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Separation of Aniline Derivatives by Micellar Electrokinetic Capillary Chromatography

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Abstract: A micellar electrokinetic capillary chromatography (MECC) was developed for the determination of aniline and 6 substituted anilines. The seven components were separated within 25 min in the buffer solution of 40 mmol/L sodium borate and 100 mmol/L SDS. It was found that the separation was dependent on operating voltage, pH value, borate and SDS concentrations. The analytical performance was examined in terms of linear response and reproducibility. Wastewater was determined by the established method.

Keywords: Aniline derivatives, separation, micellar electrokinetic capillary chromatography.

Aniline and its derivatives can originate from industrial, agricultural, and communal activities, and their presence in the environmental water can be used to characterize the nature and the origin of the pollution. Many methods have been developed for their determination1,2. However, due to the environmental samples were very complicated, the use of these means is greatly restricted.

Capillary electrophoresis (CE) is a recently developed technique that offers short analysis time. Micellar electrokinetic capillary chromatography (MECC) is a powerful separation method for both charged and neutral solutes[3] and it is a suitable method for the analysis of environmental samples. In this study, a method for determination of aniline and 6 substituted anilines by MECC was developed.

Experimental

The investigated aniline compounds included aniline, *o*-methylaniline, *m*-methylaniline, *p*-methylaniline, *o*-nitroaniline, 2,5-dimethylaniline, and *p*-bromoaniline were all in analytical grade. The buffer solution was adjusted to various pH values with 1 mol/L NaOH or 1 mol/L HCl. All the solutions were filtrated through a 0.45 μm cellulose acetate membrane filter. The water was double distilled.

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Apparatus and Operation Conditions

MECC was performed using HPCE Analyzer System model 1229 (Beijing Institute of New Technology and Application, Beijing, China) with UV detector. A fused silica capillary of 50 μm ID ×53.5 cm (39.5 cm effective) from Yongnian factory of Photoconductive Fibers (Hebei Province, China) was used as the separation channel. All the anilines were detected at 254 nm. Sample solution was introduced by siphoning sampling at 10 cm for 20 s. The temperature was kept at 25±1 ℃. The applied voltage was 17 kV. *Prior to* experiment, the capillary was washed by alkali for 5 min, by double-distilled water for 3 min, and by buffer solution for 5 min successively. Wastewater 200 mL was adjusted to pH 11.0 by NaOH, extracted by chloroform 20 mL, then condensed and dissolved in methanol to 1 mL.

Results and Discussion

In the electrokinetic sampling, a voltage is applied, which can lead to joule heat effects. So the siphoning sampling was chosen. In 25 mmol/L sodium borate and 10 mmol/L SDS buffer solution at pH 9.0, the effect of operating voltage was investigated. In the range of 15 to 17 kV, the sensibility increased when the voltage increased. But above 17 kV, the resolution was deteriorated because of joule heat. So 17 kV was suggested.

Influence of pH and Concentration of Buffer Solution

Effect of pH is significant for the separation in MECC[4]. High pH value was helpful to the separation because with the increase of pH, the solubility of the seven components in aqueous phase was enlarged. Experiments were performed with 25 mmol/L borate containing 10 mmol/L SDS at different pH values. In the pH range of 7.0~11.0, the resolution increased as pH increased. At low pH, some peaks might overlap. At pH≥10.0, discernible peaks were detected. But the resolution decreased due to zone broadening. Therefore, pH 10.0 was selected.

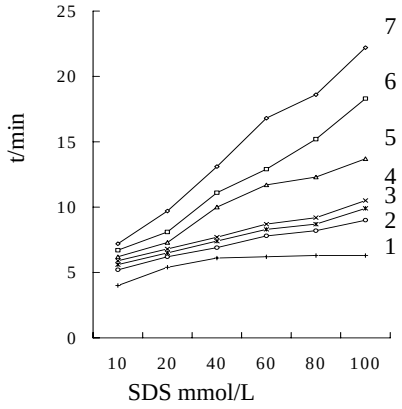
The concentration of sodium borate plays an important role in separation, it also can affect peak shape. For studying the effect of the concentration of sodium borate five different sodium borate concentrations ranging from 10 to 50 mmol/L were tested. A buffer containing 40 mmol/L sodium borate was chosen.

Effect of SDS concentration

SDS is the most widely used surfactant in MECC. To study the effect of the concentration of SDS on separation, 40 mmol/L sodium borate, pH 10.0 with different concentrations of SDS ranging from 10 to 100 mmol/L were tested. From **Figure 1**, the best resolution of seven compounds was observed at 100 mmol/L of SDS.

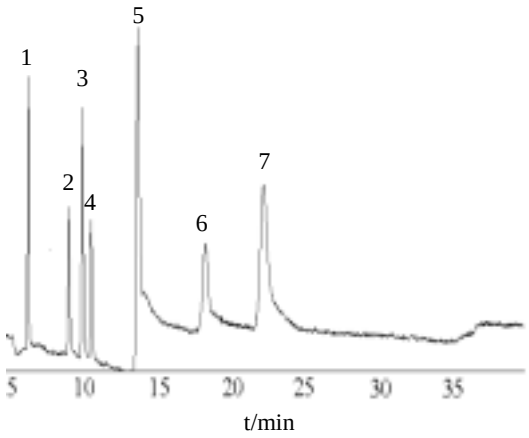
Under the selected conditions, the seven compounds were successfully separated. The electropherogram is shown in **Figure 2.** The detection limit, linearity and reproducibility were listed in **Table 1.**

Figure 1 Dependence of the migration times of aniline derivatives on concentration of SDS



Analysis: 1: aniline, 2: *o*-methylaniline, 3: *m*-methylaniline, 4: *p*-methylaniline, 5:*o*-nitroaniline, 6: 2,5-dimethylaniline, 7: *p*-bromoaniline.

Figure 2 Electropherogram of aniline derivatives under MECC



Condition: voltage: 17 kV; wavelength: 254 nm; temperature: 25±1 ℃; buffer: 40 mmol/L borate, 100 mmol/L SDS, pH=10.0; analysis: 1: aniline, 2: *o*-methylaniline, 3: *m*-methylaniline, 4: *p*-methylaniline, 5:*o*-nitroaniline, 6: 2,5-dimethylaniline, 7: *p*-bromoaniline.

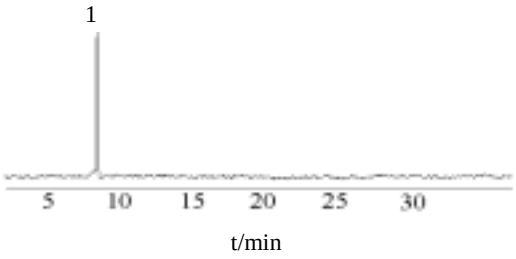
Table 1 The linear range and minimum detectable quantity

Compound	Linear equation	Correlation coeff.	RSD(%) n=8	Min. detectable quantity (mg/L)
aniline	Y= -41939+545.06X	0.997	2.67	4.22
o-methylaniline	Y= -58352+609.02X	0.996	2.79	6.29
m-methylaniline	Y= -62986+762.89X	0.996	2.55	4.58
p-methylaniline	Y= -64545+681.60X	0.996	1.57	6.61
o-nitroaniline	Y= 398.27+268.31X	0.995	2.62	3.77
2,5-dimethylaniline	Y= -65532+785.05X	0.996	2.42	7.29
p-bromoaniline	Y= 4292.5+248.65X	0.998	2.64	5.82

Sample Analysis

The system was employed for the determination of the wastewater from a factory (**Figure 3**). The actual amount of components in the wastewater is 0.97 mg/L.

Figure 3 Electropherogram of wastewater under MECC



Condition: voltage 17 kV; wavelength 254 nm; temperature 25±1 ℃; buffer: 40 mmol/L borate, 100 mmol/L SDS, pH=10.0. 1: *o*-methylaniline in wastewater.

Acknowledgments

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