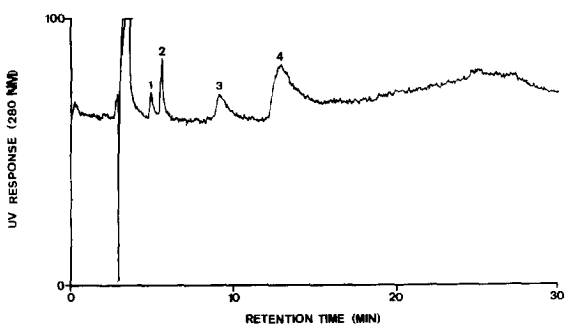

Fig. 3. LC–UV (280 nm) traces of phenolics spiked in drinking water obtained using a Hypercarb analytical column after on-line LSE with PGC sorbent. Peaks: 1 = phenol; 2 = 2-amino-4-chlorophenol; 3 = 4-methylphenol; 4 = 4-chlorophenol. Concentration, 4 μg/l. For other conditions, see Experimental.

served. On the other hand, the small particles of this sorbent (10 μm) prevent the use of high flow-rates, thus increasing the analysis time. Owing to these problems and the fact that the breakthrough volumes were in general not improved, additional studies using this sorbent were abandoned.

3.3. Validation

In order to evaluate the performance of the developed methodology, a reference material containing phenol, trichlorophenol and pentachlorophenol provided by the Aquacheck at the Water Research Centre (WRC) (Medmenhan, UK) was analysed. In earlier work by our group, inter-calibration exercises organized with the WRC were carried out using PLRP-S as a sorbent. Correct values for trichloro- and pentachlorophenol a and single flagged error for phenol were obtained. It should be noted that among all the participating laboratories (15–20 depending on the exercise), only two gave correct results for phenol and most of the others gave results with double flagged errors. That means that the determination of phenol at the 0.1–0.5 μg/l level was still unsatisfactory even using robust analytical systems as reported by Aquacheck.

Ground water samples were spiked with Aquacheck reference material according the instructions required by the WRC, and were analysed according to the protocol developed in this work using PLRP-S and LiChrolut EN. Results are given in Table 5. In both cases correct results were obtained for pentachloro- and trichlorophenol, but phenol could only be quantified using LiChrolut EN, with an error threshold of 15%. The same analysis was performed using river water but then a single flagged error (20%) was obtained for phenol. However, this deviation is acceptable, especially considering the final reports of inter-calibration exercises organized by Aquacheck, thus showing the difficulty of determining phenol.

4. Conclusions

A comparative study of the performances of three sorbents for the on-line LSE of phenolics in water samples was carried out. The results showed that LiChrolut EN and Isolute ENV sorbents give better results than with PLRP-S, and permit the detection of phenol at the 0.7 μg/l level in ground water. A few differences were found when testing polystyrene materials from different suppliers, caused by their different physico-chemical characteristics. PLRP-S did not give any appreciable band broadening but the breakthrough volumes were increased when both LiChrolut EN and Isolute ENV were used. Such differences were attributed to the open structure or LiChrolute EN and Isolute ENV, which increases the surface area available and allows higher π–π interactions. Both LiChrolut EN and Isolute ENV gave similar breakthrough volumes and recoveries. A matrix effect study showed

Table 5
Mean concentration (ng/l) and mean difference (%) in relation to reference values of phenolic compounds obtained when analysing samples provided by the WRC using PLRP-S and LiChrolut EN sorbents

Phenolic compound	Ground water				River water	
	Mean concentration (ng/l)	Mean difference (%)	Mean concentration (ng/l)	Mean difference (%)	Mean concentration (ng/l)	Mean difference (%)
Phenol	n.d.		1649.1	−15	1057.2	−20
Trichlorophenol	3852.8	−11	4372.8	8	n.d.	
Pentachlorophenol	1296.7	3	1120.5	12	n.d.	

Values were obtained from spiking ground and river water with the reference material from Aquacheck. Sample volume: 50 ml for phenol and 100 ml for trichlorophenol and pentachlorophenol.

that acidification of the sample is necessary to avoid binding of some analytes to the humic substances and to prevent their partial deprotonation.

PGC was also tested to check its performance for the trace enrichment of the most polar phenolic compounds. The breakthrough volumes and detection limits were worse than those obtained using the polymeric sorbents except in the case of 4-chloro-2-aminophenol. Moreover, PGC shows some operational drawbacks such as difficulty in recycling the precolumn and the lack of selectivity against polar humic substances.

Validation of the analytical protocol developed in this work was carried out by analysing a reference material of water samples containing phenols provided by the WRC. The results showed the good performance of the analytical protocol with ground water at the levels required by EC Directive 75/440/EEC dealing with surface water for drinking purposes, but there are still some problems with the determination of phenol in river water and a single flagged error was obtained. The results showed that polymeric sorbents such as LiChrolut EN and Isolute ENV allow the detection limits required by EC Directive 75/440/EEC dealing with surface water for drinking purposes to be achieved.

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