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Journal of Chromatography A, 719 (1996) 105–112

JOURNAL OF CHROMATOGRAPHY A

Determination of phenolic compounds at low $\mu g\ l^{-1}$ levels by various solid-phase extractions followed by liquid chromatography and diode-array detection

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Abstract

An off-line solid-phase extraction was carried out to determine thirteen phenolic compounds, which included eleven EPA priority phenols, using reversed-phase liquid chromatography and diode-array detection. Two different sorbents, carbon and a highly cross-linked styrene–divinylbenzene copolymer, were compared for the preconcentration process. To increase the retention of the most polar compounds, mainly phenol, tetrabutylammonium bromide was used as an ion-pair reagent in the extraction system. Better recoveries were obtained for the copolymer sorbent and the performance of the method was tested with tap and Ebro river water. Recoveries higher than 90% were obtained for all compounds when a 500-ml sample was preconcentrated using the optimum conditions found with the copolymer sorbent. The R.S.D. for a river water sample spiked at 1 $\mu g\ l^{-1}$ was lower than 10% ($n = 4$) and the detection limits were between 65 and 100 $ng\ l^{-1}$.

1. Introduction

RPLC is the most commonly used technique to determine phenolic compounds in water [1–4]. The use of electrochemical detection allows the detection of these compounds at lower concentrations but UV-visible detection is most often used because of its robustness. However, in both cases, it is necessary to apply a preconcentration step prior to the injection in order to reach the levels of these compounds allowed in drinking water. At present, the use of solid-phase extraction is increasing because of its advantages over liquid–liquid extraction [5,6].

Although on-line solid-phase extraction involves some very important advantages [7–9], the incompatibility between the preconcentration precolumn sorbent and the analytical column often makes on-line combination difficult. Hence the off-line procedure is still the most often used technique as it also requires simple instrumentation.

In order to determine phenolic compounds, which differ widely in polarity, with an off-line preconcentration system, several sorbents have been used. Cañas et al. [10] used anion-exchange cartridges to preconcentrate the eleven priority phenolic compounds in pure water. Good recoveries were obtained but a low volume of sample could be preconcentrated, which did not allow one to reach low limits of detection using a UV detector. However, the most often used sorbents are C_{18} to trap non-polar phenols and PLRP-S or PRP-1 to trap medium-polarity

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0021-9673/96/$15.00
SSDI 0021-9673(95)00240-5

phenols. Ruana et al. [11] used glass microcolumns filled with C_{18} with UV and electrochemical detection to determine 21 phenolic compounds. Preconcentrating only 10 ml of sample, detection limits at low μg^{-1} levels were obtained with the electrochemical detector, whereas with UV detection a higher sample volume had to be preconcentrated, which implied an important decrease in the recovery of the most polar phenols, mainly phenol. Similar results were obtained by Hoffsommer et al. [12] using C_{18} cartridges to determine nine nitrophenols. Gawdzik et al. [13] used styrene–divinylbenzene copolymer cartridges for the preconcentration of EPA phenols but no better results were obtained because less than 100 ml of sample should be preconcentrated in order to obtain good recoveries for all compounds. Mussmann et al. [14] found noticeable differences among three C_{18} sorbents from different suppliers. Brouwer and Brinkman [15] developed an on-line set-up with two precolumns in series, an ENVI-Chrom P precolumn to trap the phenol and a PLRP-S to trap the rest of the phenolic compounds.

Other sorbents which have also been used for the preconcentration of phenolic compounds include carbon [3,16] and cyclohexyl (CH) [17]. Borra et al. [16] applied graphitized carbon black to the determination of priority pollutant phenols with two different desorbing mixtures. A sample volume of 2 l gave good recoveries for all compounds except phenol, whose breakthrough volume was 200 ml. In a further study [18], a larger amount of carbon in a reversible cartridge allowed them to increase the recovery of phenolic compounds. In a previous paper [19], the breakthrough volumes obtained of phenolic compounds with cyclohexyl were low. Better results were obtained with the previously mentioned PLRP-S [19], although volumes larger than 100 ml gave lower recoveries of the most polar compounds. A highly cross-linked styrene–divinylbenzene copolymer [20] could improve the breakthrough volumes obtained with conventional PLRP-S.

The effect of an ion-pair reagent in the solid-phase extraction of phenolic compounds has been studied using C_{18}, cyclohexyl and PLRP-S [19], and it strikingly improved the breakthrough volumes of the most polar compounds.

In this work, off-line solid-phase extraction was studied to determine thirteen phenolic compounds in water using RPLC and UV detection. The aim was to develop a solid-phase extraction procedure which allows the preconcentration of the volume of sample necessary to determine phenolic compounds at levels as low $\mu g\ l^{-1}$ by RPLC with diode-array detection (DAD). Ion-pair extraction with carbon and a highly cross-linked styrene–divinylbenzene copolymer was studied in order to increase the retention of the most polar compounds, mainly phenol.

2. Experimental

2.1. Reagents and standards

The phenolic compounds studied and their abbreviations were as follows: phenol (Ph), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2-chlorophenol (2-CP), 2-nitrophenol (2-NP), 2,6-dimethylphenol (2,6-DMP), 2,4-dimethylphenol (2,4-DMP), 2-methyl-4,6-dinitrophenol (2-M-4,6-DNP), 4-chloro-3-methylphenol (4-C-3-MP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trimethylphenol (2,4,6-TMP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP). In addition to eleven EPA priority substituted phenols, two methyl phenolic compounds, 2,6-DMP and 2,4,6-TMP, were also included. All of them were obtained from Aldrich Chemie (Beerse, Belgium), except PCP, which was obtained from Jansen Chemie (Geel, Belgium).

A stock standard solution of 2000 mg l^{-1} of each compound was prepared in methanol–water (50:50) and stored in a refrigerator. Working standard solutions were prepared weekly or daily depending on their concentration by diluting the stock standard solution with water obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

HPLC-gradient grade methanol (Scharlau, Barcelona, Spain) and Milli-Q quality water

adjusted to pH 2.8 with acetic acid (Merck, Darmstadt, Germany) were used for the preparation of the mobile phase. TBA (tetrabutylammonium bromide) (Aldrich) was used as the ion-pair reagent in the extraction process. NaOH (Merck) and acetic acid (Merck) were used for pH adjustment and Na_2SO_3 (Merck) was added to remove the residual chlorine in tap water samples before the standard addition.

Dichloromethane, hexane (Riedel-de Haën, Seelze, Germany), ethyl acetate, carbon disulfide (Panreac, Barcelona, Spain), acetonitrile, and tetrahydrofuran (Scharlau) were tested as solvents in the extraction process.

2.2. Instrumentation

Chromatographic experiments were performed using a Hewlett-Packard (Waldbronn, Germany) Model 1090 ternary gradient liquid chromatograph with an HP 1040M diode-array detector. The system was controlled by an HP 79994A workstation, which also performed data acquisition from DAD. Separation was carried out using an HP stainless-steel analytical column (250 × 4 mm I.D.) containing 5-μm Spherisorb ODS-2. A loop of 5 or 20 μl was used depending on the solvent used in the solid-phase extraction process.

2.3. Chromatographic conditions and detection

The chromatographic separation was carried out using a gradient of methanol–1% acetic acid (pH 2.8) from 25:75 to 40:60 in 25 min, 100% methanol at 30 min and, after 2 min of isocratic elution with 100% methanol, the initial conditions were reached in 2 min. The flow-rate of the eluent was 1 ml min^{-1} and the column temperature was 65°C. The volume of the sample injected was 5 μl when carbon was used in the preconcentration step and 20 μl when highly cross-linked styrene–divinylbenzene copolymer was used.

For single-wavelength monitoring, the detector was set at 280 nm for all phenolic compounds except PCP (302 nm). For comparison of the spectra, data were recorded from 210 to 350 nm.

2.4. Extraction process

Off-line trace enrichment was carried out using two different cartridges: laboratory-made cartridges of carbon black (Carbopack B 120/400; Supelco, Bellafonte, PA, USA) of 300 mg and highly cross-linked styrene–divinylbenzene copolymer cartridges (ENVI Chrom P; Supelco) (80–160 μm particle size) of 500 mg. The extractions were carried out using the Bond Elut–Vac Elut system (Varian, Harbor City, CA, USA).

When carbon was used in the preconcentration process, the phenolic compounds were eluted with 5 ml of dichloromethane, and when copolymer was used, 5 ml of methanol were required. In both instances the solvent was concentrated with a rotatory evaporator to a volume of 500 μl.

In the solid-phase extraction process, the addition of TBA as ion-pair reagent was studied in order to increase the recovery of the extraction process, mainly for the most polar compounds. When TBA was used, the conditioning process consisted of rinsing the cartridge with 10 ml of solvent (methanol or dichloromethane), 10 ml of water and 2 ml of a 5 m*M* TBA solution. The cartridges were dried before sample application. Prior to elution of sample, the sample pH was adjusted to 9 with 1 *M* NaOH and different volumes of TBA were added to adjust the final concentration to 5 m*M*. The sample was passed through the cartridge and eluted with 5 ml of solvent (methanol or dichloromethane) acidified with 1% of acetic acid to decrease the effect of the ion pair and solvent was removed under vacuum with rotary evaporator (Büchi, Flawil, Switzerland) to give a volume of 1 ml.

Tap and river water samples were filtered through a 0.45-μm filter (MSI, Westboro, MA, USA) before preconcentration.

3. Results and discussion

The gradient elution profile was optimized in order to obtain good resolution between peaks. The linearity of the response of the chromato-

graphic method was checked by injecting 5 μl of a solution of phenolic compounds at levels between 1 and 30 mg l^{-1} and for some compounds the last point was considered an outlier by a statistical criterion [21], hence the linearity range was between 1 and 20 mg l^{-1}. The detection limits of the chromatographic method ($S/N = 3$) were between 30 μg l^{-1} for 4-NP, 2,4-DNP and PCP and 0.1 mg l^{-1} for 2,4,6-TCP. In Table 1, the range of linearity studied for each compound, correlation coefficients (R^2) and the detection limits of the method without preconcentration process are given.

In order to increase the sensitivity of the method, a solid-phase extraction process was chosen. In a previous study [19], sorbents such as octadecyl, cyclohexyl and styrene–divinylbenzene copolymer were tested and the effect of the addition of TBA as ion-pair reagent was studied. In this study, the positive effect of TBA on the recovery of the most polar compounds, mainly phenol, was shown. The best results involved the use of PLRP-S but only 100 ml of sample could be preconcentrated in order to obtain good recoveries for all compounds. In order to increase the volume to be preconcentrated and thus to decrease the limit of detection of the global method, two sorbents were evaluated, carbon black and a highly cross-linked styrene–divinylbenzene copolymer.

The effect of the addition of an ion-pair reagent on the retention of phenol, whose breakthrough volume is very low, was evaluated. To establish the optimum conditions of the extraction process, several variables were optimized. First, different solvents were tested for the elution of the compounds retained in each type of cartridge. Using carbon cartridges of 100 mg, 10 ml of a standard solution of 5 mg l^{-1} were passed through the cartridge and eluted with 5 ml of dichloromethane, ethyl acetate, hexane, carbon disulfide or dichloromethane–methanol (1:1). The acidification of the solvent did not improve the recovery, as other workers [18] have found. The best recoveries for all phenolic compounds were obtained using dichloromethane. However, when dichloromethane was used, a solvent peak appeared at the same retention time as 4-NP, which made it impossible to determine this peak and the use of this solvent involved the injection of only 5 μl of sample because substantial peak broadening appeared caused by the different solvent strengths between dichloromethane and the mobile phase.

Table 1
Study of the linearity of the response and detection limits of the methods

Compound	Linearity range (mg l^{-1})	R^2	Detection limit		
			Direct injection, 5-μl loop (μg l^{-1})	Carbon cartridge, 100 ml + TBA, 5-μl loop (μg l^{-1})	Polymer cartridge, 500 ml + TBA, 20-μl loop (ng l^{-1})
Ph	1.1–33.2	0.9999	75	4	100
4-NP	1.0–30.7	0.9976	30	–	65
2,4-DNP	1.0–30.6	0.9995	30	2	60
2-CP	1.0–29.9	0.9981	70	4	95
2-NP	1.0–30.3	0.9998	45	3	65
2,6-DMP	1.0–20.5	0.9988	100	6	90
2,4-DMP	1.0–19.9	0.9969	70	4	70
2-M-4,6-DNP	1.0–30.4	0.9956	40	2	65
4-C-3-MP	1.1–32.2	0.9960	80	5	95
2,4-DCP	1.0–31.1	0.9958	75	5	90
2,4,6-TMP	1.0–20.2	0.9991	75	5	90
2,4,6-TCP	1.1–21.2	0.9927	100	6	90
PCP	0.9–27.6	0.9970	30	2	70

In the next step, the mass of carbon used in the laboratory-made cartridges was studied. A mass of 300 mg was chosen because the larger the amount of carbon, the larger was the volume of solvent needed to desorb the compounds, and with this mass the recoveries were good for all compounds studied when they were eluted with 5 ml of solvent. A larger amount of carbon implied a larger volume of elution solvent and the use of a reversible cartridge [18]; although this could partially solve this problem, it was not possible with our design.

In order to determine the volume of sample that can be concentrated with good recoveries for all the compounds studied, different volumes (25, 50 and 100 ml) of a solution of phenolic compounds at the 0.1 mg l^{-1} level in Milli-Q-purified water were passed through the cartridge, eluted with 5 ml of dichloromethane and the eluate was concentrated to a final volume of 1 ml. The recovery of phenolic compounds for the different volumes was checked with and without the addition of TBA and the results obtained are given in Table 2. The addition of TBA increased the recovery of phenol, but the volume of sample that could be preconcentrated with good recoveries was low. Although for the other compounds good recoveries were obtained even when 100 ml of sample were preconcentrated, no higher sample volumes were tested because of the low recovery of phenol.

As regards the highly cross-linked styrene–divinylbenzene copolymer, better recoveries than those obtained with the conventional styrene–divinylbenzene copolymer were expected according to the literature [15,20], which would allow the preconcentration of larger sample volumes.

To select the best solvent to elute the compounds retained, 10 ml of a standard solution of 5 mg l^{-1} were passed through the cartridge and eluted with 5 ml of methanol, acetonitrile or tetrahydrofuran. No significant differences were obtained and methanol was chosen as this is the eluent for the chromatographic system.

The recoveries obtained when different volumes of a standard solution of phenolic compounds at the 10 μg l^{-1} level in Milli-Q-purified water adjusted to acidic pH (1% acetic acid) were preconcentrated are given in Table 3. Better recoveries than those obtained with carbon were achieved but at volumes larger than 250 ml the recovery of phenol decreased considerably. However, for the other compounds, good recoveries were obtained even at a sample volume of 1000 ml.

Table 2
Mean recoveries, R ($n = 3$), of solid-phase extraction with carbon for different volumes of a solution of 0.1 mg l^{-1} of phenolic compounds in Milli-Q-purified water

Compound	Volume (ml)											
	25				50				100			
	Without TBA		With TBA		Without TBA		With TBA		Without TBA		With TBA	
	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)
Ph	49	8.2	75	7.6	35	8.4	58	7.5	29	8.7	54	8.2
4-NP	–	–	–	–	–	–	–	–	–	–	–	–
2,4-DNP	83	7.4	89	6.9	82	7.4	83	7.3	80	7.6	82	7.5
2-CP	94	5.2	98	4.9	94	5.3	96	4.6	90	5.7	90	5.7
2-NP	91	4.7	95	3.8	90	4.2	91	3.6	88	4.5	91	4.1
2,6-DMP	101	3.8	103	3.7	98	4.7	100	3.8	93	4.4	95	4.6
2,4-DMP	97	4.1	100	4.8	95	4.5	97	4.2	89	5.4	92	4.8
2-M-4,6-DNP	85	6.6	91	5.7	80	6.8	85	6.5	78	6.4	80	6.7
4-C-3-MP	99	7.3	101	7.1	97	7.6	98	7.4	92	7.9	92	7.8
2,4-DCP	103	3.2	102	3.3	100	3.5	99	3.7	96	3.9	97	4.4
2,4,6-TMP	98	3.8	99	3.8	97	4.1	99	3.9	96	4.3	98	3.9
2,4,6-TCP	98	5.9	100	5.7	95	6.4	98	6.8	95	6.5	96	6.5
PCP	75	8.5	76	7.8	75	8.4	75	7.9	74	8.1	75	8.1

Table 3
Mean recoveries, R ($n = 3$), of the solid-phase extraction with the highly cross-linked styrene–divinylbenzene copolymer for different volumes of a solution of 10 $\mu g\ l^{-1}$ of phenolic compounds in Milli-Q-purified water

Compound	Volume (ml)											
	250				500				1000			
	Without TBA		With TBA		Without TBA		With TBA		Without TBA		With TBA	
	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)
Ph	76	8.4	97	4.1	44	8.3	90	4.3	17	8.7	54	8.2
4-NP	100	3.8	101	3.8	100	3.9	100	3.8	83	6.5	98	4.3
2,4-DNP	98	3.3	100	3.2	97	3.5	98	3.4	100	3.5	98	3.6
2-CP	99	4.9	102	4.7	96	5.1	98	5.5	97	5.1	96	5.2
2-NP	97	3.9	99	3.6	98	3.8	97	4.5	100	3.8	101	3.7
2,6-DMP	102	4.3	102	4.2	98	4.7	98	4.6	98	4.7	98	4.9
2,4-DMP	98	4.6	100	4.6	101	4.5	98	4.6	99	4.5	96	4.6
2-M-4,6-DNP	97	5.6	98	6.6	97	6.2	97	6.1	99	6.2	99	6.3
4-C-3-MP	102	7.6	103	6.9	99	7.3	96	7.5	100	7.3	99	7.5
2,4-DCP	100	5.8	102	5.7	93	6.4	96	6.1	92	6.4	100	5.7
2,4,6-TMP	96	3.5	99	3.9	100	3.8	101	3.7	100	3.8	102	3.9
2,4,6-TCP	95	6.5	100	6.2	90	6.7	93	6.4	90	6.7	91	6.7
PCP	76	7.6	76	7.9	76	8.4	77	7.9	75	8.4	76	7.6

To increase the recovery of phenol, ion-pair formation using TBA was tested and the recoveries obtained with different volumes of a standard solution of phenolic compounds at the 10 $\mu g\ l^{-1}$ level in Milli-Q purified water are also given in Table 3. As can be seen, the addition of TBA to the sample allowed the preconcentration of 500 ml of sample with good recoveries for all compounds, including phenol.

The detection limits obtained when 100 ml of standard solution with TBA were preconcentrated using carbon cartridges and when 500 ml of the same standard solution were preconcentrated with the copolymer cartridge are given in Table 1. When carbon cartridges were used the detection limits of the method were between 2 and 6 $\mu g\ l^{-1}$ and when polymeric cartridges were used and a loop of 20 μl the detection limits were between 60 and 100 ng l^{-1}.

The performance of the method was tested on tap and Ebro river water. The samples were filtered through a 0.45-μm filter and 300 μl of 10% Na_2SO_3 solution were added for each 100 ml of tap water to eliminate free chlorine, which could react with phenols and produce chlorophenols.

As a first step, the recovery of the compounds in real samples was checked and the values obtained were as good as those with Milli-Q-purified water. The capacity of the cartridges was also tested with real samples and recoveries at different levels of phenolic compounds in 500 ml of river water sample were checked up to 0.2 mg l^{-1}. The recoveries were similar, which meant that the capacity of the cartridges was sufficient at these levels of phenolic compounds. The repeatability of the method with real samples was tested with 500 ml of river water spiked at 1 μg^{-1} and the relative standard deviations ($n = 4$) were between 4.3 and 8.6%.

The chromatogram obtained when 500 ml of tap water were preconcentrated by using the copolymer cartridges is shown in Fig. 1a and that for the same sample spiked with a standard solution of phenolic compounds at the 1 $\mu g\ l^{-1}$ level in Fig. 1b. Both samples were adjusted to pH 9 with NaOH and 5 mM TBA was added. Na_2SO_3 was also added to the sample as mentioned previously. The phenolic compounds retained in the cartridges were eluted with 5 ml of methanol. Prior to the injection of 20 μl of sample, solvent was removed under vacuum until a volume of 1 ml was reached.

As can be seen, all compounds can be determined without interferences and a peak that could be assigned to 2-NP appeared in the

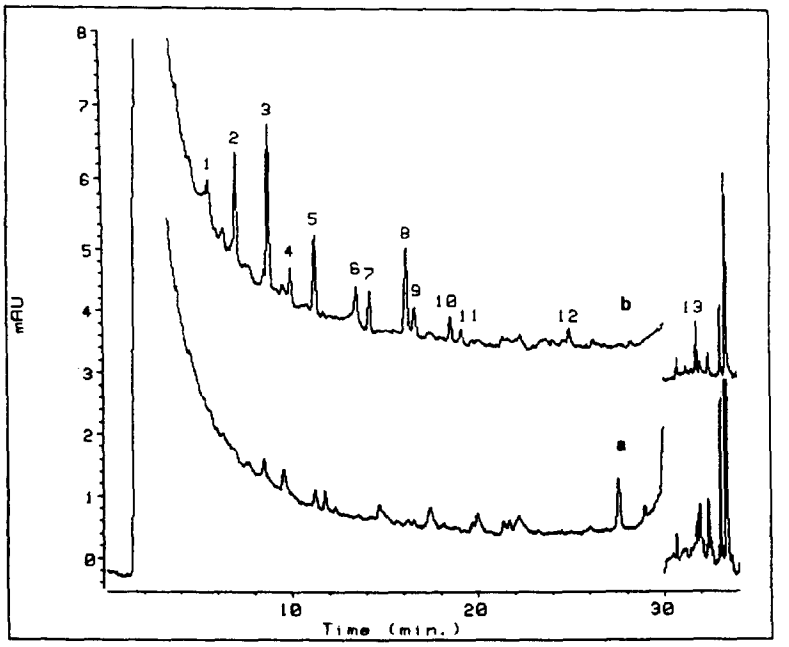

Fig. 1. Chromatograms obtained after ion-pair extraction with copolymer cartridge of (a) 500 ml of tap water and (b) 500 ml of tap water (with Na_2SO_3) spiked with a standard solution of phenolic compounds at the 1 $\mu g\ l^{-1}$ level. Peaks: 1 = phenol; 2 = 4-nitrophenol; 3 = 2,4-dinitrophenol; 4 = 2-chlorophenol; 5 = 2-nitrophenol; 6 = 2,6-dimetylphenol; 7 = 2,4-dimetylphenol; 8 = 2-methyl-4,6-dinitrophenol; 9 = 4-chloro-3-metylphenol; 10 = 2,4-dichlorophenol; 11 = 2,4,6-trimethylphenol; 12 = 2,4,6-trichlorophenol; 13 = pentachlorophenol. For conditions, see text.

chromatogram of the tap water sample. From the comparison of the spectra, it could not be assigned to 2-NP.

The same analysis was carried out with river water. A 500-ml volume of Ebro river water and the same sample spiked with 1 $\mu g\ l^{-1}$ of a standard solution of phenolic compounds were analysed using the same method and the chromatograms obtained are shown in Fig. 2. It should be pointed out that, although there was a higher retention of the most polar compounds, the band at the beginning of the chromatogram did not prevent us from detecting phenol.

On the chromatogram, two small peaks with the same retention time as 2-NP and 2-M-4,6-DNP appeared, but the low signal did not allow comparison of the spectra.

If these results are compared with those obtained in a previous study [19] in which conventional PLRP-S was used and only 100 ml could be preconcentrated in order to obtain good recoveries, this highly cross-linked stryene–divinylbenzene copolymer seems to be much more suitable for the preconcentration of phenolic compounds.

4. Conclusions

The use of a highly cross-linked styrene–divinylbenzene copolymer sorbent for the preconcentration of phenolic compounds in water gave better results than those obtained with carbon, as it allowed a higher volume of sample to be preconcentrated without breakthrough. The addition of TBA to the sample implied, in both sorbents, an increase in the breakthrough volumes, especially that corresponding to phenol, which was the most polar compound studied. The preconcentration of 500 ml of river or tap water sample allowed the determination of these compounds at $\mu g\ l^{-1}$ levels. Recoveries obtained were higher than 90% and the R.S.D. of the method for real samples was lower than 10%.

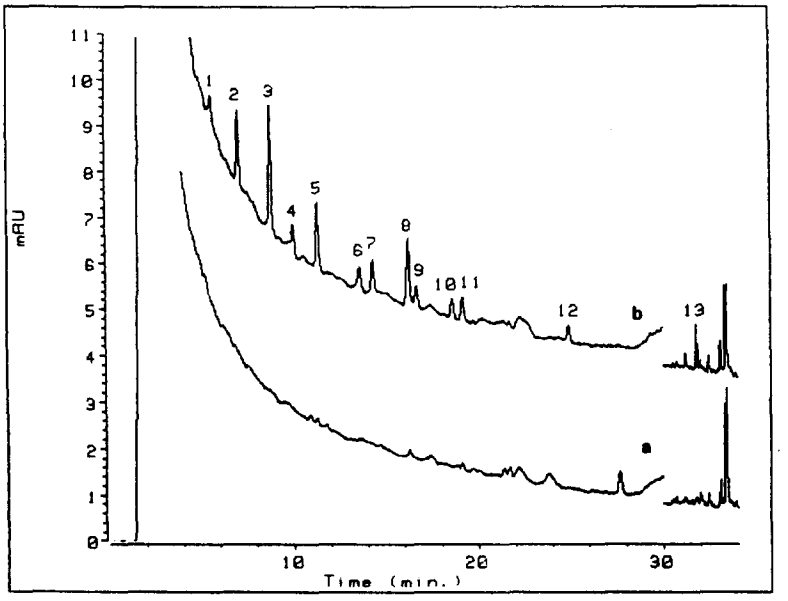

Fig. 2. Chromatograms obtained after ion-pair extraction with copolymer cartridges of (a) 500 ml of river water and (b) 500 ml of river water spiked with a standard solution of phenolic compounds at the 1 $\mu g\ l^{-1}$ level. Peaks as in Fig. 1. For conditions, see text.

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