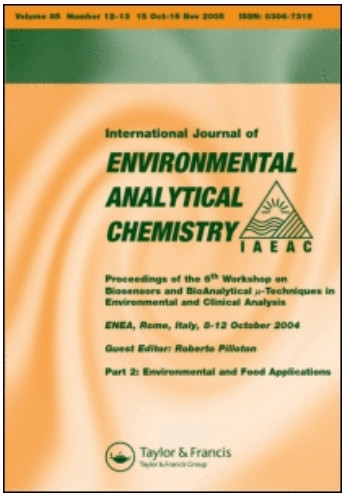

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Trace Enrichment and HPLC Analysis of Chlorophenols in Environmental Samples, Using Precolumn Sample Preconcentration and Electrochemical Detection

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A HPLC method has been developed for trace analysis of chlorophenols in the 0.2–2 ppb range from spiked water samples. Simple liquid–liquid extraction followed by on-line preconcentration of total mono- and dichlorophenols has been performed using a divinylbenzene-styrene copolymeric sorbent (PRP_1) as packing material for the precolumn. The chlorophenols have been eluted from the precolumn on an analytical column (5 μm LiChrosorb RP-18, 12.5 cm × 4 mm) by use of a switching valve system followed by separation. Detection was carried out with an electrochemical detector. The linearity of the detector response has been proved over two orders of magnitude. The detection limit of chlorophenols by means of the electrochemical method is in the lower picogram range. The recoveries of the isomeric chlorophenols from spiked river water samples having initial concentrations of 2 ppb are usually 70–90%. The procedure has been applied to drinking water and river water.

KEY WORDS: HPLC, chlorophenols in water, trace enrichment, column switching, electrochemical detection.

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INTRODUCTION

Chlorinated phenols are introduced into the environment by a multitude of pathways. They have been used extensively as fungicides and bacteriocides in industry throughout the world. The interest in chlorophenols as environmental contaminants is mainly due to the high toxicity against aquatic organisms and also to water taste, even in low concentrations. A lot of methods have been used for separation and concentration of phenolic compounds from water samples.[1–4] Usually, liquid–liquid extraction after acidification of the water samples has been applied for the determination of phenols.[5,6] Preconcentration and clean-up procedures of chlorophenols have been performed too on short precolumns[7] or commercially available cartridges packed with octadecyl-modified silica gel.[8–10] The difficulty in trapping low-chlorinated phenols, caused by the hydrophilic character of these compounds,[11] requires the investigation of a combined procedure involving an off-line preconcentration. Separation and on-line preconcentration of mono- and dichlorophenols have been done using PRP_1,[11–14] a divinylbenzene-styrene copolymeric packing material for columns. Due to the presence of aromatic rings in this type of sorbent, retention of aromatics would be expected to be higher than on C_{18} materials of comparable specific surface area, thus making it a very suitable material for preconcentration of polar compounds.[11] The method has been applied to industrial waste water and natural water.

EXPERIMENTAL

Apparatus

A chromatographic system has been used consisting of two high pressure pumps M 6000 A (Waters), an integrator model PU 4810 (Spectra-Physics), a Rheodyne-Valve (type 7120), Sep-Pak C_{18} cartridges (Waters) and a shaking machine. Electrochemical detection was carried out with a Perkin-Elmer LC4B detector with a TL-5A glassy carbon electrode. All separations were done on an 12.5 cm × 4 mm analytical column packed with 5 μm LiChrosorb RP-18 (Merk). Preconcentration was performed with a home made 1.1 cm × 5.5 mm precolumn, which was slurry packed from a

methanolic slurry with spherical 10 μm macroreticular styrene-divinylbenzene copolymer PRP_1 (Hamilton). For the mobile phase, unless otherwise noted, a 0.02 M KNO_3 solution was mixed with varying amounts of methanol, depending on the sample material.

Chemicals

All chlorophenols were purchased from EGA or Fluka and were of analytical-grade quality.

Diethylether, 0.2 M sodium hydroxide solution, conc. sulphuric acid, methanol (Merk), HPLC-water (Merk) and bidistilled demineralized water were used.

All reagents and materials were of analytical-reagent grade. For chromatographic experiments 1 ppm standard solutions of chlorophenols in HPLC-pure water were prepared and if necessary diluted to lower concentrations. Aqueous stock solutions were stored in the refrigerator. All solutions remained stable for several months.

Sampling

River water was sampled in 2.5 l dark bottles. It was stabilized with 250 mg/l ascorbic acid to prevent auto-oxidation. The following water samples were analysed:

— spring water of the River Pader (Paderborn/city)
— water of the River Ruhr (Arnsberg/monastery bridge)
— water of the River Weser (Rinteln/159 km).

Trace-enrichment step

Standard solutions containing mono- and dichlorophenols were added to 500 ml water samples. Concentration levels of 2 ppb, 0.4 ppb and 0.2 ppb were obtained. Water samples were acidified (pH = 2) with sulphuric acid and extracted twice with diethyl ether (100 ml; 50 ml). The extraction was accomplished by shaking vigorously in a reciprocal shaker for 10 min (frequency, 140/min). An aliquot was then extracted twice with 15 ml of 0.2 M sodium hydroxide solution for 10 min. In the next step the alkaline extract was acidified to pH < 2 by dropwise addition of sulphuric acid. The

sample (50 ml or less) was passed through a Sep-Pak C_{18} cartridge with the aid of a glass syringe. Before use, the Sep-Pack C_{18} cartridge is activated by passing methanol (3 ml) through it, followed by bidistilled water (20 ml). Chlorophenols were eluted with methanol (3 ml). The methanolic aliquot was then diluted with bidistilled water to 50 ml using a measuring flask. Ten ml of this sample were enriched on a short precolumn (flow: 2 ml/min), which could be switched to the analytical column in an on-line mode. A schematic diagram of the enrichment operation and the analytical determination is shown in Figure 1.

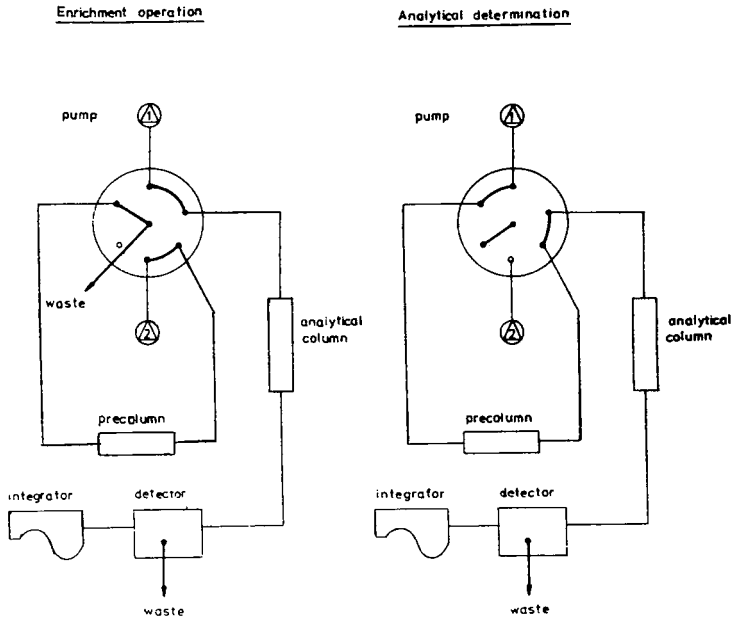


FIGURE 1 Scheme of apparatus used for trace analysis of chlorophenols in water samples by enrichment and column switching.

RESULTS AND DISCUSSION

Off-line trace enrichment

A Sep-Pak C_{18} cartridge was used for the clean-up procedure. No breakthrough on the cartridge was noticed, indicating that the

chlorophenols were quantitatively trapped on it. The experiments have shown that the enrichment volumes have to be reduced below 50 ml to prevent breakthrough. Washing the Sep-Pak C_{18} cartridge with 20 ml of distilled water after the phenols have been adsorbed[8] decreases the recovery rates. During this process breakthrough occurs for weakly retained phenols, especially 2-chlorophenol.

On-line trace enrichment

PRP_1 is well suited for the preconcentration of mono- and dichlorophenols. Breakthrough curves on a 1.1 cm × 5.5 mm long precolumn in an aqueous 0.02 M potassium nitrate solution (pH = 5.0–5.5) have been registered in the on-line mode. Breakthrough volumes and precolumn capacities for 4-chlorophenol as model compound are listed in Table I.

TABLE I

Breakthrough volume (ml) and loading capacity of 4-chlorophenol from an aqueous 0.02 M KNO_3 solution (pH = 5.0–5.5) on a 1.1 cm × 5.5 mm PRP_1 precolumn.

Solute concn. (ppm)	Sampling rate (ml/min)	Loading capacity (mg)	V_B (ml)
0.2	5	0.03	157
2.0	2	0.19	96
2.0	5	0.18	88

Optimization of the detector electrode potential

Investigations have been carried out to determine the dependence of peak height on the applied potential (vs. Ag/AgCl reference). Both the nature of the analyte and the composition of the mobile phase influence the sensitivity of the measured signals,[15] which are listed in Tables II and III, showing the values of the applied potentials corresponding with peak height in two different systems.

A decrease in sensitivity was observed, which is caused by electrode fouling; therefore several daily recalibrations were necessary using external standards. Passivation problems in the oxidation mode obviously due to adsorption or polymerization of oxidation products on the electrode surface often lead to decreasing values of peak height.[16]

TABLE II

Dependence of peak height on the applied potential (vs. Ag/AgCl reference) for some chlorophenols in the system methanol/aq. 0.02 M KNO_3 (40:60).

Chlorophenols	Peak height (cm) at		
	$E_{app} = 1.0$ V	$E_{app} = 1.1$ V	$E_{app} = 1.2$ V
2-Chlorophenol	9.7	17.5	11.5
2,6-Dichlorophenol	4.2	7.9	4.4
2,5-Dichlorophenol	2.1	4.2	2.4
3,4-Dichlorophenol	1.6	3.1	2.0
3,5-Dichlorophenol	0.3	0.9	0.8

Absolute amount of each compound: 200 ng.
Detector range: 200 nA; recorder: 10 mV full scale.

TABLE III

Dependence of peak height on the applied potential (vs. Ag/AgCl reference) for the monochlorophenols in the system methanol/aq. 0.05 M KH_2PO_4 (50:50).

Chlorophenols	Peak height (cm) at		
	$E_{app} = 0.9$ V	$E_{app} = 1.0$ V	$E_{app} = 1.1$ V
2-Chlorophenol	5.1	8.8	2.2
3-Chlorophenol	0.5	0.9	1.0
4-Chlorophenol	0.8	1.0	1.2

Absolute amount of each compound: 20 ng.
Detector range: 50 nA; integrator sensitivity: AT = 8.

RECOVERY

Recovery experiments were performed with 500 ml spiked water samples in the concentration range of 0.2–2 ppb. The results of 3–4 replicate analyses for all substances are recorded in Table IV.

The graphic in Figure 2 represents the percentage recovery, and standard deviation, of chlorophenols from three spiked river water samples at a concentration level of 2 ppb.

Standard deviations for the procedure have been calculated as follows.

TABLE IV

Recovery rates of chlorophenols from river water.

Chlorophenols	Range (%)	Average (%)	S_1(%)	S_2(%)	S (%)
2 ppb	*Spring water of River Pader*				
2-Chlorophenol	84– 89	87	3.5	0.4	3.5
3- and 4-Chlorophenol	82– 85	83	1.4	0.3	1.4
2,6-Dichlorophenol	81–100	89	9.8	1.9	10.0
2,3-Dichlorophenol	74–100	91	14.2	14.4	20.2
2,5-Dichlorophenol	89– 95	92	3.1	16.2	16.5
2,4-Dichlorophenol	94–100	97	4.5	15.3	16.0
3,4-Dichlorophenol	71– 93	83	11.3	19.2	22.3
3,5-Dichlorophenol	78– 94	87	8.0	0.2	8.0
2 ppb	*Water of River Ruhr*				
2-Chlorophenol	63– 80	72	7.1	5.4	8.9
3- and 4-Chlorophenol	78– 95	89	7.7	1.8	7.9
2,6-Dichlorophenol	54–100	78	22.9	3.5	23.2
2,3-Dichlorophenol	73– 96	83	10.7	1.6	10.8
2,5-Dichlorophenol	65–106	86	20.1	4.7	20.6
2,4-Dichlorophenol	81– 91	87	5.2	2.0	5.6
3,4-Dichlorophenol	82–115	99	16.7	4.5	17.3
3,5-Dichlorophenol	37–100	—	—	—	—
2 ppb	*Water of River Weser*				
2-Chlorophenol	72– 87	81	8.2	3.3	8.8
3-Chlorophenol	88– 99	93	6.0	0.3	6.0
4-Chlorophenol	105–118	112	6.8	7.1	9.8
2,6-Dichlorophenol	80– 88	83	4.0	3.4	5.2
2,3-Dichlorophenol	54– 66	61	6.1	3.9	7.2
2,5-Dichlorophenol	60– 70	63	5.7	4.1	7.0
2,4-Dichlorophenol	74– 82	79	4.8	2.1	5.2
3,4-Dichlorophenol	84–100	91	8.3	16.3	18.3
3,5-Dichlorophenol	56– 61	59	3.5	5.5	6.5
0.4 ppb	*Water of River Ruhr*				
2-Chlorophenol	72– 97	86	10.4	1.6	10.5
3- and 4-Chlorophenol	47– 85	61	20.8	3.1	21.0
2,6-Dichlorophenol	40– 56	48	11.0	8.3	13.8
2,3-Dichlorophenol	42– 52	48	5.9	12.9	14.2
2,5-Dichlorophenol	47– 56	53	4.6	11.5	12.4
2,4-Dichlorophenol	66– 79	73	6.6	8.3	10.6
3,4-Dichlorophenol	87– 99	92	6.0	5.2	7.9
3,5-Dichlorophenol	38– 70	—	—	—	—
0.2 ppb	*Spring water of River Pader*				
2-Chlorophenol	51– 97	80	25.1	6.2	25.9
3- and 4-Chlorophenol	74– 84	80	5.3	4.3	6.8
2,6-Dichlorophenol	68– 79	75	6.4	0.8	6.5
2,3-Dichlorophenol	61– 84	70	12.1	2.6	12.4
2,5-Dichlorophenol	80– 98	88	9.5	2.1	9.7
2,4-Dichlorophenol	77–100	94	8.1	7.1	10.8
3,4-Dichlorophenol	62– 88	72	13.9	8.8	16.5

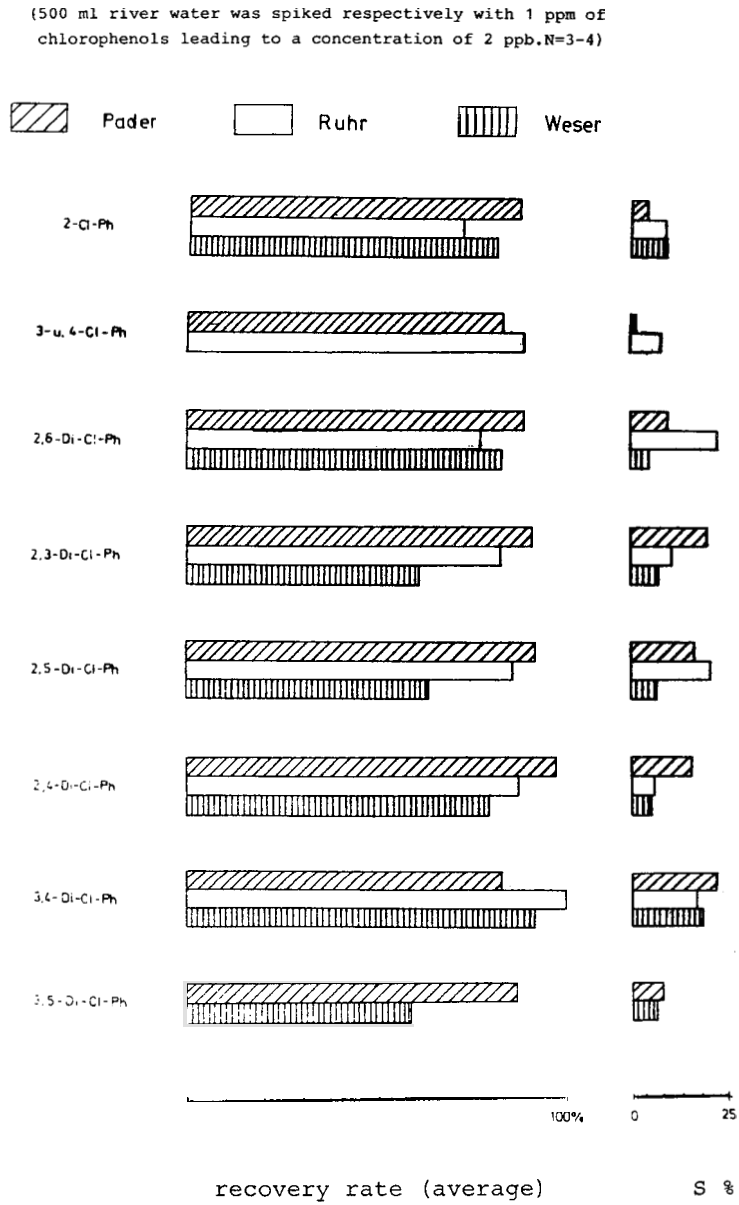


FIGURE 2 Recovery of environmental chlorophenols.

Standard deviation of the enrichment procedure:

$$S_1 = \sqrt{\frac{\sum_{a=1}^{N} (x_a - \bar{x})^2}{N-1}} \tag{1}$$

N = number of parallel samples
x_a = mean value of the analysis data from one sample
$\bar{x}$ = mean value of all x_a data.

Standard deviation of the chromatographic procedure:

$$S_2 = \sqrt{\frac{\sum_{i=1}^{N} \sigma^2}{n-N}} \tag{2}$$

σ = difference between the analysis value from one injection of the sample and the mean value of all analyses data of this sample
n = total number of injections
N = number of parallel samples.

Total standard deviation:

$$S = \sqrt{S_1^2 + S_2^2}. \tag{3}$$

Typical chromatograms for the analysis of spiked water samples are given in Figures 4 and 5, while Figure 3 shows the chromatogram of a standard mixture of chlorophenols.

Connecting the HPLC-UV output to the EC-cell input, the efficiency of the two detectors has been compared. A spiked water sample of the River Weser has been detected in the described way (Figure 5a: EC-detection; Figure 5b: UV-detection). The advantages of the electrochemical detection (selectivity and sensitivity) are clearly indicated in this example. At the bottom of Figures 4 and 5a there are shown the responses from blank extracts. The blank has been run using the same conditions as in spiked water samples. No contamination present in the water interfered with the analyses described here. These results indicate that the present analytical method is reliable.

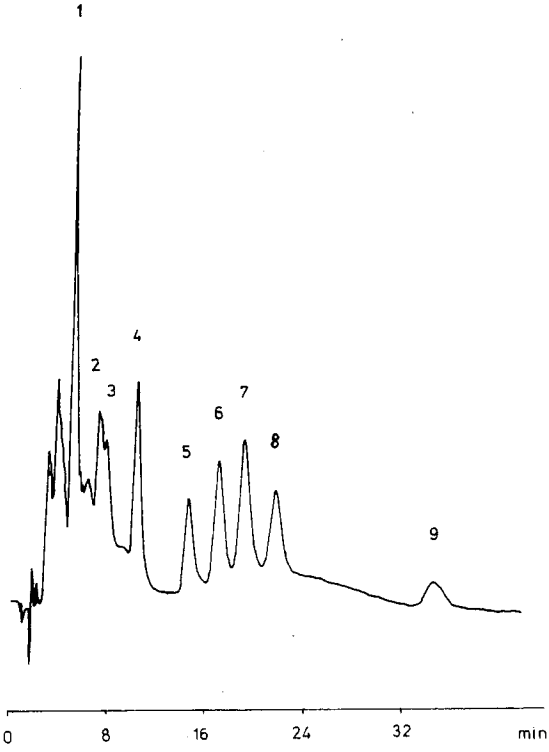


FIGURE 3 Standard test mixture (20 ppb), (1) 2-chlorophenol; (2) 4-chlorophenol; (3) 3-chlorophenol; (4) 2,6-dichlorophenol; (5) 2,3-dichlorophenol; (6) 2,5-dichlorophenol; (7) 2,4-dichlorophenol; (8) 3,4-dichlorophenol; (9) 3,5-dichlorophenol. Conditions: methanol/aq. 0.02 M KNO3 (45:55); 5 μm LiChrosorb RP-18, 12 cm × 4 mm; flow-rate: 1 ml/min; applied potential: 1 V; range: 200 nA; integrator sensitivity: AT = 4.

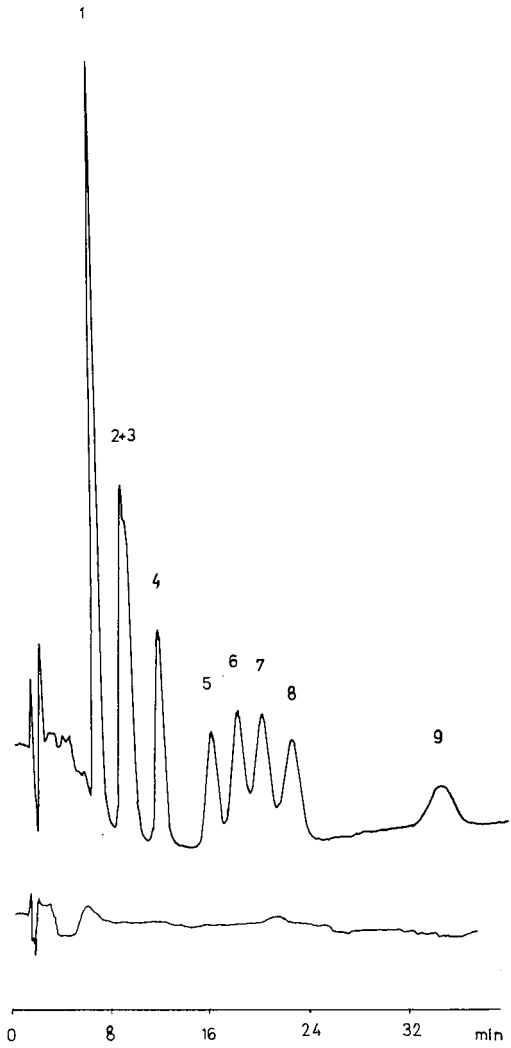


FIGURE 4 A typical chromatogram of a spiked water sample from the River Pader (2 ppb); below: unspiked water of the River Pader. Conditions, see Figure 3 except for integrator sensitivity (AT = 8).

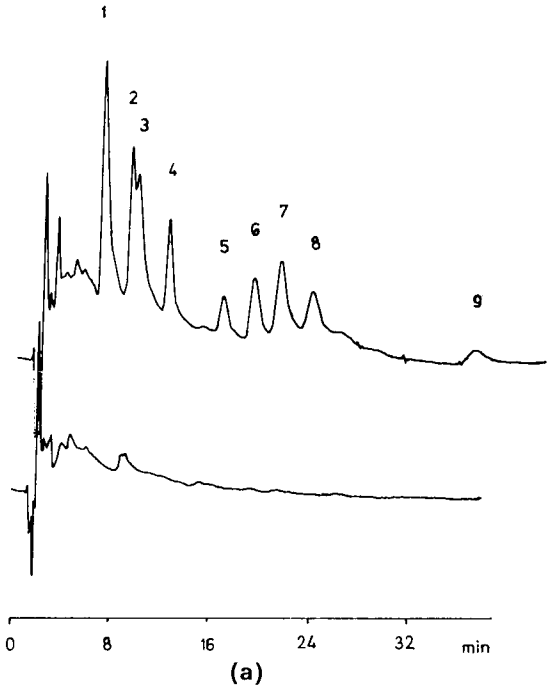
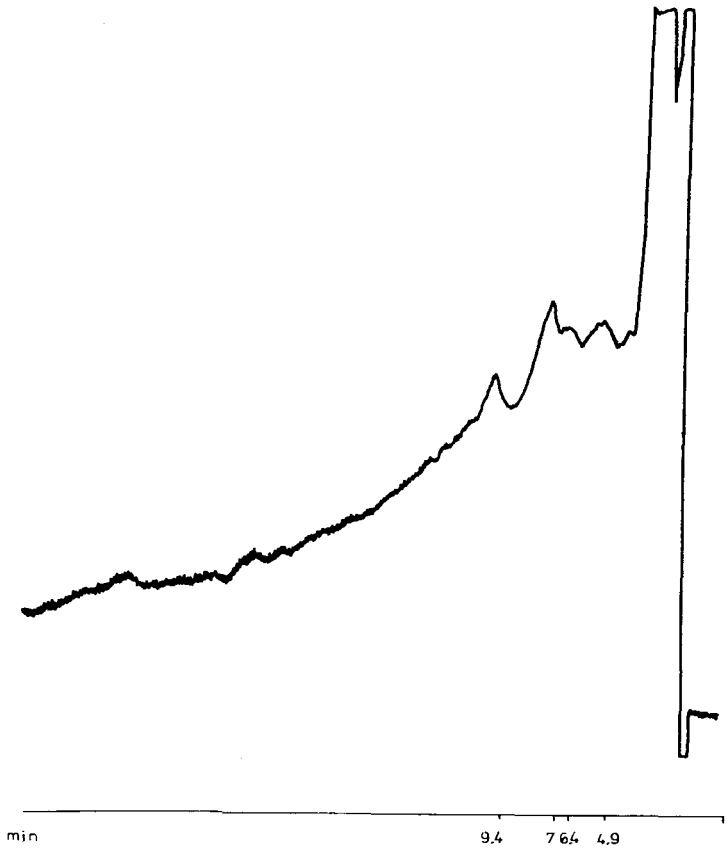


FIGURE 5 Comparison of ultraviolet detection at 254 nm with electrochemical detection at 1 V for a spiked water sample from the River Weser (2 ppb). Conditions, see Figure 3. (5a): LCEC; below: non-spiked water of the River Weser. (5b): LCUV, recorder sensitivity, 20 mV full scale; detector sensitivity, 0.01 AUFS.

CONCLUSION

A successful procedure for the determination of ng/ml levels of phenols in water has been developed. The method described has been applied to several types of water samples, including refinery waste water and natural water. Combining an off-line with an on-line enrichment operation results in good recovery rates. Electrochemical detection offers a selective and very sensitive method in detecting phenols in environmental samples. HPLC conditions for a simple isocratic separation of all mono- and dichlorophenols are shown.



(b)

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