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Determination of chlorophenols by micellar electrokinetic chromatography with electrochemical detection

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Abstract

A method has been developed for the determination of chlorophenols by micellar electrokinetic chromatography (MEKC) coupled with electrochemical detection. A mathematical model was used to predict optimal separation conditions; 17 of the 20 compounds of interest (19 chlorophenols and phenol) were baseline-separated in a 50 mmol l^{-1} ACES buffer at pH 6.1, with 22 mmol l^{-1} sodium dodecylsulfate. Detection was performed with a graphite-epoxy working electrode at a potential of 800 mV vs. Ag/AgCl. A palladium metal union was used to decouple the separation field from the electrochemical cell. A compensating pressure was applied to preserve the flat electroosmotic flow profile during analysis. Plate numbers up to 150 000 were obtained. The applied detection potential was shown to have an influence on the width of the peaks. Because the noise on the signal increased with the applied separation voltage, an optimum had to be found between detection limits and analysis time. Detection limits were in the order of 10 μg l^{-1}, one to three orders of magnitude lower than with UV detection. The repeatability was typically ±0.9% for the (electroosmotic flow corrected) mobility and ±4% for the peak area ($n=7$). Combined with off-line solid-phase extraction on a column with a polystyrene–divinylbenzene copolymer packing (PLRP-S), the method proved suitable for the analysis of river water samples. When using an internal standard, the average repeatability of the peak area was ±6% for 14 compounds ($n=5$). With this preconcentration-method, detection limits lower than 0.1 μg l^{-1} in 100 ml river water sample were obtained.

Keywords: Palladium decoupler; Detection, electrophoresis; Chlorophenols

1. Introduction

Chlorophenols are a group of persistent environmental pollutants. They can be emitted into the environment as degradation products of pesticides, by chlorination of drinking water and in industrial waste waters.

Eleven substituted phenols are currently listed by the U.S. Environment Protection Agency as priority pollutants, amongst which are 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol [1]. In the European Community, the maximum admissible concentration for chlorophenols in drinking water is 0.5 μg l^{-1} for the total content and 0.1 μg l^{-1} for each individual component [2].

Methods using liquid chromatography (LC) for

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the analysis of priority phenols [3] and chlorinated phenols [4] with UV detection have been developed. With reversed-phase LC and gradient elution, 18 of the 19 chlorophenols were separated. By using fluorescence detection after derivatization [5,6] and electrochemical detection (ED) [7–11], detection limits could be decreased considerably. However, complete separation of all chlorophenols by LC and their detection at a sufficiently low level still remains a difficult task.

One of the intrinsic advantages of capillary electrophoresis (CE) over LC is its high separation efficiency [12]. In the past decade, CE has been developed into a separation method suitable for routine applications, and in particular micellar electrokinetic chromatography (MEKC) [13] has become a popular, powerful analytical tool. MEKC has been applied for the separation of priority phenols [14] and chlorophenols, of which all isomers could be separated by Otsuka et al. [15]. The migration behaviour of several chlorophenols in MEKC has been studied systematically [16,17].

The most commonly employed detection method in CE is UV detection. However, the short light path available (the inner diameter of the capillary) limits its sensitivity. Since the sensitivity of ED is in principle not dependent on the volume scale of the measurement, and ED is known to be a very sensitive, selective and low cost effective detection method, it can provide an excellent alternative for UV detection.

Research on the coupling of ED with CE has been initiated by the group of Ewing [18] and later taken on in several other laboratories [19–25]. When using CE–ED it is essential to diminish the interference of the separation field on the electrochemical detector. For this purpose a palladium field-decoupler has been developed by us [26,27].

Because detection limits for chlorophenols in CE cannot be expected to be sufficiently low to meet the above mentioned requirements, a preconcentration step appears necessary. A sample enrichment method well suited for chlorophenols is solid-phase extraction (SPE) on PLRP-S, a polystyrene–divinylbenzene copolymer [28–30]. In the presented work, the feasibility of MEKC–ED and its combination with off-line SPE for the separation and detection of chlorophenols is investigated. River water samples have been preconcentrated and analysed.

2. Experimental

2.1. Apparatus

A set-up as described previously was used [27]. A PRINCE programmable injector for CE, including high voltage source, was obtained from Lauer Labs (Emmen, The Netherlands). Fused-silica separation capillaries (Composite Metal Service, Hallow, UK) with an inner diameter (I.D.) of 75 μm and a length of 85 cm were used. For UV detection with a UV/Vis 200 detector (Linear, Reno, NV, USA), a 2-mm detection window was created by burning off the coating at 65 cm from the capillary inlet. Detection was performed at 210 nm. The separation field was decoupled from the electrochemical cell by a palladium metal union. Inside the palladium coupling piece, the separation capillary is positioned directly against a 6-cm length poly ether ketone (PEEK) tube, 500 μm O.D. and 63.5 μm I.D. (Upchurch, Oak Harbor, WA, USA). A laboratory-made T-shaped nl-volume electrochemical cell [31], with a graphite-epoxy working electrode, stainless-steel auxiliary electrode and an Ag/AgCl reference electrode, was connected to a potentiostat/amplifier (ANTEC, Leiden, Netherlands). Signals were transferred to a strip-chart recorder Model BD 112 (Kipp and Zonen, Delft, The Netherlands) or via a HP 35900 A/D converter board to a HP ChemStation. Measurement instruments were thermostated at 30°C.

Solid-phase extraction was performed on a 10×2 mm I.D. stainless-steel column laboratory-packed with PLRP-S, particle size 15–20 μm, pore size 100 Å (Polymer Laboratories, Shropshire, UK). A high precision pump Model 300 (Gynkotek, Germering, Germany) and a gastight syringe were attached to the column by means of a Rheodyne HPLC valve.

2.2. Chemicals and solutions

Phenol and chlorophenols, N-(2-acetamido)-2-aminoethanesulfonic acid (ACES) and Sudan III were obtained from Aldrich (Milwaukee, WI, USA).

Other chemicals, obtained from standard suppliers, were all analytical-reagent grade. All chemicals were used as received. Stock solutions of chlorophenols were prepared in a mixture of methanol and water and stored at room temperature.

Unless stated otherwise, a 50 mmol l^{-1} ACES buffer, adjusted to pH 6.1 with a calculated amount of sodium hydroxide and with 22 mmol l^{-1} sodiumdodecyl sulfate (SDS) added as surfactant, was employed. 1 mmol l^{-1} sodium chloride was added to stabilize the Ag/AgCl reference electrode. All buffers were filtered through a Millipore filter (pore size 0.45 μm) and stored at 4°C. After 2 weeks of use, fresh buffer solutions were prepared. Samples of chlorophenols were prepared by diluting a mixture of stock solutions with running buffer.

2.3. Procedures

A new capillary was etched with 1 mol l^{-1} sodium hydroxide for 30 min. Daily before use the capillary was etched with 0.1 mol l^{-1} sodium hydroxide for 10 min.

Samples were injected hydrodynamically by applying 30 mbar pressure during 6 s. The injected volume was 18 nl. Before every injection the capillary was flushed with buffer for at least 5 min.

The SPE column was flushed with 3 ml methanol to remove impurities and conditioned with 3 ml 10^{-2} mol l^{-1} hydrochloric acid; flow-rates were 1.5 ml min^{-1}. After filtration through a 0.45-μm Millipore filter, standards and river water samples were acidified to pH 2 with hydrochloric acid and loaded on the column, with a flow-rate of 2 ml min^{-1}. Then, the column was flushed with 1 ml 10^{-2} mol l^{-1} hydrochloric acid. The syringe was used to elute the chlorophenols from the column with methanol. Sample volumes in the range of 10–250 ml were analysed. In the final experiments, a sample volume of 100 ml was preconcentrated and 200 μl methanol was used for elution.

An amount of 10 μl 0.1 mol l^{-1} sodium hydroxide was added to the collected extract to ionize the chlorophenols in order to avoid their evaporation. The extract was evaporated to ca. 50 μl by heating it in a water bath to 50°C while gently flushing with nitrogen. A 100-μl volume of running buffer was added before injection.

3. Results and discussion

3.1. Optimization of the separation

The effect of the pH and surfactant concentration on the separation was determined using UV detection, with a 0.02 mol l^{-1} phosphate buffer adjusted to the required pH with sodium tetraborate. The electroosmotic flow corrected apparent mobilities (μ_{app}) of six exemplary chlorophenols at four different pH values, with 40 mmol l^{-1} SDS added as surfactant, are given in Fig. 1. Compounds are numbered as in Table 1. Methanol (1) was used as indicator for the electroosmotic flow.

Because above pH 7 the degree of ionization of most chlorophenols increases (see pK_a values in Table 1), the fraction of analyte in the micellar phase

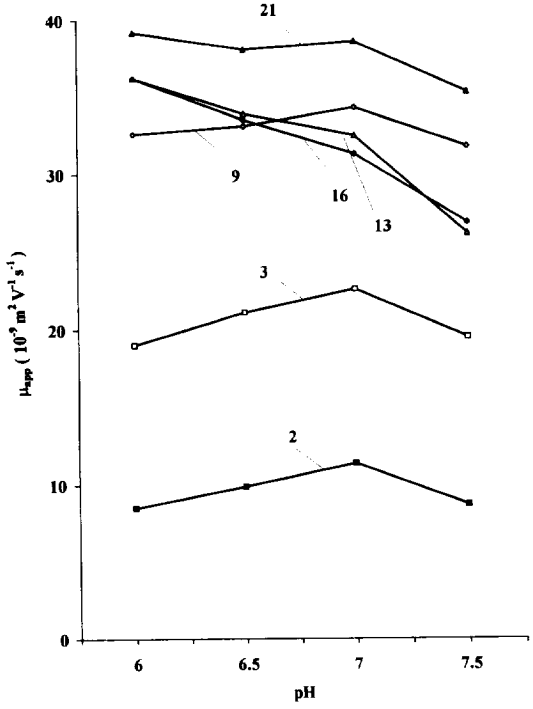

Fig. 1. Effect of pH on the apparent mobility of six chlorophenols. Conditions: see Section 2. Applied separation voltage: 25 kV.

Table 1
Migration behaviour of chlorophenols in MEKC

No.	Compound	pK_a[a]	μ_0	K_d (l mol^{-1})	Apparent mobility[b]	
					Calculated	Experimental
1	Methanol	–	μ_{eo}	–	–	–
2	Phenol	9.9	0.0	11	−7.0	−7.2
3*	2-CP	8.5	−2.0	33	−16.3	−17.1
4	3-CP	9.0	−1.0	48	−20.3	−21.2
5	4-CP	9.4	−1.4	50	−20.7	−21.2
6	2,6-DiCP	6.8	−21.2	36	−18.9	−26.9
7	2,5-DiCP	7.5	−9.2	100	−28.1	−31.8
8	2,3-DiCP	7.7	NM[c]	–	–	−33.5
9*	2,4-DiCP	7.9	−4.9	150	−32.4	−34.6
10	3,4-DiCP	8.6	−1.9	190	−34.5	−35.9
11	2,3,6-TriCP	5.8	−27.7	200	−32.9	−37.0
12	3,5-DiCP	8.3	−3.1	230	−35.7	−37.4
13*	2,4,6-TriCP	6.0	−23.2	440	−37.7	−39.3
14	2,3,5,6-TetraCP	5.0	NM	–	–	−39.3
15	2,3,4,6-TetraCP	5.2	−23.6	2200	−40.4	−41.8
16*	PentaCP	4.7	−26.4	3400	−39.2	−41.8
17	2,4,5-TriCP	6.7	NM	–	–	−41.9
18	2,3,5-TriCP	6.4	−20.2	700	−40.8	−42.2
19	2,3,4-TriCP	7.0	−12.1	620	−40.8	−42.4
20	3,4,5-TriCP	7.6	−15.0	630	−41.1	−43.2
21	2,3,4,5-TetraCP	5.6	−22.2	6100	−43.9	−44.9
22	Sudan III	–	–	–	–	−44.9

Mobilities are given in 10^{-9} m^2 V^{-1} s^{-1}. Priority chlorophenols are indicated by an asterisk.
[a] Data from Ref. [32].
[b] Conditions: 50 mmol l^{-1} ACES buffer, pH 6.1, with 22 mmol l^{-1} SDS.
[c] Not measured.

and consequently the apparent mobility decreases, leading effectively to a more compressed electropherogram. This implies that at a higher pH more SDS needs to be added to bring about a satisfactory separation, as was observed for the separation of dichlorophenols [17]. Actually, as will be explained below, for the application of ED in our set-up it is necessary to limit the electrophoretic current, so that the amount of SDS in the buffer is restricted. Therefore, a pH between 6 and 7 appeared to be preferable for the separation.

The effect of the SDS concentration on the apparent mobility was measured at pH 7, and described by the capacity factor of the micelles, k'. With the assumption that ionized analytes are not sorbed by the micelles, it can be derived [16] that k' can be obtained as:

$$k' = \frac{\mu_{app} - \mu_0}{(1-\alpha)(\mu_{mc} - \mu_{app})} \quad (1)$$

where α is the degree of ionization, μ_0 the mobility in the buffer without surfactant, μ_{app} the apparent mobility in the micellar solution and μ_{mc} the mobility of the micelles, as indicated by Sudan III.

In principle, division of μ_0 by the calculated value of α at pH 7 yields the ion mobility of a compound. For some compounds with a pK_a much higher than 7 these values are not very accurate. However, this inaccuracy is not important for the optimization of the separation, because in the pH-range 6–7 the influence of the ion mobility of these compounds on μ_{app} is limited.

From two values of k', obtained from the apparent mobilities in buffer solutions with 20 and 40 mmol l^{-1} SDS, an average value for the partition coefficient K_d (in l mol^{-1}) between the micellar and aqueous phase was calculated as:

$$K_d = \frac{k'}{[SDS] - cmc} \quad (2)$$

where *cmc* is the critical micellar concentration of SDS, equal to 5 mmol l^{-1} [33].

Results are listed in Table 1. K_d is a measure of the hydrophobicity of a compound and increases roughly with the number of substituted chlorine atoms. The values of μ_0 and K_d obtained in this way were used to predict the optimal separation conditions, with the help of Eqs. (1,2). The mobilities calculated for the separation conditions finally chosen (pH 6.1, 22 mmol l^{-1} SDS) are a fairly good estimate of the measured mobilities (Table 1).

For the separation of the chlorophenols with ED, in our set-up a phosphate–borate buffer as suggested by Otsuka et al. [15] could not be used. As has been discussed in a previous paper [26], at the palladium decoupler the electrophoretic current causes the reduction of water: $2H_2O+2e^- \rightarrow H_2+2OH^-$.

The hydrogen diffuses away through the palladium metal, while the generated hydroxide ions cause a large pH shift. With a phosphate–borate buffer, the pH shift migrates "upstream" through the separation capillary, thereby causing a disturbance of the separation and increasing the electrophoretic current. Similar effects were observed with a Tris buffer containing relatively high concentrations of SDS. A HEPES buffer also was not applicable for MEKC–ED; either by being oxidized itself, or modifying the reference electrode, HEPES prevented electrochemical detection above 600 mV vs. Ag/AgCl.

Therefore, a 50 mmol l^{-1} ACES buffer was employed. This zwitterionic buffer has a relatively low conductivity, so that its buffer capacity is high in comparison to the current. It can be calculated that the generated hydroxide-ions shift the detection pH to 7.6.

Fig. 2 presents an electropherogram of the separation of all 19 chlorophenols and phenol. Under optimized conditions, 17 compounds were baseline-separated. A similar separation could be obtained with ED (see Fig. 5).

3.2. Electrochemical detection

First, the influence of the important experimental parameters in ED, the detection potential and compensating pressure, was investigated.

In Fig. 3 the effect of the detection potential on the coulometric yield is shown. The yield was

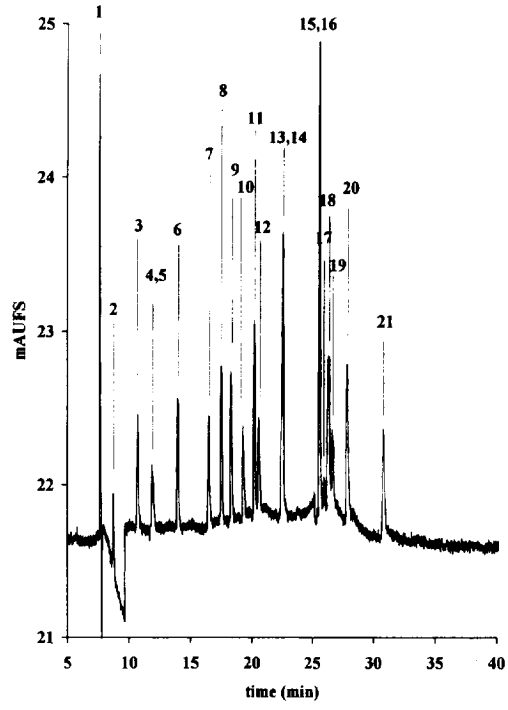

Fig. 2. Electropherogram of the separation of 19 chlorophenols and phenol in ACES buffer (UV detection). Applied voltage: 20 kV, current ca. 18 μA.

calculated with the assumption that one electron is transferred per molecule of analyte. The maximum yields observed were 45–55%. A detection potential of 800 mV vs. Ag/AgCl was chosen for further measurements. At this potential, the sensitivity for all priority chlorophenols is close to optimal; a higher detection potential would lead to an increase in baseline noise.

The PEEK coupling tube, connecting the field decoupler to the electrochemical cell, induces a backpressure against the electroosmotic flow which disturbs the flat electroosmotic flow profile, thereby causing extra peak broadening. During electrophoresis, a compensating pressure was applied on the inlet vial to restrain this effect [34]. The dependence of the observed plate number on the applied compensating pressure (Fig. 4) shows an optimum near 10 mbar, which is in agreement with the calculated backpressure, equal to 12 mbar under the conditions employed. Plate numbers up to 150 000 could be obtained. The relatively low plate number of peak 20

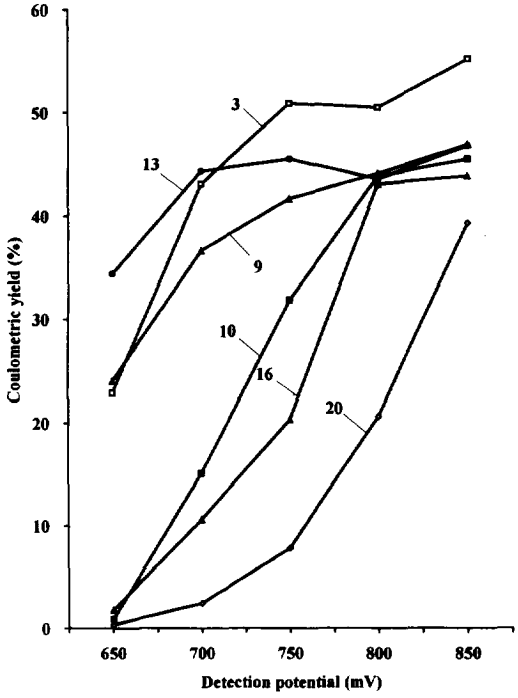

Fig. 3. Coulometric yield as a function of the detection potential. Applied voltage 30 kV, current ca. 32 μA, compensating pressure: 15 mbar.

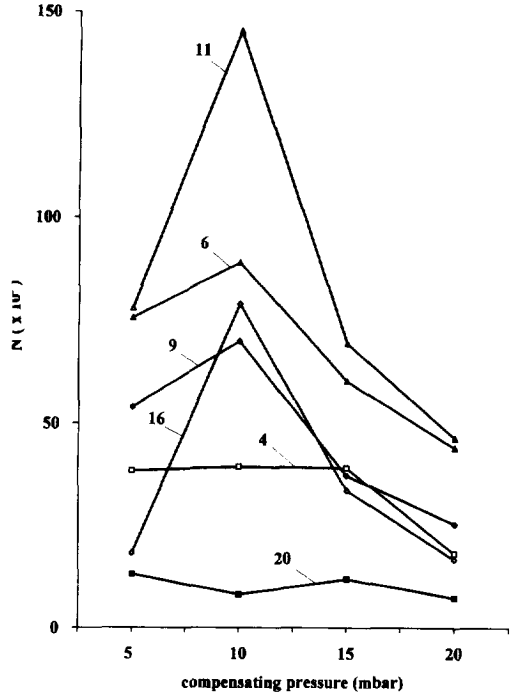

Fig. 4. Influence of compensating pressure on the observed plate number. Applied voltage: 20 kV.

will be discussed later. In following experiments, a compensating pressure of 5 mbar per 10 kV (separation voltage) was applied.

Fig. 5 shows the ED electropherogram, measured simultaneously with Fig. 2. It is evident that compared to UV detection a significantly higher signal-to-noise ratio (S/N) is obtained with ED.

Comparison of Fig. 5 to Fig. 2 also reveals that even with optimal compensation pressure, peaks obtained with ED are broader than those with UV detection. For most compounds, with UV detection about 100 000 plates are observed, while with ED on average 70 000 plates are obtained. Calculations show that this peak broadening is caused only partly by laminar flow effects in the PEEK coupling tube; peak broadening in the detection cell itself must play a role too.

In first instance, the response time of the detection cell, and with that its contribution to the peak broadening, is determined by the (effective) volume of the cell and the flow-rate of the electroosmotic flow. The coulometric yield for most compounds obtained at a high detection potential is in the order of 50%, which means that a considerable amount of analyte is depleted by the electrode reaction before being swept away by the electroosmotic flow. Because of this depletion, the response time of the detector can be shorter than expected on basis of the volume of the cell alone.

Another indication for this is the difference in peak width of compounds with similar elution times; in particular, relatively broad peaks were obtained for compounds 10, 12, 20 and 21 (Fig. 5). Remarkably, these are exactly the compounds for which the limiting current plate is not reached at the applied detection potential (800 mV). For these compounds, depletion is less complete and therefore less effective in reducing the response time.

It can be shown that in the absence of liquid flow, the response time τ (defined as the first statistical moment of the signal) of an electrochemical thin-layer cell can be written as:

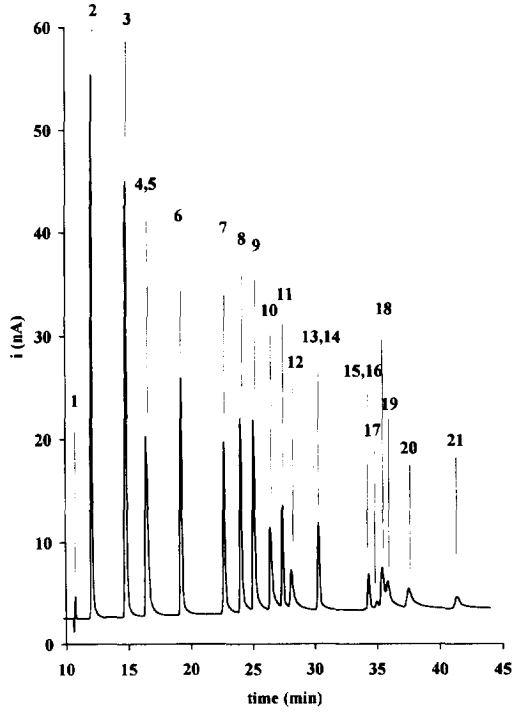

Fig. 5. Electropherogram with ED, measured simultaneously with Fig. 2.

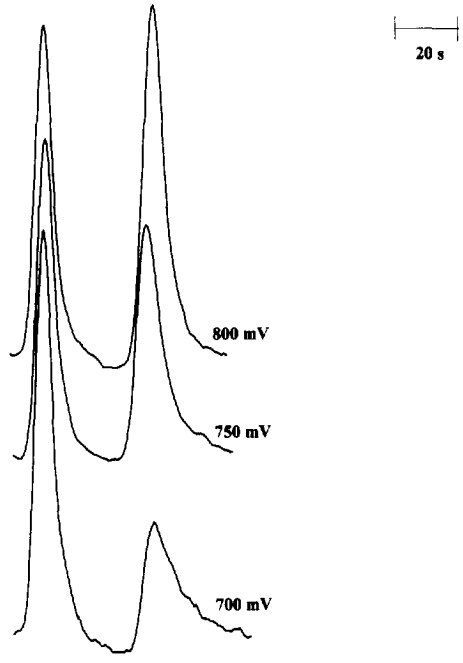

Fig. 6. Shape of peak 9 (left) and 10 (right) with different detection potentials. Conditions as in Fig. 3. Scales in the y-direction have been adjusted.

$$\tau = \frac{b^2}{3D} + \frac{b}{k_f} \quad (3)$$

where b is the thickness of the cell, D the diffusion coefficient of the analyte and k_f the heterogeneous reaction rate constant (in m s^{-1}). With fast electrode reactions the response time is diffusion limited, while with slow reactions (at a low detection potential) the response time will be increased. In a flow-through cell, as used in our experiments, the response time is set by the combined effect of the flushing of the cell and the coulometric depletion of the analyte. When the latter process is relatively slow, the resulting response time will be increased.

Fig. 6 illustrates the importance of the rate of the electrochemical reaction for the peak width in our set-up. It shows the peak shape of the two closely eluting compounds 9 and 10 at detection potentials of 700, 750 and 800 mV. For compound 9, which has a relatively low oxidation potential (Fig. 3), the increase of the detection potential only leads to some increase in height. For compound 10, which has a higher oxidation potential, the increase in height is stronger, while at the same time its width and particularly its tailing is reduced. These observations make us assume that the volume of our cell is de facto too large for CE, but that for most compounds this is not detrimental because of their fast depletion at the electrode surface.

3.3. Analytical performance

The repeatability of the method was estimated from seven consecutive injections of a standard mixture with 14 chlorophenols. From these measurements, the relative standard deviation (R.S.D.) of the mobility and peak area were calculated; the values for the priority chlorophenols are shown in Table 2. The average R.S.D. of the apparent mobility is 0.9% and of the peak area 4% for 14 compounds.

Although the separation field is decoupled from the electrochemical detection cell, its magnitude still has an effect on the baseline noise of the signal. It

Table 2
Repeatability and limit of detection (LOD) with direct injection and after SPE

No.	Compound	Direct injection				After SPE		
		R.S.D. (%)[a]		LOD[b]		R.S.D. (%)[c]		LOD[b]
		μ_{app}	Area	UV (mg l^{-1})	ED (μg l^{-1})	μ_{app}	Area	ED (μg l^{-1})
3	2-CP	0.9	4	2.9	5	0.6	4	0.07
9	2,4-DiCP	0.8	4	2.0	11	0.3	5	0.07
13	2,4,6-TriCP	0.9	5	0.4	11	0.3	7	0.08
16	PentaCP	1.1	2	0.4	36	0.4	11	0.2

[a] $n=7$.
[b] $S/N=2$.
[c] $n=5$.

was observed that changing the separation voltage from 10 to 20 and 30 kV caused an increase of the (peak-to-peak) noise level from 0.002 to 0.004 and 0.012 nA, respectively. This implies that an optimum has to be found between analysis time and detection limit.

The limits of detection (LODs) of 14 chlorophenols were estimated by extrapolating the peak heights of three measurements to $S/N=2$. In Table 2 the LODs of the priority chlorophenols are shown, measured with a separation voltage of 20 kV; the analysis time was ca. 40 min. The LODs of most chlorophenols were in the range of 4–11 μg l^{-1}, while the LOD of pentachlorophenol (16) was 36 μg l^{-1}. Due to reasons discussed before, 12, 20 and 21 were detected less favourably than other compounds under the conditions applied; their LOD was ca. 90 μg l^{-1}. Apparently, the required limit for water samples (0.1 μg l^{-1}) could not be reached; thus the method was combined with the sample enrichment method SPE.

3.4. Solid-phase extraction

Prior to the application to river water samples, SPE experiments were carried out with a standard solution containing 14 chlorophenols, to determine the minimum amount of methanol required for elution, to estimate the break through volume and to quantify the repeatability. In order to evade the error arising from the evaporation-step, in the first two experiments the collected extract was immediately made up to 2 ml with running buffer and analysed.

The required amount of desorption solvent was determined by loading 10 ml of the standard mixture on the column and extracting it with different volumes of methanol, ranging from 100 to 400 μl. From the resulting curve of the recovery vs. the volume of methanol, 200 μl methanol appeared to be sufficient for complete elution of the chlorophenols. Recoveries were between 81% (16) and 116% (3); only phenol (2) was not recovered completely (65%).

Various sample volumes, spiked with the same amount of chlorophenols were preconcentrated to investigate the effect of the sample volume on the recovery. Results are shown in Fig. 7. The results of the 250-ml sample volume are the recoveries from a preconcentrated river water sample (including the evaporation-step).

The data on the recovery from the 250-ml water sample illustrates the relatively low break through volumes of phenol (2) and 2-CP (3) on PLRP-S. Similar observations were made by other authors [28,29]. However, it appears that most chlorophenols can be preconcentrated on the column from a volume of up to 100 ml without a significant loss of recovery.

Break through volumes can be increased by the addition of an ion-pair reagent, or by the use of a second preconcentration column [30,35]. A recent article indicates it is possible to preconcentrate even the more polar phenols from a volume up to 500 ml on a highly cross-linked polystyrene–divinylbenzene copolymer packing, combined with an ion-pair reagent [36]. However, for our purposes the preconcentration of 100 ml of water sample appeared to be sufficient.

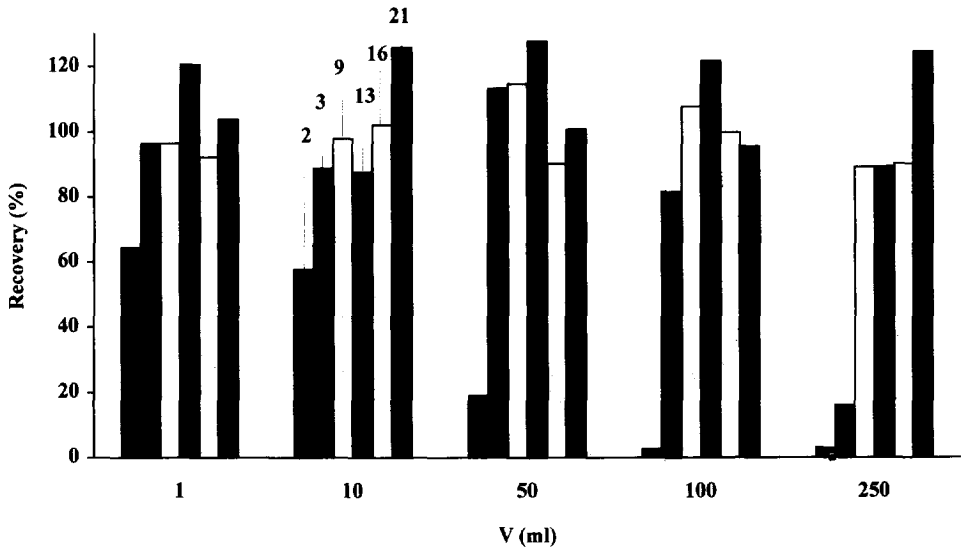

Fig. 7. SPE recoveries with different sample volumes. Conditions: see Section 2.

The repeatability of MEKC–ED combined with SPE (including the evaporation-step) was measured by 5 consecutive analyses of 10 ml of the standard mixture. The R.S.D. of the peak area was typically ±40%, probably due to adsorption of analytes to the wall of the vial during the evaporation-step. Using one of the chlorophenols (9) as internal standard can effectively reduce the R.S.D. of the peak area. Results for the priority chlorophenols are given in Table 2. The R.S.D. varies from 2% (7) to 12% (20), with an average of 6% for 13 compounds.

3.5. Application to river water samples

Several river water samples, taken from various locations near Amsterdam have been preconcentrated and analysed simultaneously with UV and electrochemical detection. Two electropherograms of 250 ml preconcentrated river water are visible in Fig. 8a. Compounds 2, 6 and 9 could be identified in the river water sample when ED was applied.

Fig. 8b shows electropherograms of 250 ml of the same river water sample spiked with 14 chlorophenols, with concentrations in the range of 0.5–6 $\mu g\ l^{-1}$. Comparison of Fig. 8b2 to Fig. 8b1 again clearly demonstrates the gain in sensitivity made by employing ED. It can be seen in Fig. 8a2 Fig. 8b2 that the high selectivity of the presented method limits the interference of the river water matrix on the determination of the chlorophenols.

Limits of detection ($S/N=2$) in river water are estimated from three analyses of 100 ml spiked river water sample, measured with a separation voltage of 30 kV. Average LODs of the priority chlorophenols are given in Table 2. The values for 9 and 13 (0.07 $\mu g\ l^{-1}$) are representative for most of the other chlorophenols, with the exception of 12, 20 and 21, for which the LOD is about 0.4 $\mu g\ l^{-1}$, and 16 (0.2 $\mu g\ l^{-1}$). It should be noted that these LODs were measured with a relatively high separation voltage; with a lower separation voltage certainly the limit of 0.1 $\mu g\ l^{-1}$ can be reached for the most important compounds. The LODs are comparable to those obtained with LC–ED, which are typically about 0.03 $\mu g\ l^{-1}$ after preconcentration on a polystyrene-divinylbenzene disk from 250 ml to 1.5 ml [11]. However, the degree of interference by other sample components in the HPLC chromatograms appeared to be higher than in our experiments.

A gain in sensitivity can be made by the above mentioned improvements for the SPE-procedure, which would allow a larger sample volume to be preconcentrated on the column. Presumably, our instrumental set-up can still be improved to decrease

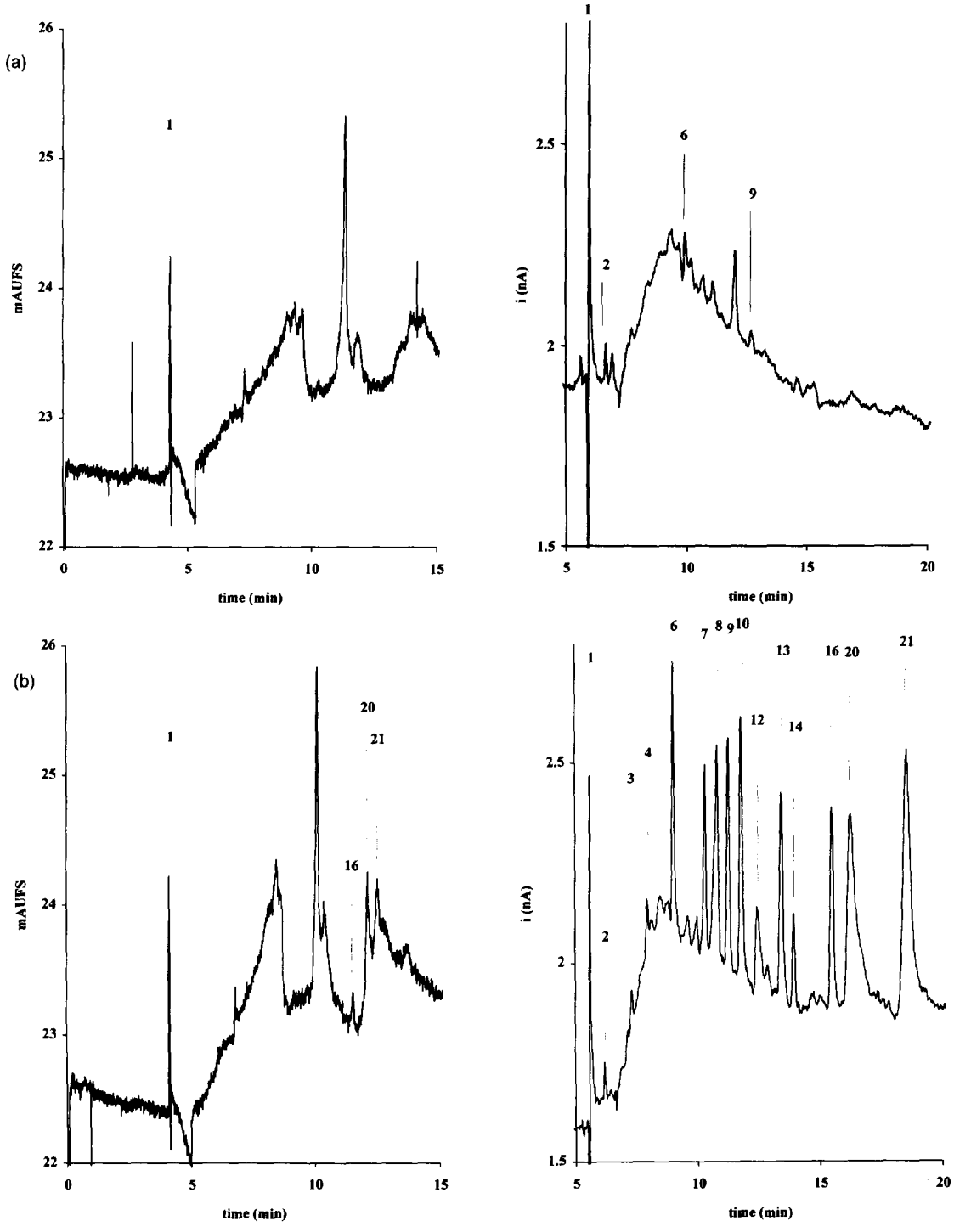

Fig. 8. Electropherograms of 250 ml unspiked (a) and spiked river water sample (b), with UV (1) and ED (2). Unmarked peaks have not been identified.

detection limits, e.g., by applying a glassy carbon working electrode or a smaller volume detection cell. Work in this direction is currently in progress.

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