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Determination of phenols at the ng/l level in drinking and river waters by liquid chromatography with UV and electrochemical detection☆

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ABSTRACT

Solid–liquid extraction of samples and liquid chromatography with UV and electrochemical detection with laboratory-made microcolumns were applied to the separation and identification of phenols and substituted phenols in waters. The compounds mainly studied were the eleven phenols considered as priority pollutants by the US Environmental Protection Agency. Chromatographic separation was carried out with several water–methanol isocratic mobile phases; use of the autoincrement mode of the electrochemical detector allowed the compounds in the samples to be confirmed. The chromatographic system worked automatically. The detection limits obtained with prior concentration of the samples were 40–600 ng/l, depending of the phenol. Electrochemical detection was used for the determination of phenols in river and drinking waters; phenols at the ng/l level was detected

INTRODUCTION

The determination of phenols in drinking and river waters is of great importance now that the MAC (Maximum Admissible Concentration) in the EEC countries for phenols in drinking water is 0.5 μg/l, excluding those natural phenols which do not react with chlorine [1]. The official methods [1] recommended for their determination are based on the measurement of an index of phenols using spectrophotometric methods based on 4-aminoantipyrine or 2-nitrophenol [2,3]. These methods are subject to interferences and only with difficulty can phenolic compounds be detected at the 0.5 μg/l level [4,5] demanded at present.

Chlorophenols and nitrophenols, which are used in industry and agriculture and as wood preservatives, etc., can be present in raw waters as a result of spillages or accidents. Because of this, in the 1970s the US Environmental Protection Agency (EPA) [6] created a list of the eleven most important phenol contaminants as priority pollutants. Chlorophenols can be formed during water chlorination [7], causing problems of taste and odour in waters at very low concentrations, near the μg/l level.

There are numerous standard methods for determining and for confirming the presence of

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phenols [2,3,5,8]. The most recent [8] are based on their concentration by liquid–liquid extraction, derivatization and measurement by gas chromatography with electron-capture detection. This is the official method of the EPA [9] and gives limits of detection between 0.58 to 2.2 μg/l for the eleven priority pollutant phenols.

Methods of liquid chromatography (LC) with UV detection [5,10–12] have also been used, together with LC with UV detection and derivatization "on-line" [13]. In this way, LC has been used with electrochemical detection (ED) [14–16], achieving excellent limits of detection with easy sample preparation.

In this work, the determination of a wide range of phenols, nitrophenols chlorophenols, methylphenols, hydroxyphenols and other phenols, mainly those considered to be priority pollutants by the EPA, was studied. LC–ED was applied, employing an amperometric detector which uses the electronic treatment technique to correct for the electrodeposition, as proposed by Wang and Lin [17,18]. This detector was studied by Gretzfeld-Hüsgen and Schuster [16] in the determination of certain phenols, but here all the phenols listed by the EPA were considered. ED and UV detection were compared in order to check the improvement in sensitivity and limits of detection for the former method.

To confirm the presence of phenols, a method similar to that proposed by Shoup and Mayer [14] and by Hennion *et al.* [15] was used. In this method the amperometric detector was equipped with two working electrodes to which different potentials were applied. The detector produced two signals and their ratio was used to confirm the compounds. In this work we used the detector function defined as the "autoincrement mode". This allowed us to obtain automatically the chromatograms of phenols and signal ratios at different potentials using only one working electrode.

To improve the limits of detection of phenolic compounds, solid-phase extraction with reversed-phase C_{18} microcolumns, prepared in the laboratory, was used. The proposed technique was applied to determine phenols in drinking and river waters, giving limits of detection lower than those of the EPA standard method [9]. With prior concentration, the limits of detection were 1.2–15 pg (40–600 ng/l), depending on the phenol.

EXPERIMENTAL

Equipment

The system of gradients, pump, furnace, automatic injector/autosampler and programmable UV detector were from a Series HP 1050 from Hewlett-Packard (Waldbron, Germany). The electrochemical amperometric detector was an HP 1049 A (Hewlett-Packard) connected in series to the output of the UV detector. All the modules of the configuration were connected by interfaces, and the whole system in turn was controlled by an HP QS/20 87 personal computer (Hewlett-Packard) with outputs to a screen and printer. The interface to connect the start–stop orders and to control the signals input from the two detectors was an HP 35900 C (Hewlett-Packard). The data analysis, results and system control were executed using the chromatographic software Chemstation HP 3365 Series II (Hewlett-Packard), which is controlled by Windows 3.0 (Microsoft).

The stability of the HP 1049 A electrochemical detector was studied by Gretzfeld-Hüsgen and Schuster [16] for tetrachlorophenol and pentachlorophenol, giving an R.S.D. lower than 2.5% for 200 injections, based on both area counts and peak heights.

Chromatographic separation and detection

The separation of the compounds was achieved using a 5-μm LiChrospher 100 RP-18 precolumn (4 × 4 mm I.D.) connected to a 5-μm Spherisorb ODS-2 column (250 × 4 mm I.D.), both supplied by Hewlett-Packard. The temperature of the column was kept at 40°C and the flow-rate of the eluents was 0.8 ml/min. The volume of sample injected by automatic injection was 25 μl in all instances (blanks, standards and samples).

The wavelength of the UV detector was set at 280 nm, except for pentachlorophenol, which was determined at 300 nm by programming the detector before its elution. The electrochemical detector worked in the amperometric mode with

a glassy carbon electrode at a potential of 1000 mV between the working and the reference electrodes. A solid-state AG/AgCl reference electrode was used, so the eluents used with the electrochemical detector contained KCl (0.05 g/l). This detector has a pretreatment function to clean the working electrode automatically, which was used every fifteen injections, applying in a cyclical form (two cycles) alternate potentials of −800 and +1300 mV during 500 ms. The working electrode was polished in the conventional way every 60 injections.

Mobile phases

The water–methanol gradients used for UV detection were prepared with HPLC-grade water acidified with 28 μl/l of 98% H_2SO_4 (pH 3), to which were added different proportions of methanol. The mobile phases used with the UV detector were as follows: gradient A, 0 min 35% of methanol, 10 min 40% of methanol, 25 min 80% of methanol; and gradient B, 0 min 40% of methanol, 20 min 80% of methanol. Gradient A was used for the general separation of 21 phenols and gradient B to separate the eleven EPA priority pollutant phenols.

The isocratic mobile phases of water–methanol used with the electrochemical detector were as follows: eluent A, 25% of methanol, eluent B, 50% of methanol and eluent C, 75% of methanol, with HPLC water acidified with 28 μl/l of 98% H_2SO_4 (pH 3) that contained KCl (0.05 g/l) and KNO_3 (2 g/l). Eluents B and C were used to screen for the eleven phenols being studied, and the eluent A exclusively for the determination of phenols in the real samples. The background currents registered for these three eluents with the working electrode in the correct state were 40–80 nA. The retention times obtained with the gradient and isocratic conditions used are given in Table I.

Sample treatment and solid-phase extraction

Samples were placed in glass bottles (1 l) with a PTFE-covered stopper and kept in the dark at 4°C. Volumes of 100 ml of these samples were

TABLE I

RETENTION TIMES (min) OF DIFFERENT PHENOLS UNDER THE ELUTION CONDITIONS USED

Phenol	UV detection		ED detector		
	Gradient A	Gradient B	Isocratic A	Isocratic B	Isocratic C
Hydroquinone	3.24				
Resorcinol	3.79				
Pyrocatechol	4.59				
Phenol	7.08	6.21	10.50	4.77	
4-Nitrophenol	9.53	8.20	16.80	5.60	
2,4-Dinitrophenol	11.33	9.65		6.50	
p-Cresol	11.80				
o-Cresol	12.10				
2-Chlorophenol	12.98	11.40		6.98	
2-Nitrophenol	14.56	13.20		8.25	
4-Chlorophenol	15.81				
2,6-Dimethylphenol	17.37				
2,4-Dimethylphenol	18.23	17.16		10.21	
2,6-Dichlorophenol	18.92				
2-Methyl-4,6-dinitrophenol	19.84	18.46		12.18	
4-Chloro-3-methylphenol	20.61	19.61		12.97	
2,4-Dichlorophenol	21.93	20.25		15.83	
2,4,6-Trimethylphenol	21.93				
2,4,6-Trichlorophenol	25.75	23.00		30.75	6.23
2,4,5-Trichlorophenol	26.14				
Pentachlorophenol	32.12	28.51			13.10

treated with 0.3 ml of 10% Na_2SO_3 solution to eliminate the free chlorine and with 100 μl of 65% HNO_3 (pH 2). The treated samples were then filtered through a 0.45-μm membrane filter from Schleicheir & Schüll (Dassell, Germany). Glass microcolumns (100 × 8 mm I.D.) filled with 500 mg of phase Bakerbond C_{18} type 7025-00 (J.T. Baker, Deventer, Netherlands) were used to concentrate phenols. The microcolumns were previously conditioned with 10 ml of acetonitrile, 10 ml of methanol and 100 ml of water (pH 2, adjusted with HNO_3). An aliquot of 25 ml of treated sample was taken and passed through the column, which was then washed with 2 ml of 0.01 *M* HNO_3 and the phenols were eluted with 1 ml of methanol. This methanolic solution was placed in 2-ml vials and injected into the chromatograph by the automatic injector/autosampler. The passage of the solvents and samples through the extraction equipment for microcolumns (J.T. Baker, type 70180) was accomplished under vacuum (250–500 mmHg); 1 mmHg = 133.322 Pa). Microcolumns were prepared and conditioned in the laboratory and before being used the column blanks were obtained with 1-ml samples of methanol, which were run to obtain the corresponding chromatograms.

Reagents and standards

The standards used were: 4-nitrophenol, 2,4-dinitrophenol, 2-nitrophenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, *p*-cresol, *o*-cresol, 2,4-dimethylphenol, 2,6-dimethylphenol, resorcinol, hydroquinone, pyrocatechol, phenol, 4-chloro-3-methylphenol and 2-methyl-4,6-dinitrophenol from Merck (Darmstadt, Germany), 2,4,5-trichlorophenol and 2,4,6-trimethylphenol from Fluka (Buchs, Switzerland) and pentachlorophenol from Janssen (Geel, Belgium). Stock standard solutions of 1000 mg/l were prepared in water–methanol (1:1) and kept in the dark at 4°C. Dilutions of the stock standard solutions were made with HPLC water immediately before use. All of the general reagents used, 98% H_2SO_4 and 65% HNO_3 (Merck), KCl, KNO_3 and Na_2SO_3 (Probus) were of analytical-reagent grade. The water, methanol and acetonitrile (Merck) used to prepare the eluents were of HPLC grade. The eluents were filtered using 0.45-μm membrane filters (Schleicher & Schüll) and were degassed with helium.

RESULTS AND DISCUSSION

Comparison between UV and electrochemical detection

The initial study was carried out to compare the detection of phenols with UV and electrochemical detectors. As water–methanol gradients allow UV detection the separation of the compounds in systems A and B described above was studied first. Fig. 1a shows the chromatogram of the 21 phenols studied (250 ng of each compound) with gradient A. Under these conditions 2,4-dichlorophenol and 2,4,6-trimethylphenol (retention time t_R = 21.92 min) did not separate, and it was possible partially to separate *p*-cresol and *o*-cresol (t_R = 11.79 and 12.02 min, respectively). This chromatogram was obtained using a wavelength of 280 nm, changing to 300 nm at 28 min, before pentachlorophenol was eluted. The wavelength change did not affect the baseline. Fig. 1b shows the chromatogram obtained for the eleven EPA priority phenols (250 ng of each phenol) with gradient B, measured at 280 nm and changed to 300 nm at 25 min (before the elution of pentachlorophenol). With this gradient all eleven phenols were well resolved in less than 30 min.

With an electrochemical detector it is not possible to work with gradients because the flow stability can be affected, causing baseline drift and random noise. Also, not all the solvents used in LC can be used, as some of them attack certain internal parts of the detector. Initially, we used the solvent mixture used by Gretzfeld-Hüsgen and Schuster [16] [water–methanol (40:60) at pH 3], modified to give eluents A, B and C described above. Eluant B (50% methanol) was used as screening for the nine more polar phenols. Under these conditions, 2,4,6-trichlorophenol and pentachlorophenol had a high t_R of 45 min. This meant that we had to use a solvent containing more methanol, *i.e.*, eluent C (75% methanol), with which we obtained the separation of the most non-polar phenols is less than 15 min. Eluent A (25% methanol) was used exclusively in the determination of phenol in real

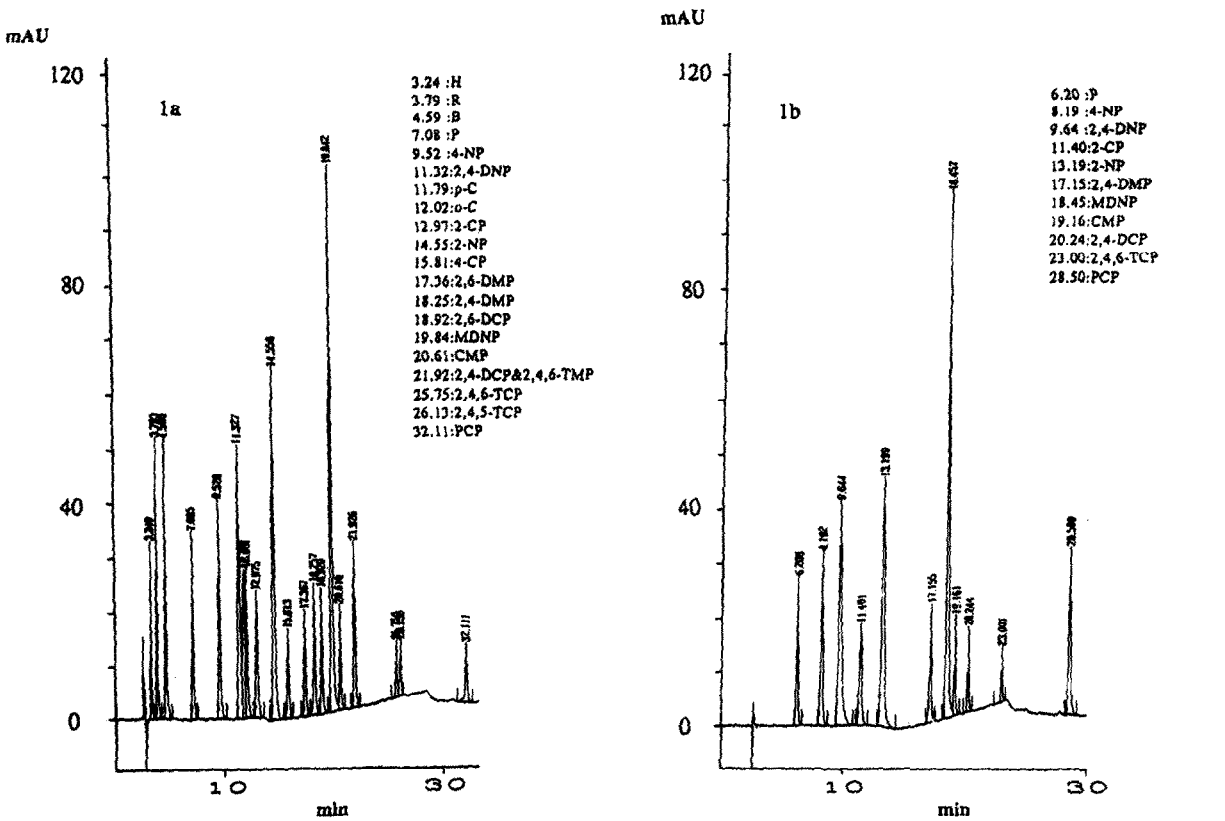


Fig. 1. Chromatograms obtained with UV detection: (a) separation of the 21 phenols and (b) separation of the EPA priority pollutant phenols (10 mg/l of each). H = hydroquinone; R = resorcinol; B = pyrocatechol; P = phenol; 4-NP = 4-nitrophenol; 2,4-DNP = 2,4-dinitrophenol; p-C = *p*-cresol; o-C = *o*-cresol; 2-CP = 2-chlorophenol; 2-NP = 2-nitrophenol; 4-CP = 4-chlorophenol; 2,6-DMP = 2,6-dimethylphenol; 2,4-DMP = 2,4-dimethylphenol; 2,6-DCP = 2,6-dichlorophenol; MDNP = 2-methyl-4,6-dinitrophenol; CMP = 4-chloro-3-methylphenol; 2,4-DCP = 2,4-dichlorophenol; 2,4,6-TMP = 2,4,6-trimethylphenol; 2,4,6-TCP = 2,4,6-trichlorophenol; 2,4,5-TCP = 2,4,5-trichlorophenol; PCP = pentachlorophenol.

samples because the matrix components of the sample caused a large peak at the beginning of the chromatogram and masked the results. With eluent B, the t_R of phenol was 4.77 whereas using eluent A phenol appeared at 10.50 min, far enough from the initial zone of the chromatogram to avoid the interferences mentioned. In Fig. 2a and b the sequential chromatograms of the eleven phenols (625 pg of each) are shown, with isocratic mobile phases B and C at a potential of 1000 mV. In these chromatograms all the peaks are measured in less than 35 min (analysis of both injections).

Table II gives the detection limits (DL) for the UV and electrochemical methods and the sensitivity ratios of the two methods, illustrating the sensitivity gain obtained by using the electrochemical detector. The DLs were obtained from calibration graphs constructed for each phenol and were calculated as the analyte concentration than caused a signal three times the standard error. Calibration graphs were also used to calculate the sensitivity expressed as area counts/concentration (μg/l) (in Table II only sensitivity ratios between the detectors are shown). The calibration graphs obtained had correlation coefficients >0.99 and were achieved with five points in the concentration range 2000–10 000 μg/l for the UV detector and 1–20 μg/l for the electrochemical detector. From Table II it can be observed that the sensitivity of electrochemical detection was more than 100 times better than that of UV detection for all the phenols except the nitrophenols, with gains of 566- and 728-fold

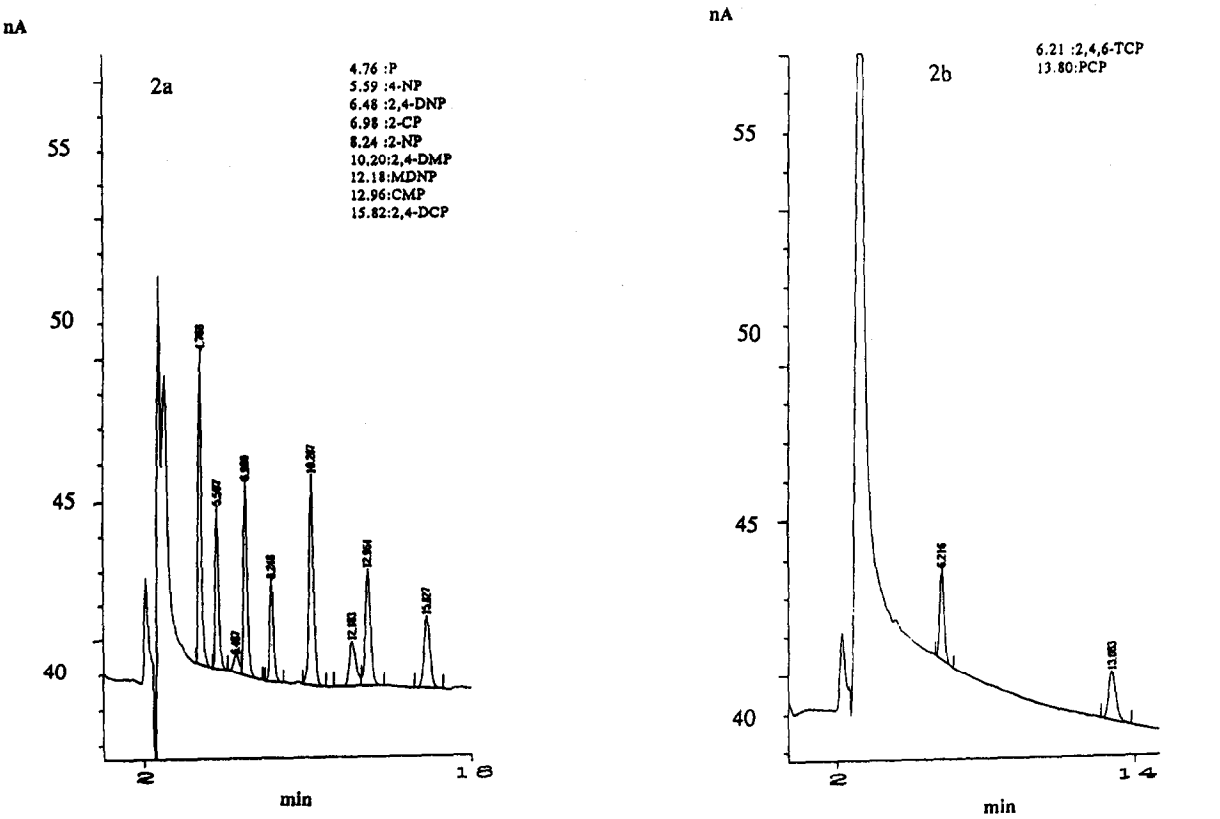


Fig. 2. Chromatograms of the EPA priority pollutant phenols (25 μg/l of each) obtained with ED: (a) eluent B and (b) eluent C. P = phenol; 4-NP = 4-nitrophenol; 2,4-DNP = 2,4-dinitrophenol; 2-CP = 2-chlorophenol; 2-NP = 2-nitrophenol; 2,4-DMP = 2,4-dimethylphenol; MDNP = 2-methyl-4,6-dinitrophenol; CMP = 4-chloro-3-methylphenol; 2,4-DPC = 2,4-dichlorophenol; 2,4,6-TCP = 2,4,6-trichlorophenol; PCP = pentachlorophenol.

TABLE II

DETECTION LIMITS AND RATIOS OF SENSITIVITY BETWEEN ELECTROCHEMICAL AND UV DETECTION

Phenol	Detection limit (μg/l)		Sensitivity ratios (ED/UV)
	UV detection	ED	
Phenol	22	0.9	566
4-Nitrophenol	341	1.5	47
2,4-Dinitrophenol	266	4.3	4
2-Chlorophenol	454	1.7	390
2-Nitrophenol	531	1.3	75
2,4-Dimethylphenol	240	0.9	403
2-Methyl-4,6-dinitrophenol	187	5.2	21
4-Chloro-3-methylphenol	292	1.6	633
2,4-Dichlorophenol	326	1.9	179
2,4,6-Trichlorophenol	263	4.2	728
Pentachlorophenol	809	6.1	419

for phenol and 2,4,6-trichlorophenol, respectively. For nitrophenols the sensitivity ratios are much lower, especially for 2,4-dinitrophenol (ratio only 4). This may be due to the fact that the working potential used (1 V) was not optimum for determining nitrophenols, as it is known that 1.2 V is to be preferred.

Concentration by solid–liquid extraction

The concentration technique studied was solid–liquid extraction of the sample with microcolumns containing 500 mg of C_{18} reversed-phase material. Aliquots of 25 ml of standard solutions of different initial concentrations were subjected to solid–liquid extraction. Standard solutions of 10 μg/l–1 mg/l were prepared for the UV detector, while for the electrochemical detector the starting concentration ranged from 0.5 to 1 μg/l; greater sensitivity and lower DLs were achieved in the latter separation mode, as mentioned above. In all instances the final volume was 1 ml of methanol solution in a concentration factor of 25.

Table III presents the recovery results for standard solutions of 50 μg/l of each phenol with UV detection and 0.5 μg/l of each phenol with electrochemical detection. Table III also gives the detection limits obtained for both methods. With the UV detector phenol concentrations between 4 and 85 μg/l could be detected whereas with the electrochemical detector concentrations between 0.04 and 0.59 μg/l could be detected, depending of the type of phenol. For the electrochemical detector the R.S.D. for the nine recovery experiments was of the order of 10%. With the UV detector an insufficient number of experiments (three) to allow the calculation of a reliable R.S.D. were carried out, owing

TABLE III

RECOVERY OF PHENOLS BY SOLID–LIQUID CONCENTRATION

Initial concentration of phenols: 50 μg/l for UV detector and 0.5 μg/l for electrochemical detector

Phenol	UV detection		ED		
	Recovery (%)	Detection limit (μg/l)	Recovery (%)	R.S.D. (%) ($n = 9$)	Detection limit (μg/l)
Hydroquinone	ND[a]	–	–	–	–
Resorcinol	ND	–	–	–	–
Pyrocatechol	18	85	–	–	–
Phenol	19	5	80	8	0.05
4-Nitrophenol	72	19	62	10	0.10
2,4-Dinitrophenol	95	11	65	11	0.27
p-Cresol	93	4	–	–	–
o-Cresol	79	14	–	–	–
2-Chlorophenol	90	20	102	5	0.07
2-Nitrophenol	103	21	102	7	0.05
4-Chlorophenol	91	13	–	–	–
2,6-Dimethylphenol	88	13	–	–	–
2,4-Dimethylphenol	98	10	93	7	0.04
2,6-Dichlorophenol	97	15	–	–	–
2-Methyl-4,6-dinitrophenol	91	8	64	8	0.33
4-Chloro-3-methylphenol	93	13	88	8	0.07
2,4-Dichlorophenol	102	13	116	6	0.07
2,4,6-Trimethylphenol	102	13	–	–	–
2,4,6-Trichlorophenol	78	14	81	5	0.21
2,4,5-Trichlorophenol	91	8	–	–	–
Pentachlorophenol	48	67	41	9	0.59

[a] ND = not detected.

to a lack of sensitivity in our application. Recovery data with UV detection were only used for comparison with electrochemical data.

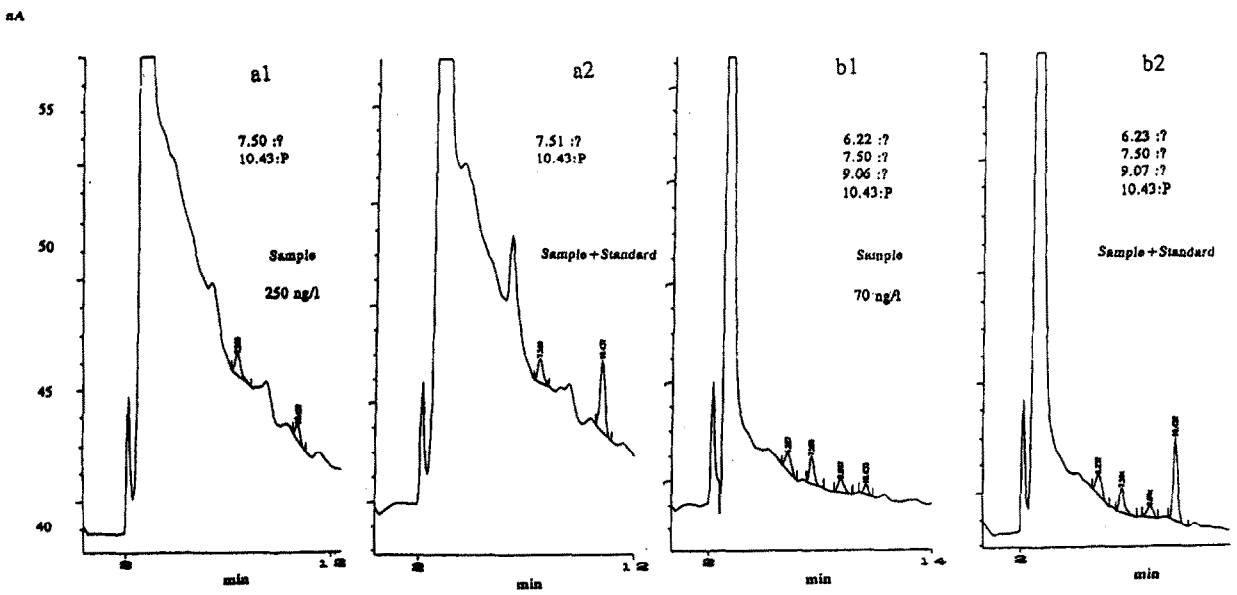
Determination of phenols in samples of river and drinking water

Fig. 3 shows two examples of chromatograms for river and drinking waters. Fig. 3a for a concentrated sample of river water; Fig. 3a1 is for the concentrated sample alone and Fig. 3a2 is for the same sample spiked with 0.5 μg/l of phenol. Fig. 3b is for a concentrated sample of drinking water; Fig. 3b1 is for the sample alone and Fig. 3b2 is for the sample spiked with 0.5 μg/l of phenol. In both instances the peak at $t_R = 10.43$ min was identified as phenol; its concentration was calculated to be 250 and 70 ng/l in river and drinking water, respectively (using the standard addition method). These chromatograms were achieved using eluent A; with eluents B and C no electrochemically active substances attributable to the phenols studied were detected.

Na_2SO_3 was added to samples of drinking water to eliminate free chlorine, which could interfere in the determination using the standard addition method, because when the standard of phenols is added to samples of chlorinated water the chlorine can react with the phenols added and produce chlorophenols. The effect of sulphite addition was studied and no interference was observed in the analyses of samples extracted with microcolumns. Only direct injection of samples treated with sulphite showed a distorted area at the beginning of the chromatogram.

Confirmation of the peaks with electrochemical detection

The general working potential for the electrochemical detector was 1000 mV, although to confirm the phenolic compounds a feature of the detector called the "autoincrement mode" was used, in which a sample was injected repeatedly and automatically at different potentials, so obtaining chromatograms at several working voltages. The initial and final potentials, the voltage increments and the allowed baseline drift were fixed before the equipment made the injection. Here the conditions were initial potential



a) RIVER WATER b) DRINKING WATER

Fig. 3. Chromatograms of concentrated samples of (a) river and (b) drinking waters (eluent A). P = phenol.

TABLE IV

ELECTROCHEMICAL RATIOS OF THE AREAS AT DIFFERENT VOLTAGES

Phenol	Ratio of voltages					
	0.8/0.9	0.8/1.0	0.8/1.1	0.9/1.0	0.9/1.1	1.0/1.1
Phenol	0.45	0.40	0.40	0.90	0.90	1.00
4-Nitrophenol	0.00	0.00	0.00	0.00	0.00	0.17
2,4-Dinitrophenol	0.00	0.00	0.00	0.00	0.00	0.18
2-Chlorophenol	0.60	0.55	0.50	0.90	0.80	0.90
2-Nitrophenol	0.00	0.00	0.00	0.00	0.00	0.55
2,4-Dimethylphenol	0.85	0.85	0.85	1.00	1.00	1.00
2-Methyl-4,6-dinitrophenol	0.00	0.00	0.00	0.00	0.00	0.18
4-Chloro-3-methylphenol	0.75	0.65	0.50	0.85	0.70	0.80
2,4-Dichlorophenol	0.75	0.70	0.60	0.95	0.85	0.90
2,4,6-Trichlorophenol	0.80	0.80	0.80	1.00	1.00	1.00
Pentachlorophenol	0.30	0.35	0.40	1.00	1.20	1.20

800 mV, final potential 1100 mV, increments of 100 mV and allowed baseline drift 1 nA/min.

Table IV gives the electrochemical ratios found for standard solutions of 25 μg/l of each phenol. As can be seen, the nitrophenols did not respond to 800 or 900 mV in the range of concentrations studied. The most interesting ratios were 0.8/0.9, 0.8/1.0, 0.8/1.1, except for nitrophenols, for which the best ratio was 1.0/1.1. A similar confirmation technique had been used via ED with two working electrodes each at a different potential. In this way, for example, Shoup and Mayer [14] used potentials of 850 and 900 mV *versus* Ag/AgCl/3 *M* NaCl.

CONCLUSIONS

Using LC coupled to a UV detector, concentrations of phenols down to *ca.* 10 μg/l can be detected employing the concentration technique studied, whereas an electrochemical detector can reach levels below 500 ng/l, which is actually the MAC in drinking waters in EEC countries. Further, with ED phenols present in samples can be confirmed using the "autoincrement mode" and the retention times obtained with different eluents.

The electrochemical detector used in this study has a pretreatment function that allows the cleaning of the working electrode surface electrochemically, before or between analyses, so avoiding premature fouling of the electrode surface. This feature improves the stability of the response with this type of detector.

LC–ED has the advantage over the EPA standard method [9] that it is possible to obtain lower DLs in shorter analysis times because derivatization of the phenols is not required.

We consider that LC–ED could replace the standard official methods using 4-aminoantipyrine and 2-nitrophenol, which do not allow the determination of the specified levels (0.5 μg/l) and which are much less able to distinguish the types of phenols present in the samples.

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