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Determination of phenolic compounds in natural waters by liquid chromatography with ultraviolet and electrochemical detection after on-line trace enrichment

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Abstract

The eleven phenolic EPA priority pollutants were determined by liquid chromatography followed by UV and electrochemical detection. Modified on-line trace enrichment was used to detect lower concentrations of phenolic compounds, which enables stronger sorbents to be used without broadening the peaks. PLRP-S and a highly cross-linked styrene–divinylbenzene copolymer were compared for the on-line trace enrichment. Higher breakthrough volumes were obtained with the latter sorbent but the selectivity was lower. The performance of the methods developed was checked with tap and river water and the methods studied enabled phenolic compounds at levels of 0.1 $\mu g\ l^{-1}$ to be determined in real samples. The repeatability and reproducibility between days ($n = 5$) for real samples spiked at 1 $\mu g\ l^{-1}$ were lower than 10%.

Keywords: Water analysis; Environmental analysis; Sample preparation; Phenolic compounds

1. Introduction

The environmental interest of phenol and substituted phenols is well known. These compounds are formed in the course of several industrial processes, particularly in pulp processing [1], and many phenols, especially chlorophenols, have a well established reputation for their toxicity and their persistence in the environment.

For this reason, many phenols are subject to legislation. European Community (EC) Directive 80/778/EEC specifies 0.5 $\mu g\ l^{-1}$ of total phenols as the maximum admissible concentration (MAC) in water intended for human consumption, excluding those phenols which do not react with chlorine, or 0.1 $\mu g\ l^{-1}$ for the individual compounds [2]. Some of the chlorinated compounds are listed in EC Directive 76/464/EEC and in the US Environmental Protection Agency (EPA) list as priority pollutants [3–5].

High-performance liquid chromatography is the most suitable technique to determine phenolic compounds in water using UV or diode-array detection (DAD) [6–12] or electrochemical detection (ED) [13–16] but, although amperometric detection is more sensitive than UV detection, a preconcentration step is necessary in both cases in order to achieve the low levels allowed in real samples.

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Solid-phase extraction is widely used instead of a liquid–liquid process to concentrate phenolic compounds, using several alkylsilica bonded phases such as phenyl [10,12], octyl [10,12], octadecyl [7–13,17] and cyanoyl [12], or poly-(styrene–divinylbenzene) [11,12] by itself or containing quaternary ammonium groups [6] and some other higher cross-linked poly(styrene–divinylbenzene) materials such as ENVI-Chrom P [18,19], LiChrolut [20] and Hysphere [21]. In general, low breakthrough volumes are obtained with alkylsilica bonded phases, mainly for the most polar compounds. On the other hand, poly(styrene–divinylbenzene) involves higher breakthrough volumes, which are even higher with the highly cross-linked sorbents. Graphitized carbon black has also been used for the extraction of phenolic compounds [21,22] with different results. Some workers [23] obtained better results by using a reversible graphitized carbon black cartridge because of the higher retention capacity of the carbon.

Membrane extraction discs, either with C_{18} or poly(styrene–divinylbenzene) adsorbent, have also been used for the extraction of phenolic compounds [13,24–27] and have the advantage of a faster elution rate and hence a shorter extraction time.

The main problem with all sorbents is the low recoveries obtained for the most polar phenolic compounds. It has been demonstrated that using tetrabutylammonium bromide as an ion-pair reagent increases the recovery of some of these compounds [9,11].

In order to decrease the detection limits of the method and increase the reproducibility and automation potential, several workers have used on-line solid-phase extraction instead of off-line solid-phase extraction to determine phenolic compounds in water using C_{18} [11,12,14], PLRP-S [11,12,28] or some more specific sorbents such as ENVI-Chrom P [28]. The most important limitation of these systems is the incompatibility between the sorbent in the precolumn and the stationary phase in the analytical column. Hence the use of sorbents that strongly retain phenolic compounds, such as ENVI-Chrom P [28] and graphitized carbon [29], can cause peak broadening because of the low solvent strength used for the chromatographic separation.

The main objective of this study was to use on-line solid-phase extraction with PLRP-S and ENVI-Chrom P coupled to liquid chromatography with UV and electrochemical detectors connected in series, to compare the performance of the two detection systems and select the best analytical conditions to establish a protocol capable of determining the eleven phenolic EPA priority pollutants in tap and river water at the levels required by the current legislation. To prevent peak broadening when a strong sorbent is used, the design of the equipment was modified in accordance with a previous paper [30].

2. Experimental

2.1. Equipment

Chromatographic experiments were performed using two Shimadzu (Tokyo, Japan) LC-10AD pumps with a Shimadzu SPD-10A UV spectrophotometric detector and an HP-1049A electrochemical detector (Hewlett-Packard, Palo Alto, CA, USA) connected in series. The temperature of the column was controlled by a Shimadzu CTO-10A 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 steel cartridge with a particle size of 5 μm purchased from Teknokroma (Barcelona, Spain).

To check the response of the instrument, standard solutions were injected through a Rheodyne valve with a 20-μl loop, but an automatic Must column-switching device (Spark Holland, Emmen, Netherlands) was used with on-line solid-phase extraction. The trace enrichment experiments were performed using two precolumns, one of which was 10 × 3 mm I.D. and laboratory-packed with the highly cross-linked styrene–divinylbenzene copolymer ENVI-Chrom P (Supelco, Bellefonte, PA, USA) (80–160 μm

particle size) and the other was a commercial 10×2 mm I.D. packed with styrene–divinlybenzene (Spark Holland). A Waters (Milford, MA, USA) M45 pump was used to deliver the sample.

2.2. Reagents and standards

The phenolic compounds studied were phenol (Ph), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2,4-dimethylphenol (2,4-DMP), 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), pentachlorophenol (PCP), 4-chloro-3-methylphenol (4-C-3-MP) and 2-methyl-4,6-dinitrophenol (2-M-4,6-DNP), all obtained from Aldrich Chemie (Beerse, Belgium) except pentachlorophenol, which was supplied by Jansen Chemie (Geel, Belgium). A stock standard solution (2000 mg l^{-1}) of each compound was prepared in methanol–water (50:50) and stored in a refrigerator. Working standard solutions were prepared every day by diluting the stock standard solutions with water obtained from a Milli-Q system (Millipore).

HPLC-grade methanol (Scharlau, Barcelona, Spain) and Milli-Q quality water adjusted to pH 2.8 with acetic acid (Merck, Darmstadt, Germany) were used in the preparation of the mobile phase. To adjust the ionic strength of the eluent, potassium chloride (Probus, Badalona, Spain) was added. Tetrabutylammonium bromide (TBA) used as the ion-pair reagent in the extraction process was supplied by Aldrich (Beerse, Belgium).

2.3. Chromatographic conditions

The eluents for the chromatographic separation were a solution of acetic acid (1%) containing 0.05 g l^{-1} of KCl as solvent A and methanol as solvent B. The flow-rate was 1 ml min^{-1} and the temperature was set at 65°C. The gradient profile was 25% B, initially 60% B after 25 min, 100% B at 30 min, isocratic for 2 min and then returned to initial conditions in 2 min.

The wavelengths used in the UV detector were 316 nm for 4-NP and 280 nm for the other nitrophenols: 2,4-DNP, 2-NP and 2-M-4,6-DNP. The potential used in the electrochemical detector to determine the remainder of the phenolic compounds studied was 1.0 V. This detector worked in the amperometric mode with a glassy carbon electrode. A solid-state Ag/AgCl reference electrode was used, so the eluent had to contain KCl (0.5 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 [14].

2.4. On-line trace enrichment

On-line trace enrichment was carried out in the two precolumns previously mentioned. In both cases, and prior to the preconstruction step, the pH of the sample was adjusted to 9.0 with NaOH and TBA was added at a concentration of 5 m*M* to form the ion pair.

To desorb the phenolic compounds from the sorbents, a modification of the common elution design was used [30], shown in Fig. 1. A Must column-switching device with two switching valves was used to clean up the tubes, activate the precolumn and more accurately measure the sample volume to be preconcentrated. First, the preconcentration system was washed with methanol for 5 min to remove all solvents between the delivery system and the pump delivering sample. Then the precolumn was cleaned up and conditioned with methanol for 1 min. After washing the tubes with water–5 m*M* TBA, the precolumn was activated with 2 ml of this solution and again the tubes were cleaned with the sample solution. Then different sample volumes were preconcentrated depending on the sorbent used. Before elution, when ENVI-Chrom P was used as the sorbent, there was a clean-up step with 10 ml of methanol–water (10:90, v/v) to reduce the influence of the matrix. In the next step the analytes trapped on the precolumn were desorbed in the backflush mode for 1 min with methanol and transferred on-line to the analytical column [30] after being mixed with solvent

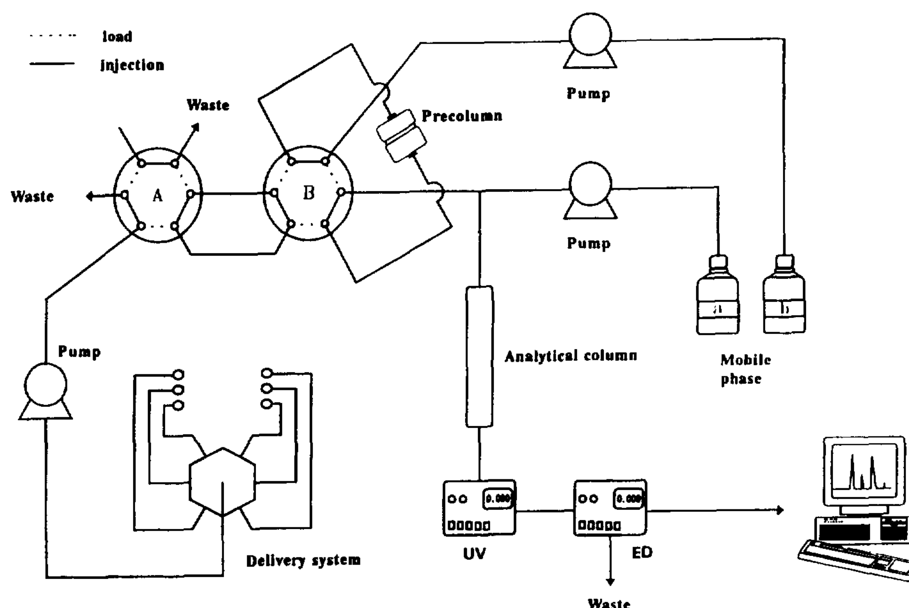

Fig. 1. Set-up of the system used.

A of the mobile phase. The flow-rate was 2 ml min^{-1} throughout the process. The different steps are summarized in Table 1.

Real samples were filtered through a 0.45-μm filter before preconcentration. When tap water was analysed, and prior to the standard addition, 300 μl of 10% Na_2SO_3 solution were added for each 100 ml of water in order to eliminate free chlorine.

3. Results and discussion

3.1. Analytical LC separation

The use of two detectors in series enabled the eleven EPA phenolic compounds to be determined at low levels since the nitrophenolic compounds, which have a low response in the electrochemical detector, have a higher response in

Table 1
Programme for the extraction process

Step	Time (min)	Event	Valve A	Valve B
1	0	Washing tubes with methanol	Inject	Load
2	5	Conditioning cartridge with methanol	Load	Load
3	6	Washing tubes with water–TBA (pH 9)	Inject	Load
4	11	Activation of cartridge with water–TBA (pH 9)	Load	Load
5	12	Washing tubes with sample	Inject	Load
6	17	Sample preconcentration	Load	Load
7	29:30	Washing tubes with–water methanol (90:10)[a]	Inject	Load
8	34:30	Clean-up with water–methanol (90:10)[a]	Load	Load
9	39:30	Analyte desorption	Inject	Inject
10	40:30	End desorption	Inject	Load

[a] Only for the highly cross-linked styrene–divinylbenzene copolymer.

the UV detector. For nitrophenols to respond better with electrochemical detection (ED) it is necessary to work at higher potentials, as was shown in another paper [14], and this involves a higher background in the chromatogram, especially in the present method in which gradient elution is applied. For this reason, these compounds were better detected using a UV detector working at the maximum absorbance wavelength of these compounds (316 nm for 4-NP and 280 nm for 2,4-DNP, 2-NP and 2-M-4,6-DNP). On the other hand, the other compounds studied had a better response using an electrochemical detector at 1.0 V. For this reason, the electrochemical detector was set at 1.0 V during the analysis and the UV detector was set at 316 nm until 8 min, then changed to 280 nm. The ratio of the responses from the two detectors may also be used to confirm the presence of some phenolic compounds.

To determine the linearity of the response of the chromatographic method, 20 μl of the standard solutions of the phenolic compounds studied were injected. Using an electrochemical detector good linearity was observed for the compounds studied between 15 $\mu g\ l^{-1}$ and 1 mg l^{-1}, except for Ph, whose last point was statistically considered to be an outlier, 2,4,6-TCP and PCP, their linearities being between 15 and 500 $\mu g\ l^{-1}$ for Ph and between 50 $\mu g\ l^{-1}$ and 5 mg l^{-1} for 2,4,6-TCP and PCP. When using a UV detector to determine the nitro compounds (4-NP, 2,4-DNP, 2-NP and 2-M-4,6-DNP), good linearity was obtained between 15 $\mu g\ l^{-1}$ and 20 mg l^{-1}. In both instances the regression coefficients (r^2) were higher than 0.996.

It should be pointed out that lower sensitivity was obtained with gradient elution than isocratic elution [14], owing to distortion of the baseline in the electrochemical detector.

3.2. On-line trace enrichment

Solid-phase extraction was selected to decrease the detection limits of the method by using two different sorbents, styrene–divinylbenzene commercially available in 10×2 mm I.D. cartridges and a highly cross-linked styrene-divinylbenzene copolymer (ENVI-Chrom P) in a 10×3 mm. I.D. laboratory-packed cartridge. As ENVI-Chrom P was not available commercially as precolumns, it was laboratory packed and a 10× 3 mm I.D. column was selected in order to obtain higher breakthrough volumes than with a 10×2 mm I.D. column. The modification of the elution system, which involves the phenolic compounds retained in the precolumn being eluted only by the methanol in the mobile phase instead of the initial conditions of gradient elution, allowed these stronger sorbents to be connected on-line to a C_{18} analytical column with no peak broadening, because of the higher solvent strength of methanol compared with the initial gradient mixture and, also, the subsequent rapid formation of the proper LC eluent [30].

In previous studies [11,30], breakthrough volumes with these two precolumns were determined using TBA as the ion-pair reagent because it increased the volume of the sample to be concentrated without important losses of phenolic compounds. When PLRP-S was used, a good recovery for phenol was obtained by concentrating 10 ml of Milli-Q water, but when a volume of 20 ml was preconcentrated, recoveries higher than 85% were obtained for 4-NP, 2-CP, 2-NP and 2,4-DMP and about 25% for phenol. For the other compounds the breakthrough volumes were higher than 30 ml and for some of them, such as 2-M,4,6-DNP, 2,4,6-TCP and PCP, even higher than 100 ml [11]. Therefore, 10 ml of sample were selected for further studies and the chromatograms obtained under these conditions by preconcentrating 10 ml of Milli-Q water are shown in Figs. 2a and 3a for electrochemical and UV detection, respectively.

When the highly cross-linked styrene–divinylbenzene copolymer was used as the sorbent, it was possible to concentrate 50 ml of Milli-Q water with no important losses of phenolic compounds, including phenol, whose recovery was about 80%. When this sorbent was used with real samples, there was a large system peak at the beginning of the chromatogram and therefore a clean-up step before eluting the sample was carried out in order to reduce this matrix effect. For this reason, 25 ml of sample were preconcen-

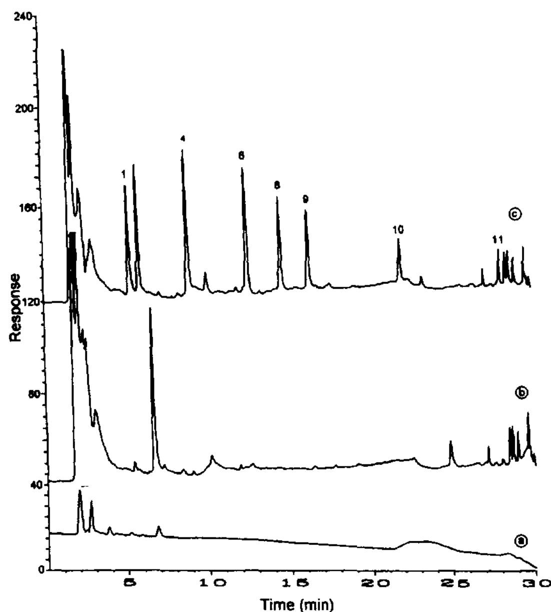

Fig. 2. Chromatograms obtained by on-line trace enrichment with a PLRP-S precolumn of a 10-ml sample using ED (a) Milli-Q water; (b) tap water; (c) tap water spiked at 1 μg l^{-1} with each phenolic compound. Peaks: 1 = Ph; 2 = 4-NP; 3 = 2,4-DNP; 4 = 2-CP; 5 = 2-NP; 6 = 2,4-DMP; 7 = 2-M-4, 6-DNP; 8 = 4-C-3-MP; 9 = 2,4-DCP; 10 = 2,4,6-TCP; 11 = PCP.

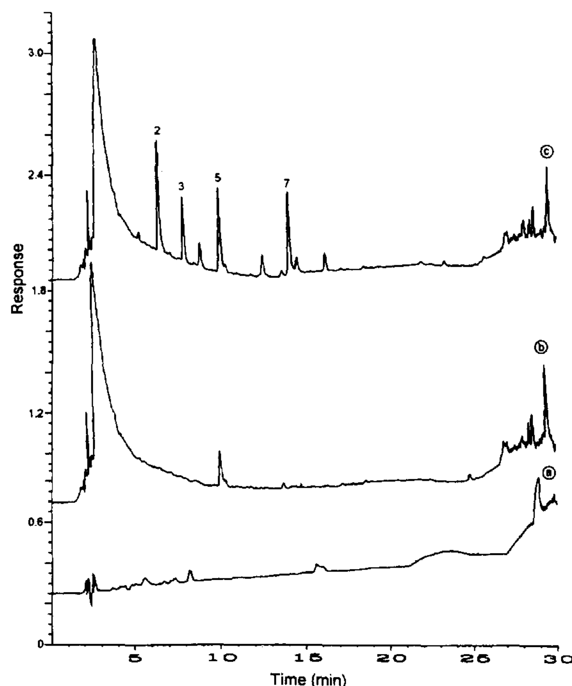

Fig. 3. Chromatograms obtained by on-line trace enrichment with a PLRP-S precolumn of a 10-ml sample using UV detection. (a) Milli-Q water; (b) tap water; (c) tap water spiked at 1 μg l^{-1} with each phenolic compound. Peaks as in Fig. 1.

trated and then 10 ml of methanol–water (10:90, v/v) were used as a clean-up step to reduce the large band appearing at the beginning of the chromatogram when real samples were analysed. The clean-up step allowed phenol and 2-NP to be determined with good recoveries in real samples whereas without the clean-up these peaks were overlapped by the band [30]. Under these conditions, recoveries obtained by preconcentrating a sample of 5 μg l^{-1} of phenols in Milli-Q water were higher than 80% for all compounds studied.

3.3. Application

The performance of the two sorbents was checked with tap and river water. Fig. 2b and c shows the chromatograms obtained with ED when 10 ml of tap water, with TBA as ion-pair reagent and adjusted to pH 9 with NaOH, were analysed with a PLRP-S precolumn and when the same sample was spiked with 1 μg l^{-1} of the standard solution of phenolic compounds, after the addition of Na_2SO_3 to eliminate free chlorine. A peak with the same retention time as phenol appeared in the chromatogram. This peak was identified as phenol by comparing the ratios of the peak areas at different potential values [14]. On the other hand, Fig. 3b and c show the chromatograms obtained with UV detection, in which there is a peak with the same retention time as 2-NP. The ratio of the responses with UV and ED did not enable us to assign this peak to 2-NP. Moreover, no signal appeared at the retention time of phenol, which confirmed that the compound appearing with ED could be phenol.

The same experiment was carried out with Ebro river water. In this case, it was only necessary to add TBA and NaOH to adjust the pH to 9. Na_2SO_3 was not added because there was no free chlorine in the sample. Fig. 4 shows the chromatograms obtained for 10 ml of Ebro river water with TBA as ion-pair reagent and adjusted to pH 9 with NaOH and the same sample spiked with 1 μg l^{-1} of standard solution of phenolic compounds. The results obtained

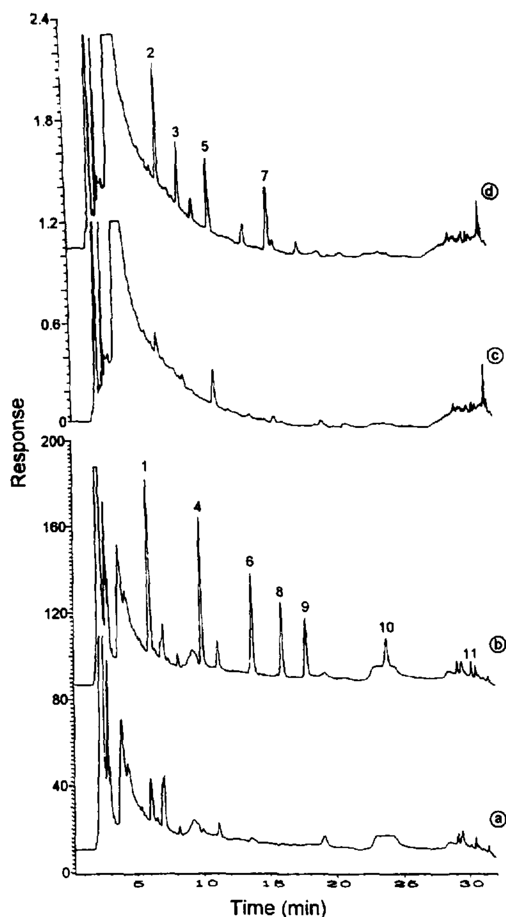

Fig. 4. Chromatograms obtained by on-line trace enrichment with a PLRP-S precolumn and (a, b) ED and (c, d) UV detection of 10 ml of (a, c) Ebro river water and (b, d) Ebro river water spiked at 1 μg l^{-1} with each phenolic compound. Peaks as in Fig. 1.

with ED (Fig. 4a and b) enabled a peak to be detected with the same retention time as phenol, but no positive identification could be made on the basis of the ratio of peak areas at different potentials. Using UV detection, only a peak with the same retention time as 2-NP appeared in the chromatogram, but, like the analysis of tap water, no positive identification could be confirmed.

For both samples the recoveries were determined, and the results obtained were similar to those with Milli-Q water, higher than 80% for all compounds. The linearity of the method with tap and river water was also checked and in both cases it was good ($r^2 > 0.994$) for all compounds in the range 0.1–2 μg l^{-1}, except for 2,4,6-TCP and PCP, where it was 0.2–10 μg l^{-1} when ED was used and 0.1–20 μg l^{-1} for nitro compounds when UV detection was used. The limits of detection (LODs) of the method when 10 ml of real sample were analysed were between 0.02 μg l^{-1} for 2-NP and 0.1 μg l^{-1} for PCP. In river water the LOD of phenol could not be determined because of the presence of a peak with the same retention time. The repeatability and the reproducibility between days were determined by preconcentrating five samples of tap water spiked at 1 μg l^{-1}; the R.S.D. was lower than 7% and 10%, respectively.

The use of the highly cross-linked styrene–divinylbenzene allows a larger volume of sample to be preconcentrated and thus lower limits of detection to be achieved. The chromatograms obtained by preconcentrating 25 ml of tap water with TBA to pH 9.0 and the same sample spiked with 0.5 μg l^{-1} of the eleven compounds studied using this sorbent are shown in Fig. 5. It should be pointed out that the use of ED enabled phenol to be determined when it could not be with UV detection because of the band appearing at the beginning of the chromatogram [30]. In the chromatograms corresponding to ED (Fig. 5a and b), various peaks appeared, some of them at the same retention time as the compounds studied. One peak appeared at the same retention time as phenol and another at the same retention time as 4-NP, 2,4-DNP, 2-NP and 2,4-DMP, but none of them could be identified from the ratio of the responses of the two detection systems. A peak corresponding to phenol appeared with the same retention time as another interfering peak, and so it could not be identified in tap water. In the chromatograms corresponding to UV detection (Fig. 5c and d), a peak appeared at the same retention time as 2-NP but it could not be identified as such.

The linearity of the method with tap water was checked and results are given in Table 2 together with the limits of detection and the reproducibility (R.S.D.).

Fig. 6 shows the chromatograms obtained by preconcentrating 25 ml of Ebro river water with

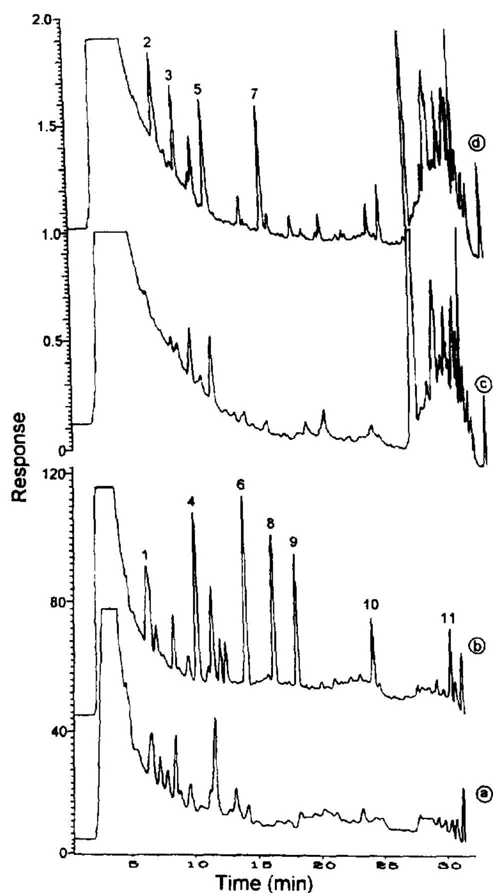

Fig. 5. Chromatograms obtained by on-line trace enrichment of 25 ml of tap water with a clean-up step using (a, b) (ED) and (c, d) UV detection using a highly cross-linked styrene–divinylbenzene copolymer as the sorbent. (a, c) Tap water; (b, d) tap water spiked at 0.5 μg l^{-1} with each phenolic compound. Peaks as in Fig. 1.

TBA to pH 9.0 and the same sample spiked with 0.5 $\mu g\ l^{-1}$ of all the compounds studied. It can be observed that in both chromatograms corresponding to ED and UV detection, a peak appeared at the same retention time as 2-NP, but it was not assigned to this compound since at the levels corresponding to UV detection no peak should have appeared in the chromatogram obtained with ED.

The linearities were similar to those obtained with tap water and the regression coefficients were higher than 0.992. The only exception was phenol because of a slight increase in the background noise. The detection limits were between 0.03 μg l^{-1} for 2,4-DMP and 2-M-4,6-DNP and 0.1 μg l^{-1} for Ph.

Table 2
Linearity range, correlation coefficients, detections limits and relative standard deviations ($n = 5$) for the analysis of tap water under optimum conditions using ENVI-Chrom P.

Phenolic compound	Linearity range ($\mu g\ l^{-1}$)	r^2	LOD ($\mu g\ l^{-1}$)	R.S.D. (%) ($n = 5$)
Ph	0.05–5	0.997	0.02	8.7
4-NP	0.10–5	0.999	0.03	8.6
2,4-DNP	0.10–5	0.998	0.04	8.6
2-CP	0.05–2	0.999	0.02	3.3
2-NP	0.10–5	0.999	0.03	3.5
2,4-DMP	0.05–2	0.999	0.03	5.8
2-M-4,6-DNP	0.10–5	0.999	0.03	3.9
4-C-3-MP	0.05–2	0.999	0.02	8.4
2,4-DCP	0.05–5	0.999	0.03	3.1
2,4,6-TCP	0.10–5	0.998	0.05	7.9
PCP	0.10–5	0.994	0.05	8.2

The precision of the method for real samples was also checked with river water samples spiked at 1 μg l^{-1} and the repeatability and reproducibility of the method expressed as R.S.D. ($n = 5$) were lower than 10% in both instances.

4. Conclusions

The coupling of a UV detector in series with an electrochemical detector allows the determination of nitrophenolic compounds which have a low response to ED with RPLC and gradient elution in less than 30 min. When the compounds retained in a precolumn connected on-line to the analytical column are eluted only with methanol and not the initial conditions of the mobile phase, sorbents in which phenolic compounds are highly retained and which broaden peaks considerably in the common design can be used. This allows a higher sample volume to be preconcentrated and, thus, lower limits of detection.

Although the highly cross-linked styrene–divinylbenzene copolymer allowed lower detection limits than PLRP-S, the latter is more selective and so the number of interfering peaks appearing

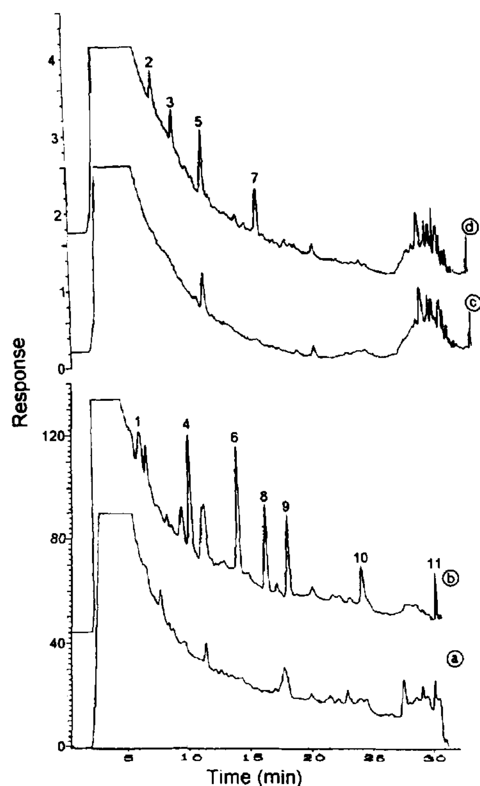

Fig. 6. Chromatograms obtained by on-line trace enrichment of 25 ml of Ebro river water with a clean-up step using (a, b) ED and (c, d) UV detection using a highly cross-linked styrene–divinylbenzene copolymer as the sorbent. (a, c) Ebro river water; (b, d) Ebro river water spiked at 0.5 μg l^{-1} with each phenolic compound. Peaks as in Fig. 1.

in the chromatogram when real samples are analysed decreases considerably.

The methods developed enable phenolic compounds to be determined at levels of 0.1 μg^{-1} in real samples, the maximum concentration allowed in water for human consumption.

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