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Automated on-line trace enrichment and determination of phenolic compounds in environmental waters by high-performance liquid chromatography

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Abstract

Automated trace enrichment of phenolic compounds on a 10 × 2.0 mm I.D. precolumn packed with PLRP-S was coupled on-line with reversed-phase column liquid chromatography and electrochemical detection. Two different eluents were used owing to the different polarities of the phenolic compounds and the difficulty of combining gradient elution with electrochemical detection. In the analysis of real samples (tap and river water), each step of the automatic method was optimized taking into account the complexity of the matrix. In tap water, the preconcentration of 4-ml samples allowed phenolic compounds to be determined at the ng l^{-1} level and the limits of detection (LODs) were between 1 and 10 ng l^{-1} (except for 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenol, for which the LODs were 75 and 50 ng l^{-1}, respectively). When river water was analyzed, only 1 ml of sample could be preconcentrated because of humic and fulvic acid interference and the detection limits were about four times higher.

1. Introduction

The determination of phenol and substituted phenols is receiving increasing attention because of their toxicity. Further, the presence of chlorinated phenols, which can be present in drinking waters as a consequence of the disinfection process with chlorine, has an adverse effect on the taste and odour of water [1,2]. The maximum admissible concentration (MAC) according to EC directives for phenols in drinking water is 0.5 $\mu g\ l^{-1}$, excluding those phenols which do not react with chlorine [3].

There are various methods for determining phenols in water. The spectrophotometric method based on the reaction of 4-aminoantipyrine with phenols [4] is recommended but only the total content of phenols can be determined. Another much used method is based on gas chromatography with derivatization and electron-capture detection, which is the standard EPA method [5].

Recently, these compounds have been determined by RPLC using mainly UV [6–8] or amperometric detection [9–11], although other detection techniques such as mass spectrometry [12], fluorescence or chemiluminescence after derivatization [13] have also been described.

When amperometric detection is used, it is necessary to develop the chromatographic sepa-

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ration by isocratic elution to avoid baseline distortion. In this case, when isocratic elution is used, the main problem in the separation is the different polarities of the compounds, which results in long analysis times and the appearance of broader peaks for the last-eluted compounds, with a consequent loss of sensitivity.

Although amperometric detection is very sensitive, the low concentration allowed in drinking water by EC regulations implies a preconcentration process. Liquid–liquid extraction has been the most often used technique, but in the last few years solid-phase extraction (SPE) has become more popular [14,15]. Various packing materials with different selectivity such as octadecyl-bonded silica, styrene–divinylbenzene copolymer and graphitized carbon black are currently available. Some of them have been applied to the determination of phenolic compounds [16–19], with varying results. On-line solid-phase extraction procedures involve better sensitivity, lower sample volume, lower consumption of organic solvents, higher automation potential and better reproducibility [20–25].

In this paper, the eleven phenolic compounds considered as priority pollutants by the EPA were determined using a liquid chromatographic system with an electrochemical detector. Isocratic elution was selected and two eluents had to be used. In order to decrease the limit of detection, an automatic on-line preconcentration system with a styrene–divinylbenzene copolymer precolumn and with the addition of the ion-pair reagent tetrabutylammonium bromide (TBA) to the sample was developed. The performance of the total system was checked with tap and river water.

2. Experimental

2.1. Equipment

Chromatographic experiments were performed using a Shimadzu (Tokyo, Japan) LC-9A pump with an HP-1049A electrochemical detector (Hewlett-Packard, Palo Alto, CA, USA). The temperature of the column was controlled by a Bio-Rad (Veenendaal, Netherlands) oven and chromatographic data were collected and recorded using an HP-3365 Series II Chemstation, which was controlled by Windows 3.1 (Microsoft). The separation was performed using a 250 × 4 mm I.D. Spherisorb ODS-2 column with a particle size of 5 μm.

The sample was injected through a Rheodyne valve with a 20-μl loop or with an automatic method using a Must column-switching device (Spark-Holland, Emmen, Netherlands) that allowed the sample to be injected after the preconcentration process. To carry out the solid-phase extraction, a precolumn (10 × 2 mm I.D.) packed with a styrene–divinylbenzene copolymer (PLRP-S) (15–25 μm particle size) (Spark Holland) and a Waters (Milford, MA, USA) M45 pump to deliver the sample were used.

2.2. Reagents and standards

Phenol (Ph), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2-chlorophenol (2-CP), 2-nitrophenol (2-NP), 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) and 2,4,6-trichlorophenol (2,4,6-TCP) were obtained from Aldrich Chemie (Beerse, Belgium) and pentachlorophenol (PCP) from Janssen Chemie (Geel, Belgium). Standard solutions (2000 mg l^{-1} of each compound) were prepared in methanol–water (50:50). If stored in a refrigerator, the solutions were stable for several months. A mixture of all phenolic compounds was prepared weekly by diluting the standard solution in water obtained with a Milli-Q system (Millipore, Bedford, MA, USA), and more diluted working solutions were prepared every day by diluting the solution with Milli-Q-purified, tap and river water.

HPLC-grade methanol (Scharlau, Barcelona, Spain) and Milli-Q quality water were used in the preparation of the eluent and in the solid-phase extraction system.

The pH values of the eluent were adjusted with sulphuric acid (Panreac, Barcelona, Spain) and acetate buffer (Merck, Darmstadt, Germany). To adjust the ionic strength of the

eluent, potassium nitrate (Probus, Badalona, Spain) and potassium chloride (Probus) were added. The tetrabutylammonium bromide used as an ion-pair reagent in the extraction process was supplied by Fluka (Buchs, Switzerland).

2.3. Chromatographic conditions and detection

Two eluents with different solvent strength were used. For the separation of the nine most polar compounds studied, the eluent used was methanol–water (45:55) acidified to pH 3.0 with H_2SO_4 and containing KCl and KNO_3 at final concentrations of 0.05 and 2 g l^{-1}, respectively (eluent A). The eluent used for the separation of 2,4,6-TCP and PCP was methanol–water (65:35) adjusted at pH 4.7 with acetic acid–sodium acetate buffer and KCl and KNO_3 at final concentrations of 0.05 and 2 g l^{-1}, respectively (eluent B). In both instances, the flow-rate was 1 ml min^{-1}, the column temperature was kept at 50°C and the volume of sample for direct injection was 20 μl.

The potential values used in the electrochemical detector were 1.1 V for the nine most polar compounds and 0.8 V for 2,4,6-TCP and PCP. The electrochemical detector worked in the amperometric mode with a glassy carbon electrode. A solid-state Ag–AgCl reference electrode was used, so the eluents had to contain KCl (0.05 g l^{-1}). The electrochemical cleaning technique was used every twenty injections to correct the electrodeposition on the surface of the electrode, applying a cyclic treatment with alternate potentials. The working electrode was polished in the conventional way every 60 injections [8,26].

2.4. On-line trace enrichment

The on-line solid-phase extraction process was carried out using a 10×2 mm I.D. precolumn packed with the styrene–divinylbenzene copolymer (PLRP-S). The pH of the samples was adjusted at about 9.0 and TBA was added at a concentration of 5 m*M*. The addition of TBA to the sample meant an increase in breakthrough volumes, mainly for the most polar compounds, as had been shown previously [27].

Fig. 1 shows a diagram of the programmable delivery system used for automatic preconcentration. Two switching valves were used in order to clean up the tubes, activate the precolumn and measure more accurately the sample volume to be preconcentrated. Table 1 shows the programme followed in the extraction process. The flow-rate was 2 ml min^{-1} in all processes. First,

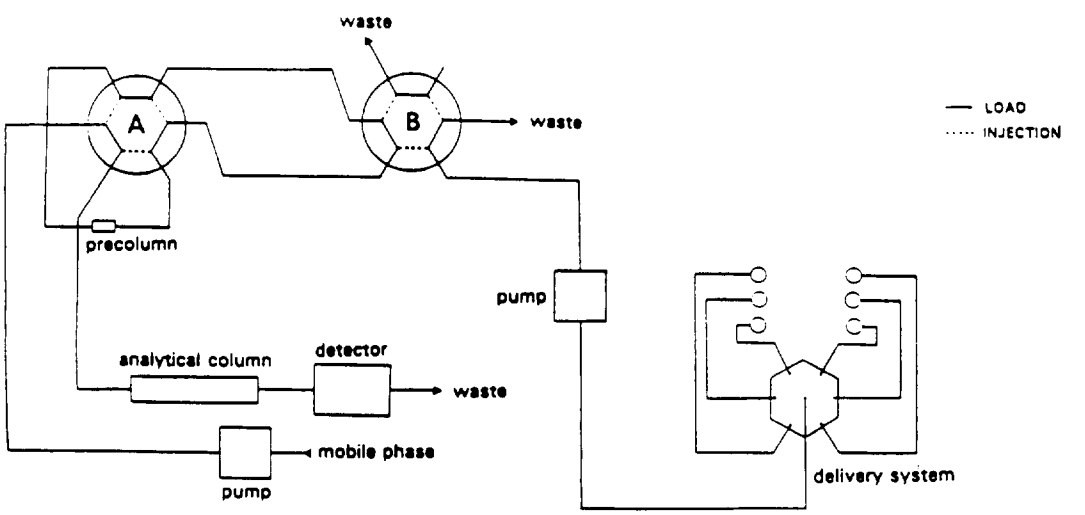

Fig. 1. Set up for automated preconcentration of sample.

Table 1
Programme for the extraction process

Step	Time (min)	Event	Valve A	Valve B
1	0	Washing tubes with methanol	Load	Load
2	2	Conditioning cartridge with methanol	Load	Inject
3	8	Washing tubes with water–TBA	Load	Load
4	10	Activation of cartridge with water–TBA	Load	Inject
5	11	Washing tubes with sample	Load	Load
6	13	Sample preconcentration	Load	Inject
7[a]	15	Washing tubes with water–TBA	Load	Load
8[a]	17	Clean-up with water–TBA	Load	Inject
9	15/18.5	Analyte desorption	Inject	Inject

[a] Only applied when river water was analysed.

the preconcentration system was washed with methanol for 2 min to remove all the solvents between the delivery system and the pump delivering sample. Then, in step 2, the cartridge was cleaned up and conditioned with methanol for 6 min. Another step (3) was introduced to remove the methanol with a 5 m*M* solution of TBA. After activating the cartridge with the TBA solution for 1 min and cleaning the tubes with the sample for 2 min, the preconcentration step started (at 13 min). The length of this step can be changed depending on the matrix sample (2 min for standard solution and tap water or 0.5 min for river water). In the next step, the analytes trapped on the precolumn were desorbed in the backflush mode and transferred on-line to the analytical column.

When river water was analysed, prior to the injection of the sample two additional steps were introduced in the programme to remove humic and fulvic acids, which may introduce an important distortion peak at the beginning of the chromatogram. In this case, two steps (7 and 8) to clean up the tubes and the cartridge were included in the programme.

3. Results and discussion

As mentioned above, two eluents were optimized to carry out the isocratic separation: one to separate the nine most polar phenolic compounds studied (eluent A, which contains 45% methanol) and another, with a higher solvent strength (eluent B, with 65% of methanol), to separate 2,4,6-TCP and PCP, which are the least polar compounds studied. The best results for the more polar compounds were obtained at pH 3.0, but for the other compounds (eluent B), the pH had to be increased in order to shorten the analysis time, because the retention time of PCP is highly pH dependent, although the retention time of 2,4,6-TCP does not change very much with pH. Of the different pH values tested, between 3 and 5, pH 4.7 allowed the separation of both compounds in less than 10 min. Although some workers used gradient elution [11], lower sensitivity was obtained because of the baseline drift and two runs are preferred [8].

In order to select the best working potential, different potential values were tested and for eluent A the potential had to be fixed at 1.1 V, because at lower potentials nitrophenols had a very low response in the range of concentrations studied and a considerable background appeared in the chromatogram at higher potential values, which meant that it took a longer time to stabilize the detector. On the other hand, for 2,4,6-TCP and PCP, with the eluent specified previously, the highest signal was obtained at 0.8 V.

The electrochemical ratios of the peak areas at different voltages for each phenolic compound were determined under the experimental conditions used so that they could be used as confirmation data when real samples were ana-

Table 2
Electrochemical ratios of the peak areas at different voltages

Compound	0.8/1.1 V	0.9/1.1 V	1.0/1.1 V	0.7/0.8 V	1.0/0.8 V	1.1/0.8 V
Ph	0.05	0.28	0.71			
4-NP	0.00	0.00	0.11			
2,4-DNP	0.00	0.02	0.08			
2-CP	0.13	0.44	0.74			
2-NP	0.00	0.01	0.29			
2,4-DMP	0.51	0.74	0.91			
2-M-4,6-DNP	0.00	0.00	0.07			
4-C-3-MP	0.27	0.60	0.76			
2,4-DCP	0.41	0.77	0.88			
2,4,6-TCP				0.89	0.94	0.91
PCP				0.29	0.86	0.81

lysed. The results are given in Table 2 and the relative standard deviations of the values ($n = 4$) were between 1.5 and 7.9%.

Fig. 2 shows the chromatograms obtained after a 20-μl injection of a standard solution of 20 μg l^{-1} of each phenol except 2-M-4,6-DNP (40 μg l^{-1}) and 2,4-DNP (200 μg l^{-1}) with the two optimum eluents. Good resolution between the different peaks was observed. The linearity of the response was checked for different ranges depending on the sensitivity of each compound and in all instances good linearity was achieved. The detection limits of the chromatographic method were determined for a signal-to-noise ratio of about 3, and the results of linearity ranges and limits of detection are given in Table 3.

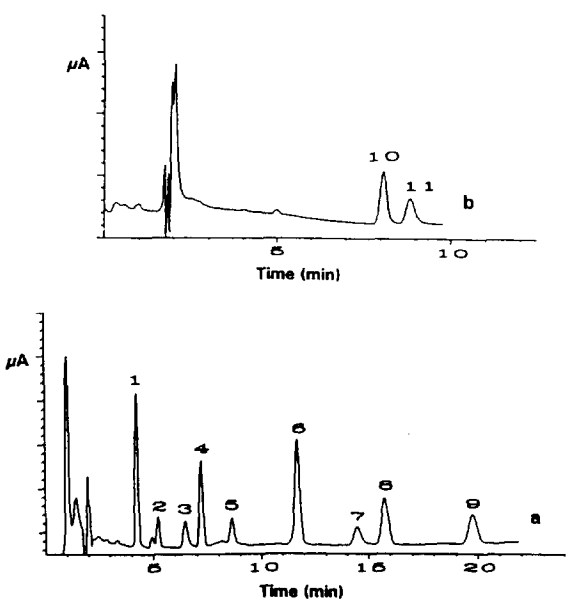

Fig. 2. Chromatograms obtained under optimum conditions for a standard solution of phenols of 20 μg l^{-1}, except 2-methyl-4,6-dinitrophenol (40 μg l^{-1}) and 2,4-dinitrophenol (200 μg l^{-1}). (a) Eluent A; (b) eluent B. 1 = phenol; 2 = 4-nitrophenol; 3 = 2,4-dinitrophenol; 4 = 2-chlorophenol; 5 = 2-nitrophenol; 6 = 2,4-dimethylphenol; 7 = 2-methyl-4,6-dinitrophenol; 8 = 4-chloro-3-methylphenol; 9 = 2,4-dichlorophenol; 10 = 2,4,6-trichlorophenol; 11 = pentachlorophenol.

In order to determine lower concentrations of phenols, a preconcentration system was required. On-line trace enrichment systems improve the limit of detection as all of the preconcentrated sample is injected into the chromatographic system whereas only an aliquot is injected when an off-line system is used.

Different packing materials were used for on-line SPE. In a previous paper [17] the off-line SPE of phenolic compounds was studied and it was shown that a styrene–divinylbenzene copolymer meant a higher breakthrough volume than C_{18} or cyclohexyl and the addition of an ion-pair reagent such as TBA also increased the breakthrough volumes of phenolic compounds. Some workers [20] recommend the use of two precolumns in series, one with PLRP-S for all phenolic compounds except for phenol, because of the low breakthrough volume, for which they recommended a non-ionic styrene–divinylbenzene copolymer with a large number of active aromatic sites (ENVI-Chrom P) and, conse-

Table 3
Linearity ranges, R^2 and limits of detection of phenolic compounds by direct injection and with on-line trace enrichment of 4 ml of Milli-Q-purified water adjusted to pH 9 and with TBA added

Compound	Direct injection			On-line trace enrichment		
	Linear range ($\mu g\ l^{-1}$)	R^2	LOD ($\mu g\ l^{-1}$)	Linear range ($\mu g\ l^{-1}$)	R^2	LOD ($ng\ l^{-1}$)
Ph	1–20	0.9990	0.1	0.01–1.0	0.9996	2
4-NP	5–25	0.9984	1	0.025–5.0	0.9982	10
2,4-DNP	25–200	0.9996	10	0.1–10.0	0.9984	75
2-CP	1–20	0.9994	0.5	0.01–1.0	0.9996	5
2-NP	5–25	0.9986	1	0.025–5.0	0.9986	10
2,4-DMP	1–20	0.9994	0.1	0.01–1.0	0.9996	2
2-M-4,6-DNP	5–25	0.9990	2	0.075–5.0	0.9980	50
4-C-3-MP	1–20	0.9990	0.5	0.01–1.0	0.9990	5
2,4-DCP	1–20	0.9980	0.5	0.01–1.0	0.9980	5
2,4,6-TCP	1–50	0.9990	0.1	0.01–1.0	0.9978	1
PCP	1–50	0.9988	0.1	0.01–1.0	0.9962	1

quently, a higher retention of phenolic compounds. In a recent paper [27], on-line SPE of phenolic compounds was studied and the influence of the different parameters, including the addition of TBA to the sample, on the breakthrough volumes was studied. Most compounds had breakthrough volumes considerably higher with PLRP-S than with other precolumns, whereas for the most polar compounds, mainly phenol, the breakthrough volumes were low and were considerably increased by the addition of TBA to the sample.

According to the values obtained, 4 ml of sample with TBA added was chosen as the volume for preconcentration, mainly determined by the phenol breakthrough volume. It should also be pointed out that higher sample volumes would cause overlap of the phenol peak with the peak that appeared at the beginning of the chromatogram and owing to the polar compounds retained in the precolumn.

Fig. 3 shows the chromatograms of 4 ml of Milli-Q-purified water spiked at 0.1 $\mu g\ l^{-1}$ with each phenolic compound, except 0.2 $\mu g\ l^{-1}$ for 2-M-4,6-DNP and 1 $\mu g\ l^{-1}$ for 2,4-DNP when the on-line trace-enrichment process was used. Good resolution between the different peaks can be observed, in addition to the presence of several unknown peaks with different retention times from the peaks of the compounds studied. Only slight peak broadening was observed for the compounds when the automatic on-line preconcentration method was used.

The linearity of the response for the total

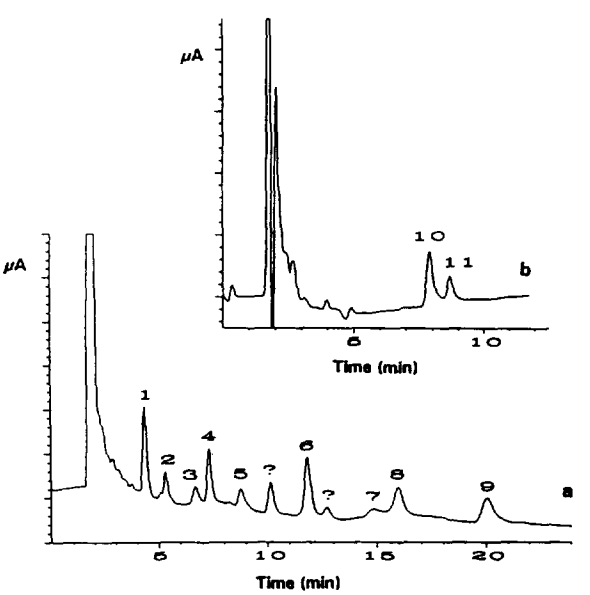

Fig. 3. Chromatograms obtained by on-line trace enrichment of 4 ml of Milli-Q-purified water spiked at 0.1 $\mu g\ l^{-1}$ with each phenolic compound, except 2-methyl-4,6-dinitrophenol (0.2 $\mu g\ l^{-1}$) and 2,4-dinitrophenol (1 $\mu g\ l^{-1}$). (a) Eluent A; (b) eluent B. For peak designation, see Fig. 2; ? = unknown.

analytical system, including the preconcentration step, was checked for a sample volume of 4 ml of Milli-Q-purified water spiked at different concentrations depending on the sensitivity of each phenolic compound. The results obtained for the linearity range are included in Table 3 together with the limits of detection (signal-to-noise ratio = 3). The recoveries for a sample of 0.2 $\mu g\ l^{-1}$ were >85% for all compounds except 2,4-DNP and 2-M-4,6-DNP, the recoveries of which were about 75%. The repeatability of the method was checked with a 4-ml Milli-Q-purified water sample spiked at the 0.1 $\mu g\ l^{-1}$ level and the R.S.D. were between 1.5 and 7.7% ($n = 4$).

The analytical performance of the system was tested with tap and river water. When tap water was analysed, 300 μl of a 10% solution of Na_2SO_3 were added to 100 ml of water before adding the standard solution of phenolic compounds in order to eliminate free chlorine, which could react with phenols and produce chlorophenols [13].

The linearity of the method was checked with tap water and it was essentially as good as for Milli-Q-purified water (R^2 values between 0.995 and 0.9994). Recoveries were calculated from the calibration graph including a preconcentration step with Milli-Q-purified water [28] and they were >90% for all compounds. The repeatability of the method was checked with a 4 ml of tap water sample spiked at the 0.1 $\mu g\ l^{-1}$ level. The R.S.D.s were between 1.9 and 8.2% ($n = 4$). The limits of detection were also similar to those obtained with Milli-Q-purified water and allowed pollutants to be determined at the levels required by present EC regulations.

On-line trace enrichment for river water showed a large, distorted peak at the beginning of the chromatogram, owing to the presence of humic substances in the river water. When eluent A was used, a volume of 4 ml of sample could not be preconcentrated because of interference with the first compounds eluted. It was necessary to decrease the volume for preconcentration.

A volume of 1 ml of sample was chosen to be preconcentrated. Under these conditions, a less distorted peak at the beginning of the chromatogram also appeared. Different clean-up steps were studied and the optimum one, with a decrease in the peak due to fulvic and humic acids and no decrease in the recoveries of phenolic compounds, is given in Table 1. The linearity of the response of the complete system was checked and linear ranges were found to be 0.05–5 $\mu g\ l^{-1}$ for all the compounds analysed with eluent A, except 2,4-DNP (0.5–40 $\mu g\ l^{-1}$) and 2-M-4,6-DNP (0.5–20 $\mu g\ l^{-1}$) ($R^2 = 0.994$–0.998). The repeatability of the method in river water was checked with a sample spiked at 0.5 $\mu g\ l^{-1}$ and the R.S.D.s found were between 3.2 and 8.5% ($n = 4$). The limits of detection (LOD) were between 5 and 50 $ng\ l^{-1}$, except for 2-M-4,6-DNP and 2,4-DNP (0.2 and 0.3 $\mu g\ l^{-1}$, respectively).

In Figs. 4a and b the chromatograms of a river water sample and the same sample spiked with a standard solution of the nine phenolic compounds at the 0.5 $\mu g\ l^{-1}$ level are shown. Different peaks also appeared but none of them could be assigned to any phenolic compound.

Fig. 4c shows the chromatogram obtained after the on-line preconcentration of 4 ml of tap water with the addition of Na_2SO_3. Several peaks appeared, one of them at the same retention time as phenol, which was assigned to phenol using electrochemical ratios. The concentration of phenol was 43 $ng\ l^{-1}$. The chromatogram obtained for a 4-ml tap water sample spiked with a phenolic compounds at the 0.1 $\mu g\ l^{-1}$ level with the addition of Na_2SO_3 is shown in Fig. 4d. Samples treated with Na_2SO_3 showed a larger peak at the beginning of the chromatogram.

The same study was carried out with the other two compounds and the results obtained in the analysis of 4-ml tap water sample and a 4-ml tap water sample spiked with a standard solution of 0.1 $\mu g\ l^{-1}$ and addition of sulphite solution are shown in Fig. 5a and b, respectively. It can be seen that a peak with a retention time similar to that of 2,4,6-TCP appears, but a study of the response at several potential values did not confirm the presence of this compound. It should be pointed out that the narrower peak at the beginning of the chromatogram is due to the

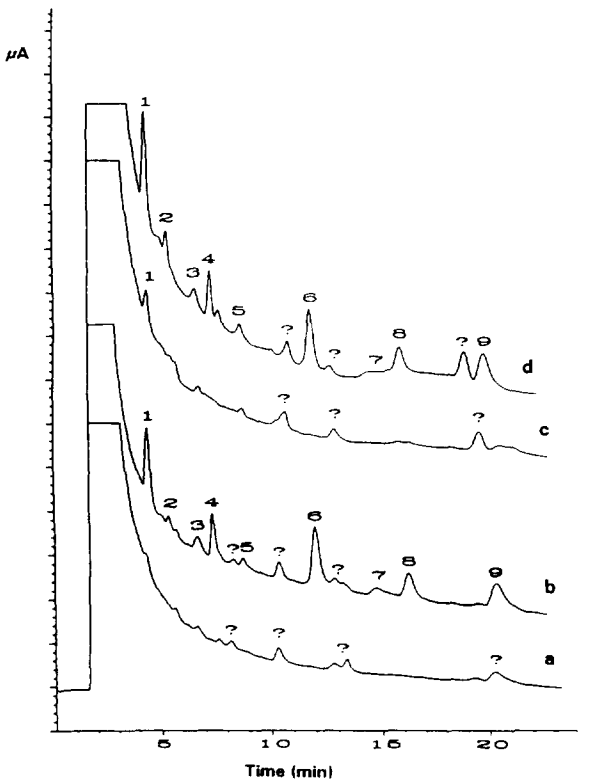

Fig. 4. Chromatograms with eluent A of (a) 1 ml of river water sample followed by the clean-up step (3 ml of water–TBA); (b) 1 ml of river water sample spiked at 0.5 $\mu g\ l^{-1}$ with each phenolic compound, except 2-M-4,6-DNP (1 $\mu g\ l^{-1}$) and 2,4-DNP (4 $\mu g\ l^{-1}$), followed by the clean-up step; (c) a 4-ml sample of tap water with Na_2SO_3 added; (d) a 4-ml sample of tap water with Na_2SO_3 added and spiked with a standard addition as in Fig. 3. For peak designation, see Fig. 2.

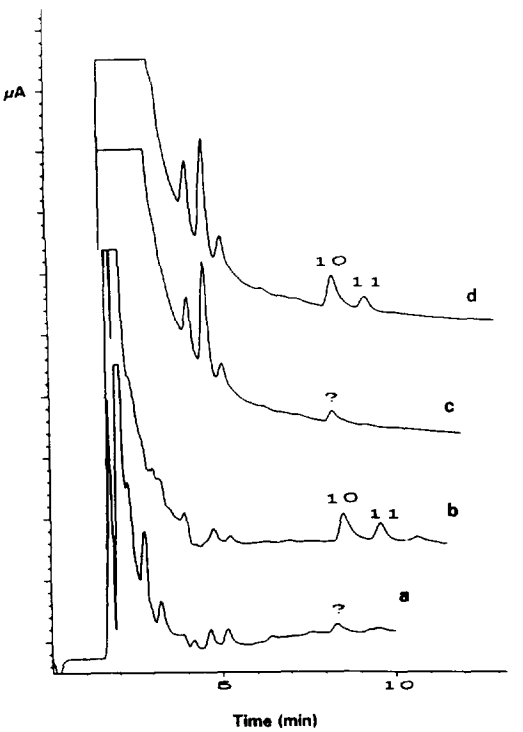

Fig. 5. Chromatogram with eluent B of (a) a 4-ml sample of tap water; (b) a 4-ml sample of tap water spiked at 0.1 $\mu g\ l^{-1}$ with 2,4,6-TCP and PCP; (c) a 4-ml river water sample; (d) a 4-ml river water sample spiked at 0.1 $\mu g\ l^{-1}$ with 2,4,6-TCP and PCP. For peak designation, see Fig. 2.

higher solvent strength of eluent B compared with eluent A.

For the determination of 2,4,6-TCP and PCP in river water, no clean-up step was required. In this instance, the volume of sample for the analysis was 4 ml and no large peak appeared at the beginning of the chromatogram, owing to the higher solvent strength. The linearity ranges for tap and river water were the same as those obtained for Milli-Q-purified water. The R.S.D.s for a 4-ml river water sample spiked at 0.1 $\mu g\ l^{-1}$ with 2,4,6-TCP and PCP were 3.2 and 5.1%, respectively ($n = 4$), and L.O.D. were 1 ng l^{-1} for both compounds. Chromatograms for a 4-ml river water sample and a 4-ml river water sample spiked at 0.1 $\mu g\ l^{-1}$ with each compound are shown in Fig. 5c and d, respectively. The peak that appeared at the same retention time as TCP was not assigned to this compound using the electrochemical ratios.

4. Conclusions

An on-line trace-enrichment–reversed-phase liquid chromatographic method with electrochemical detection has been developed for the determination of phenolic compounds in environmental waters. Two different eluents had to be optimized owing to the different polarities of the compounds studied. The addition of an ion-pair reagent to the sample allowed higher volumes of sample to be preconcentrated with

better recoveries, mainly for the most polar compounds. The preconcentration of only 4 ml of tap water allowed most compounds to be determined in the range 0.01–0.5 $\mu g\ l^{-1}$ and the LODs were at the low ng l^{-1} level. When river water samples were analysed, it was only possible to preconcentrate 1 ml of sample and the LODs were about four times higher.

References

[1] P.A. Realini, *J. Chromatogr. Sci.*, 19 (1981) 124.
[2] D.A. Baldwin and J.K. Debowski, *Chromatographia*, 26 (1988) 186.
[3] *Drinking Water Directive 80/778/EEC*, Commission of the European Communities, Brussels, 1980.
[4] *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, New York, 16th ed., 1985.
[5] *Fed. Regist.*, 233, No. 44, Dec. 3 (1979) 69464.
[6] C.P. Ong, H.K. Lee and S.F.Y. Li, *J. Chromatogr.*, 464 (1989) 405.
[7] O. Busto, J.C. Olucha and F. Borrull, *Chromatographia*, 32 (1991) 566.
[8] J. Ruana, I. Urbe and F. Borrull, *J. Chromatogr. A*, 655 (1993) 217.
[9] E. Nieminen and P. Heikkila, *J. Chromatogr.*, 464 (1989) 405.
[10] R.E. Shoup and G.S. Mayer, *Anal. Chem.*, 54 (1982) 1164.
[11] D.A. Baldwin and J.K. Debowski, *Chromatographia*, 26 (1988) 186.
[12] D.F. Hunt, J. Shabanowitz, T.M. Harvey and M. Coates, *Anal. Chem.*, 57 (1985) 525.
[13] P.J.M. Kwakman, D.A. Kamminga, U.A.Th. Brinkman and G.J. de Jong, *J. Chromatogr.*, 553 (1991) 345.
[14] I. Liska, J. Krupcík and P.A. Leclerq, *J. High Resolut. Chromatogr.*, 12 (1989) 577.
[15] B. Gawdzik, J. Gawdzik and U. Czerwinska-Bil, *J. Chromatogr.*, 509 (1990) 136.
[16] E. Pocurull, M. Calull, R.M. Marcé and F. Borrull, *Chromatographia*, 38 (1994) 579.
[17] A. Di Corcia, S. Marchese and R. Samperi, *J. Chromatogr.*, 642 (1993) 175.
[18] C. Borra, A. Di Corcia, M. Marchetti and R. Samperi, *Anal. Chem.*, 10 (1991) 317.
[19] L. Schmidt, J.J. Sun, J.S. Fritz, D.F. Hagen, C.G. Markell and E.E. Wisted, *J. Chromatogr.*, 641 (1993) 57.
[20] E.R. Brouwer and U.A.Th. Brinkman, *J. Chromatogr. A*, 678 (1994) 223.
[21] M.W. Nielen, U.A.Th. Brinkman and R.W. Frei, *Anal. Chem.*, 57 (1985) 806.
[22] I. Liska, E.R. Brouwer, H. Lingeman and U.A.Th. Brinkman, *Chromatographia*, 37 (1993) 13.
[23] P. Subra, M.C. Hennion, R. Rosset and R.W. Frei, *J. Chromatogr.*, 456 (1988) 121.
[24] U.A.Th. Brinkman, *J. Chromatogr. A*, 665 (1994) 217.
[25] M.C. Hennion, *Trends Anal. Chem.*, 10 (1991) 317.
[26] A.G. Huesgen and R. Schuster, *Selective HPLC Analysis in River Water (Application Note)*, Hewlett-Packard, Waldbronn, 1990.
[27] E. Pocurull, R.M. Marcé and F. Borrull, *Chromatographia*, in press.
[28] V. Pichon and M.C. Hennion, *J. Chromatogr. A*, 665 (1994) 269.