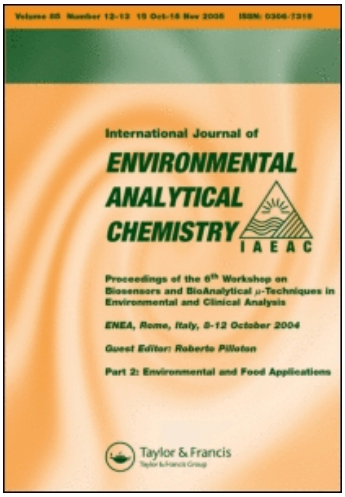

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CAPILLARY ELECTROPHORETIC SEPARATION AND DETERMINATION OF CHLOROPHENOLIC POLLUTANTS IN INDUSTRIAL WASTE WATERS

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Capillary zone electrophoresis was applied to analyze chlorophenols in industrial waste waters. 17 chlorophenols could be all resolved from each other within 12 min using acetone as the organic modifier in 10 mmol/L phosphate electrolyte at pH 8.23. Effects of pH and organic modifiers on the separation selectivity were investigated. The results indicated that the elution order was related with the pKa order of analytes. Reproducibilities termed in R.S.D.% of migration times and peak areas of 17 chlorophenols were in the range 0.48–0.67% and 3.9–5.1%, respectively. When 2,3,4-trichlorophenol was used as the internal standard, R.S.D.% of migration times was reduced to 0.03–0.28%. Detection ranges of all chlorophenols were linear over two orders of magnitude of concentrations with correlation coefficients 0.998–1.000 except for 4-chlorophenol, the peak area of which could not be measured accurately because of the interference from electroosmotic flow (EOF). Limits of detection were 100–270 μg/L. With the method developed chlorophenolic pollutants in industrial waste waters could be analyzed by direct injection without any pretreatment.

Keywords: Capillary zone electrophoresis; organic modifiers; chlorophenols

INTRODUCTION

Chlorophenols are a major class of pollutants that can contaminate environment and can be enriched in the food chain. They have been widely used as fungicides, herbicides, insecticides, pesticides and precursors in the synthesis of other pesticides since the early 1930s. Therefore, they have been widespreadly distributed in the environment.[1,2] In water, chlorophenols may appeares degradation products of herbicides,[3] or during the chlorination of drinking or waste waters from petroleum, steel or pulp and paper industry.[2] They possess high toxicity even at low concentrations and usually impart a strongly disagreeable taste to water. Several chlorophenols have been designated as priority pollutants by the United

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States Environmental Protection Agency.[4] Chlorophenols are generally measured by GC and HPLC. But these methods are commonly time-consuming and often require derivatization or gradient elution.[5,6]

As a novel micro-separation method with a rapid development in the last decade, capillary electrophoresis (CE) has been undergoing an exploding growth in environmental analysis.[7,8]Many typical pollutants including PAHs,[9,10] pesticides[11,12] and others have been separated and determined by different CE separation modes.

Chlorophenols were once separated by capillary zone electrophoresis (CZE) and micellar electrokinetic chromatography (MEKC).[13,14] With MEKC separations were completed in 30 min, but baseline separation was not achieved for all 19 chlorophenolic isomers.[14] At present, many attempts with MEKC focused on separations of those lower chlorinated chlorophenolic congeners.[15,16] It should be noted that with MEKC the possible interference from neutral compounds, which always exist in complex samples, has to be considered, because neutral compounds may take part in the partition process with the pseudostationary phase. However, in CZE separations the selectivity depends on the surface charges/mass ratio of analytes. Therefore, Interference from neutral contaminants can be disregarded because with no surface charges, neutral analytes will have no electrophoretic mobilities and can only comigrate with EOF. This is one of the major advantages of CZE separations of chlorophenols. But resolutions of all chlorophenols with CZE were very difficult.[8] The best result obtained so far with CZE indicated that 13 chlorophenols were baseline separated in 20 min.[13] Recently, all chlorophenolic isomers and phenol were separated in the coelectroosmosis mode.[17] Hexadimethrine bromide (poly (N,N,N′,N′-tetramethyl-N-trimethylene-hexamethylenediammonium)) was used as the modifier to reverse EOF direction.

In this paper, a fast convenient CZE method was developed to separate 17 chlorophenols. Acetone was used as the organic modifier. Effects on the selectivity of electrolyte pH and kinds and concentrations of organic modifiers were investigated. Reproducibilities of migration times, linear ranges and limits of detection using UV detector were also determined. With the method developed chlorophenolic pollutants in industrial waste waters were analyzed.

EXPERIMENTAL

Chemicals

Sodium dihydrogen phosphate, disodium hydrogen phosphate, methanol, acetonitrile and acetone are of analytical grade. The solvents were redistilled before

use. Stock solutions of chlorophenols (about 50 mg/L each) were made in methanol. Other concentrations of standard samples were prepared from their stock solutions by dilution with methanol. Stock solutions of 0.1 mol/L sodium dihydrogen phosphate and 0.1 mol/L disodium hydrogen phosphate were prepared by dissolving the respective chemicals in water. The running background electrolyte of 10 mmol/L phosphate consisted of sodium dihydrogen phosphate and disodium hydrogen phosphate with an appropriate ratio. After adding organic modifiers, pH value of electrolyte was readjusted with a few drops of 1 mol/L sodium hydroxide or 1 mol/L hydrochloric acid.

Apparatus

Measurements were carried out on a P/ACE system 5510 (Beckman, Palo Alto, CA, USA), equipped with a UV absorbance detector. 0.05 mm I.D. fused-silica capillary column (Yongnian Optical Fibre Factory, Hebei Province, P.R. China) was used. All experiments were performed at 25.0°C. Separation voltage was 30.0 kV and electric current was about 22 μA. Samples were introduced pneumatically. Solutes were monitored at 214 nm. Peak areas and electrophoretic mobilities were measured using Beckman P/ACE™ Station.

Procedure

New capillary columns were washed with 1 mol/L sodium hydroxide, 1 mol/L hydrochloric acid, and water successively for 1 h each. Before an actual electrophoretic experiment, the capillary was firstly conditioned with the background electrolyte for 10 min. Between runs, the column was systematically washed with 0.1 mol/L sodium hydroxide (2 min), then rinsed with water (5 min) and the electrolyte (5 min).

RESULTS AND DISCUSSION

Capillary zone electrophoretic separation of chlorophenols

In CZE separations, electrophoretic mobilities mainly depend on the degree of solutes' dissociation in the electrolyte, their solvated ion weight and electrolyte viscosity, etc. According to Gonnord, these factors can be inversely combined in the following equation:[13]

$$\mu_{ep} = \frac{\varepsilon\alpha f(\kappa r)}{6\pi\eta\alpha(1+\kappa r)}$$

where ε is the permittivity of the background electrolyte, η is the viscosity of the electrolyte, $f(\kappa r)$ is a function dependent on the analyte double layer thickness ($1/\kappa$) and the solute solvated radius (r), assuming that chlorophenols can be considered as spherical particles.

α is the degree of dissociation of chlorophenols in the electrolyte, which can be calculated by

$$\alpha = \frac{1}{1 + 10^{pH - pK_a}}$$

By this equation, the pH value of the electrolyte solution and solvation weight of solutes become two key factors in practice for controlling the selectivity on chlorophenols in capillary zone electrophoresis. But the wide range of pKa values made almost impossible to separate all chlorophenols only through changing the pH without other additives in the electrolyte. After addition of methanol, acetonitrile or acetone in the electrolyte, all 17 chlorophenolic compounds were baseline resolved at pH 8.23. The volume ratios used for the three solvents were 50%, 50% and 40%, respectively. The separation is achieved due to the modifications of pKa values as well as influence on chlorophenolic solvation process in the electrolyte, which leads to changes in the solvation weight of solutes by replacing some water molecules within the solvation radius with organic solvent molecules.

Figure 1.a shows a representive electrophoregram of the chlorophenolic standard mixture obtained with 35%v/v acetone as the organic modifier. The separation was finished within 12 min. The analysis time is greatly reduced comparing to GC (about 60 min)[5,6] or MEKC.[14]

Separation results indicated that the elution order for most chlorophenols was in agreement with their pKa order. The relatively small 2,3,6-trichlorophenol with the highest acidity among trichlorophenols had the largest electrophoretic mobility and migrated most slowly. Though pentachlorophenol is the most acidic congener, its electrophoretic mobility was less than that of 2,3,6-trichlorophenol because of its highest molecular weight. The elution order of three tetrachlorophenols clearly showed the influence of molecular solvation weight on electrophoretic mobilities. The chlorophenols' pKa values are given in Table I [13,18].

By running eight replicates of the standards (10 mg/L each) each chlorophenol showed high reproducibility in terms of peak areas and migration times, giving standard deviations between 0.48 and 5.1%. Table II shows the reproducibilities of migration times and peak areas termed in R.S.D.% for the 17 chlorophenols. The concentration of acetone used was 35%v/v. As the peak of 4-chlorophenol was fully overlapped with the peak of EOF, 4-chlorophenol had the largest R.S.D.% of migration time and its area could not be measured accurately.

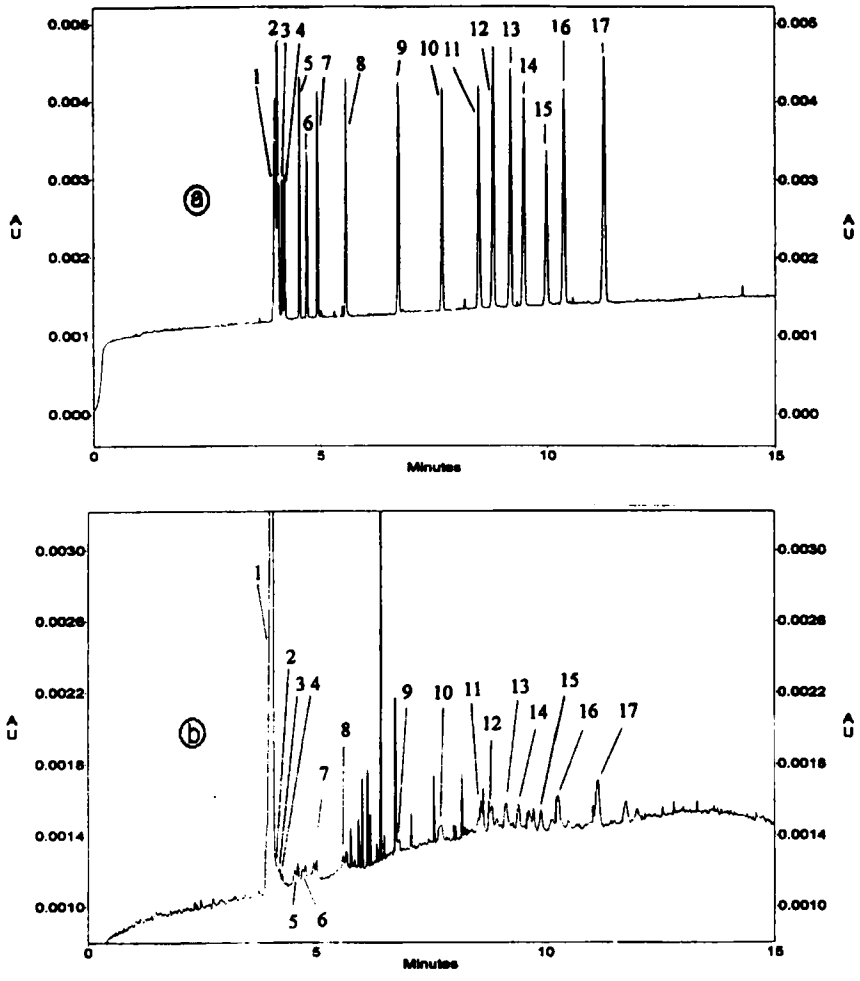

FIGURE 1 Capillary Zone Electrophoretic Separation of Chlorophenol 10 mmol/L phosphate, pH 8.23, acetone 35% v/v, a) standard sample, b) waste water sample spiked with 0.4 mg/L each 17 chlorophenol standard. Numbers over the peaks refer to the congeners listed in Table II

Figure 1a shows that positions of peaks of 2,3,4-trichlorophenol and 2,4,5-trichlorophenol were in the middle of all 17 chlorophenols, implying that these two compounds were suitable to be used as internal standards. When 2,3,4-trichlorophenol was chosen as the internal standard, R.S.D.% for migration times all decreased dramatically (Table II). Average plate numbers given in Table II were more than 200,000 for most chlorophenols, indicating a higher efficiency achieved during the separations. The lower efficiency for 3-chlorophenol was also due to the interference from EOF.

TABLE I pKa Values of Chlorophenols[13,18]

Peak No.	*Congener*	*pKa (water)*	*pKa (methanol/water: 60/40)*
1	4-chlorophenol	9.37	9.70
2	3-chlorophenol	8.97	9.53
3	2-chlorophenol	8.52	9.13
4	3,4-dichlorophenol	8.62	8.87
5	3,5-dichlorophenol	8.25	8.54
6	2,4-dichlorophenol	7.90	8.51
7	2,3-dichlorophenol	7.71	8.52
[a]	3,4,5-trichlorophenol	7.55	7.57
8	2,5-dichlorophenol	7.51	7.69
9	2,3,4-trichlorophenol	6.97	7.34
11	2,6-dichlorophenol	6.80	7.15
10	2,4,5-trichlorophenol	6.72	7.20
12	2,3,5-trichlorophenol	6.43	6.92
[a]	2,4,6-trichlorophenol	5.99	6.51
17	2,3,6-trichlorophenol	5.80	6.10
13	2,3,4,5-tetrachlorophenol	5.64	5.92
15	2,3,4,6-tetrachlorophenol	5.22	5.53
16	2,3,5,6-tetrachlorophenol	5.03	5.76
14	pentachlorophenol	4.74	4.92

a. Not tested in this study.

TABLE II Reproducibilities termed in R.S.D.% and Average Plate Numbers (n=8)

peak No.	*congener*	*peak area*[a]	*migration time*[b]	*migration time*	*average plates*
1	4-chlorophenol	–	0.28%	0.67%	–
2	3-chlorophenol	4.5 %	0.19%	0.64%	39,000
3	2-chlorophenol	4.0 %	0.15%	0.62%	240,000
4	3,4-dichlorophenol	4.4 %	0.17%	0.62%	240,000
5	3,5-dichlorophenol	4.5 %	0.19%	0.64%	240,000
6	2,4-dichlorophenol	4.0 %	0.12%	0.60%	260,000
7	2,3-dichlorophenol	4.2 %	0.10%	0.54%	250,000

peak No.	*congener*	*peak area*[a]	*migration time*[b]	*migration time*	*average plates*
8	2,5-dichlorophenol	4.2 %	0.13%	0.51%	240,000
9	2,3,4-trichlorophenol	4.9 %	0.00%	0.59%	280,000
10	2,4,5-trichlorophenol	4.9 %	0.03%	0.58%	290,000
11	2,6-dichlorophenol	4.8 %	0.32%	0.48%	240,000
12	2,3,5-trichlorophenol	5.0 %	0.09%	0.59%	230,000
13	2,3,4,5-tetrachlorophenol	3.9 %	0.09%	0.58%	210,000
14	pentachlorophenol	5.1 %	0.08%	0.57%	230,000
15	2,3,4,6-tetrachlorophenol	4.2 %	0.14%	0.56%	250,000
16	2,3,5,6-tetrachlorophenol	4.8 %	0.15%	0.57%	230,000
17	2,3,6-trichlorophenol	4.5 %	0.24%	0.56%	200,000

a. Corrected peak areas Ac=AmVapp, Am is measured peak areas, Vapp is apparent mobilities of solutes.
b. 2,3,4-trichlorophenol was used as the internal standard.

Detection linear ranges and limits of detection

The linearity was determined from repeated injections at 9 different concentrations of each chlorophenol. Table III Summarizes the results of linear detection ranges and detection limits acquired by three parallel experiments at every concentration with on-line UV direct detection. All the 17 chlorophenolic congeners were monitored at 214 nm. Detection ranges for the chlorophenolic compounds were linear all over two orders of magnitude of concentrations except for 4-chlorophenol, of which peak area could not be measured accurately because of the interference from EOF. The main disappointing feature of UV detector is its relatively lower sensitivity, although adopting a Z-shaped flow cell[19] or a bubble cell[20] the UV absorbance detection can be improved. This drawback also limited the detection sensitivity towards chlorophenolic congeners. LODs obtained commonly were 1 order magnitude higher than that with electrochemical detection.[21] LODs for higher chlorinated congeners were slightly better than those for lower chlorinated congeners.

APPLICATION

Chlorophenols in a waste water sample from a coke plant in DT area, northern China, was analyzed with the method developed. During analysis, the waste

water sample was directly injected into the separation column without any pretreatment. Figure 1b shows the electrophoregram of the water sample spiked with about 0.4 mg/L of each chlorophenol standard. The result validated the advantages of CZE methods for the determination of chlorophenolic pollutants in water, such as short separation time, avoidance of interference from neutral contaminants, etc. Without any pretreatments before injection, the peak symmetry of chlorophenols at low concentrations was deteriorated somewhat with the complexity of sample matrix. In addition, the low sensitivity of UV detector also made it difficult to measure chlorophenolic pollutants at very low concentrations, especially those with low chlorination. That is why the concentrations of 2,4-dichlorophenol (peak no. 6), 2,5-dichlorophenol (peak no. 8) and 2,4,5-trichlorophenol (peak no. 10) were not given here, although these three pollutants were tentatively detected in the waste water sample. The higher chlorinated chlorophenols and their concentrations detected in the water sample were 2,3,6-trichlorophenol, 0.2 mg/L (peak no. 17), 2,3,5,6-tetrachlorophenol, 0.6 mg/L (peak no. 16), 2,3,4,6-tetrachlorophenol, 0.4 mg/L (peak no. 15), pentachlorophenol 0.4 mg/L (peak no. 14) and 2,3,4,5-tetrachlorophenol, 0.4 mg/L (peak no. 13).

TABLE III Detection Linear Ranges and Limits of Detection of Chlorophenols

peak No.	*congener*	*linear equation*	*correlation coeffi.*	*Linear range (mg/L)*	*LOD (μg/L)*
1	4-chlorophenol	–	–	–	–
2	3-chlorophenol	Y=71.9+86.6*X	0.997	0.4–40	190
3	2-chlorophenol	Y=-8.5+65.5*X	0.998	0.4–40	270
4	3,4-dichlorophenol	Y=-0.1+60.9*X	0.998	0.4–40	200
5	3,5-dichlorophenol	Y=-14.7+98.7*X	0.998	0.4–40	150
6	2,4-dichlorophenol	Y=-3.1+68.3*X	0.998	0.4–40	160
7	2,3-dichlorophenol	Y=-19.3+92.9*X	0.998	0.4–40	160
8	2,5-dichlorophenol	Y=-27.6+98.1*X	0.998	0.4–40	160
9	2,3,4-trichlorophenol	Y=-17.6+91.9*X	0.998	0.4–40	150
10	2,4,5-trichlorophenol	Y=-18.9+89.4*X	0.998	0.2–40	100
11	2,6-dichlorophenol	Y=-32.4+101.2*X	0.998	0.2–40	100
12	2,3,5-trichlorophenol	Y=-20.3+111.7*X	0.998	0.2–40	100
13	2,3,4,5-tetrachlorophenol	Y=-12.3+101.8*X	0.997	0.2–40	100
14	pentachlorophenol	Y=27.6+81.8*X	0.999	0.2–40	100
15	2,3,4,6-tetrachlorophenol	Y=6.8+61.7*X	0.999	0.2–40	110
16	2,3,5,6-tetrachlorophenol	Y=12.3+87.4*X	0.999	0.2–40	110
17	2,3,6-trichlorophenol	Y=-24.9+116.8*X	0.999	0.2–40	100

It is evident that with more sensitive detectors other than the UV detector, relatively lower concentrations of chlorophenolic pollutants could be determined without any pretreatment in the capillary electrophoretic system, otherwise some sample pre-concentration should be adopted before injection.

CONCLUSION

Capillary zone electrophoresis is a fast and convenient separation method with higher separation efficiency for the determination of chlorophenolic pollutants in waste waters when using acetone as the organic modifier. The method can avoid the interference from neutral contaminants to chlorophenol measurements. The analysis time was reduced greatly comparing to GC and MEKC methods. Reproducibilities of migration times and peak areas were excellent. Due to the wide range of detection linear range and the strong resolution power, the samples did not require any pretreatment before analysis. If other kinds of detectors with higher sensitivity than UV detector is adopted, LODs will be improved dramatically and the method can be used to monitor the lower concentrations of chlorophenolic pollutants in water directly.

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