

Separation of carcinogenic aromatic amines in the food colourants plant wastewater treatment

Ye Shengquan^{a,b,*}, Wu Hui^a, Zhang Chaohua^b, Huang Fu^c

^aCollege of Light Industry and Food, South China University of Technology, Guangzhou 510640, China

^bCollege of Food Science and Technology, Guangdong Ocean University, P.O. Box 302, Hai Ning Road No. 67, Xiashan, Zhanjiang, Guangdong 524005, China
Tel. +86 759 2669688; Fax +86 759 2669826; email: yeshengq@163.com

^cDepartment of Applied Chemistry, Guangdong Ocean University, P.O. Box 302, Hai Ning Road No. 67, Xiashan, Zhanjiang, Guangdong 524005, China

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Abstract

A new method of separation of carcinogenic aromatic amines in wastewater is given. With SDS ($C_{12}H_{25}O_4SN_a$) and β -CD (β -cyclodextrin) addition, it is effective to improve separation. At the same time, it forms mixed micelle.

As a result, a micellar electrokinetic capillary chromatography (MECC) system was established. Nine aromatic amines were separated by the MECC with added lower concentration of β -CD. In the system, the sample entered the capillary at the in positive electrode and was detected at the negative electrode. The experiment revealed that the separation of aromatic amines increased quickly with a slight increase in β -CD concentration in MECC. Nine analytes reach the baseline separation in 13 min.

The retention order of peaks of aromatic amines is related to the number of carbon atoms of the solute molecules and the numbers of amino. When the number of amino groups gets larger, the number of carbon atoms of the solute molecules becomes smaller, and the peaks elute earlier, the 110 mmol/L SDS and 10 mmol/L β -CD were chosen. When the NaH_2PO_4 concentration is from 20 to 60 mmol/L, the separation of aromatic amines increased quickly. And then the 40 mmol/L is chosen. The optimal conditions were 40 mmol/L NaH_2PO_4 (pH 9.6).

Keywords: Wastewater treatment; Separation; Lower electroosmotic flow; Micellar electrokinetic capillary chromatography; Aromatic amine

1. Introduction

Aromatic amines are popular as important environmental pollutants. Aromatic amines and

their *N*-nitroso derivatives are potential carcinogenic agents [1–4]. Aromatic amines are widely used as raw material or at an intermediate stage in the manufacturing of industrial chemicals such as pesticides, medicines, dyestuffs, polymers,

*Corresponding author.

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surfactants, cosmetics and corrosion inhibitors [5,6], especially in the dyestuff plant. As these amines are discharged into the atmosphere and water, they constitute an important class of environmental pollutants. This has increased attention for the development of reliable, sensitive and rapid analytical methods. Several analytical methods have been reported for the determination of aromatic amines. Among them, GC methods are most commonly employed [7–11]. However, it is difficult to analyze aromatic amines by GC due to their polar nature. To overcome these difficulties, it is usually necessary to derivatize them before GC. Flow injection coupled with voltammetry has been employed with diazotization [12] or bromination [13] reactions. These methods involve tedious and time consuming sample preparation. Capillary electrophoresis (CE) has also emerged as fast and efficient tool for chemical analysis, and a few methods for the analysis of aromatic amines using CE are reported in the literature [14–16]. Nevertheless, liquid chromatography (LC) is known as the most convenient technique for aromatic amines. Variety of separation and detection methods for the analysis of anilines has been reported [17–22].

According to the EU regulations the limit of detection of analytical methods should be as low as $0.1 \mu\text{g L}^{-1}$ for the study of environmental pollutants in water [23]. It is difficult to obtain such a low detection limit with path length dependent UV and fluorescence detectors. Although, better sensitivities could be achieved using laser induced fluorescence detector (LIF), expensive instrumentation makes its routine use difficult. Moreover, LIF detection of aromatic amines requires adding a fluorescent tag to them. Mass spectrometer can be used with LC for qualitative and quantitative analysis of aromatic amines but mass spectra of aromatic amines are often not ideal if these compounds are present in low concentrations [24]. Aromatic amines are well known to show good electrochemical behaviour due to the presence of amino group that permits

their sensitive electrochemical detection (ECD) without making derivatization a prerequisite. There are reports on the analysis of aromatic amines by LC-ECD [25–31] but they involve tedious procedures leading to analysis period longer than 1 h. In an ion-exchange method with ECD and gradient elution [32] the analysis time for nine anilines was 30 min. To date, many sample preconcentration methods have been developed as alternatives of the conventional liquid–liquid extraction and the well-developed solid phase extraction for enrichment of aromatic amines [33,34]. Solid phase microextraction (SPME) [35,36], and liquid–liquid–liquid microextraction with hollow fibers [37] were well documented. Membrane extraction is another kind of useful sample preconcentration technique [38–40], in which microporous liquid–liquid extraction has been used for trace enrichment prior to HPLC [41,42], but there are very few research reports about β -CD (β -cyclodextrin) addition coupled with micellar electrokinetic capillary chromatography (MECC) [43–45]. And no papers based on β -CD-MECC focusing analysis of aromatic amines are found.

The high sensitivity and selectivity of lower β -CD concentration micellar electrokinetic capillary chromatography (β -CD-MECC), as reported here, offer considerable advantages in the separation of aromatic amines. This paper presents a simple method for the separation of nine carcinogenic aromatic amines in the synthetic food colourants plant wastewater. The subject is to establish a method for effective analysis of the level of aromatic amines in water samples by making use of β -CD addition coupled with MECC. The different aspects affecting the extraction efficiency such as SDS, β -CD, NaH_2PO_4 concentration and flow rate effect were optimized. The separation was complete within 13 min using β -CD-MECC. The proposed study provides a simple, fast, sensitive method for determination of aromatic amines in water samples. The method has also been applied to the analysis of aromatic

amines in sea water and the dyestuff plant wastewater treatment.

2. Experimental

2.1. Instrumentation

CE separations were performed on a HP^{3D} CE system (Agilent Technologies, USA) equipped with an on-column diode array detection (DAD) system. Detection wavelength of 214 nm and experiment temperature at 25°C was kept throughout. Uncoated fused quartz capillaries (obtained from Hebei Yongnian Implements, Hebei, China), a total length of 56.5 cm and effective length of 41.5 cm, inner diameter of 50 µm were used. New capillary was flushed with ultrapure water and 1 mol L⁻¹ sodium hydroxide each for 10 min. Before injections, the capillary was conditioned by sequential flushing with 1 mol L⁻¹ sodium hydroxide, ultrapure water, and run buffer for 10, 20 and 15 min, respectively. After each run the capillary was washed for 5 min with the separation electrolyte. Spectra 100 UV–vis (Thermo Separation Products, USA) was used for UV detection.

2.2. Chemicals and reagents

Nine aromatic amines including *p*-aminobenzenesulfonamide, aniline, *p*-nitroaniline, *p*-aminobenzenesulfonic, *o*-toluidine, *N,N*-dimethylaniline, benzidine, diphenylamine, *o*-toluidine were purchased from Acros Organics (NJ, USA). Ethanol, SDS, β-CD, NaH₂PO₄, sodium dihydrogen phosphate, phosphoric acid, ethylene diamine were from Beijing Chemical Factory (Beijing, China). The water used throughout was purified from a Milli-Q ultrapure water purification system (Millipore).

The nine aromatic amines were dissolved in ethanol to achieve a stock solution with a concentration of 0.5 mg mL⁻¹. All these standard solutions were kept at 4°C. Working solution was obtained from dilution of stock solution.

The NaH₂PO₄ was prepared with ultrapure water of concentrations as 0.02, 0.04, 0.06 and 0.08 M, respectively. Electrophoresis buffer was freshly prepared daily from sodium dihydrogen phosphate, phosphoric acid, ethylene diamine stock solutions, organic solvent was added into the electrophoresis buffer based on the study for achieving better separation.

2.3. Electrophoresis conditions

Capillary electrophoresis separation was investigated, and the affecting factors such as SDS, β-CD, NaH₂PO₄ concentration and flow rate effect were optimized. In this process, the sample entered the capillary at the in positive electrode, pressure injection mode with 10 cm high and 10 s was adapted, and 26 kV was selected as the application voltage. The optimized buffer matching parameters and the injection and separation parameters were used for optimizing conditions of LEOF-MECC.

2.4. Procedures

Standard solutions of nine aromatic amines were spiked into purified water to obtain testing concentration, respectively. A 100 mL sample was used as the test volume for all the optimization process. The sample flow rate was set as 0.05 µL min⁻¹. After enrichment, the acceptor phase was taken out with a volume of 2 mL, and then dried with a mild nitrogen stream. Finally, analytes were dissolved in 0.08 M NaH₂PO₄ for electrophoresis analysis.

3. Results and discussion

3.1. Separation of nine aromatic amines

The results showed that nine aromatic amines including *p*-aminobenzenesulfonamide, aniline, *p*-nitroaniline, *p*-aminobenzenesulfonic, *o*-toluidine, *N,N*-dimethylaniline, benzidine, diphenylamine

and *o*-toluidine have performance for the separation. The electrophoresis separation conditions was optimized, and the optimal separation buffer solution contained 110 mmol/L SDS, 10 mmol/L β -CD, 40 mmol/L NaH_2PO_4 , pH 9.6 and 26 kV. The separation was complete within 13 min.

3.2. Optimization of SDS and β -CD concentration

To obtain the optimum separation performance, several probable factors were investigated and discussed in conditions detail, respectively.

3.3. SDS concentration selection

With the higher SDS concentration ($C \geq 100$ mmol/L), it is effective to improve separation. At the same time, the migration time of electro-osmotic flow is more 110 min, and the migration time of aromatic amines is less 13 min. When the NaH_2PO_4 concentration is from 20 to 60 mmol/L, the migration time of aromatic amines increased quickly. And then the 110 mmol/L SDS, 40 mmol/L NaH_2PO_4 are chosen.

3.4. Effect of β -CD concentration

The distribution of β -CD in the micellar phase increases with added β -CD when the concentration of β -CD is lower. The β -CD concentration was optimized over the range of 5–15 mmol/L while keeping the other conditions unchanging. When the β -CD concentration to be changed, the separation of aromatic amines increased quickly. And then the 10 mmol/L β -CD was chosen.

3.5. Effect of NaH_2PO_4 concentration on sample migration time

As β -CD was concerned, the sample migration time posed a profound influence on the separation efficiency. High-migration time give rise to

low- NaH_2PO_4 concentration efficiency. Effect of NaH_2PO_4 concentration on sample migration time had been explored in the range of 0.02–0.08 M, with the results exhibited in Fig. 1 and Table 1. As Fig. 1 elucidated, generally the aromatic amine has higher separation performance at lower NaH_2PO_4 concentration. When the NaH_2PO_4 concentration was larger than 0.06 M, the separation efficiency decreased. To obtain the higher trapping and decrease the time needed, 0.06 M was adopted for application.

3.6. Linear range, detection limit, separation efficiency

In order to check the feasibility of established method for quantitative analysis, we have investigated the linearity and detection limits and repeatability of the nine aromatic amines under the optimal separation conditions.

The repeatability was investigated by analyzing nine aliquots spiked with 4 mg L^{-1} *p*-aminobenzenesulfonamide, 4 mg L^{-1} aniline, 3 mg L^{-1} *p*-nitroaniline, 4 mg L^{-1} *p*-aminobenzenesulfonic, 4 mg L^{-1} *o*-toluidine, 4 mg L^{-1} *N,N*-dimethylaniline, 4 mg L^{-1} benzidine, 6 mg L^{-1} diphenylamine and 4 mg L^{-1} *o*-toluidine. The results of separation

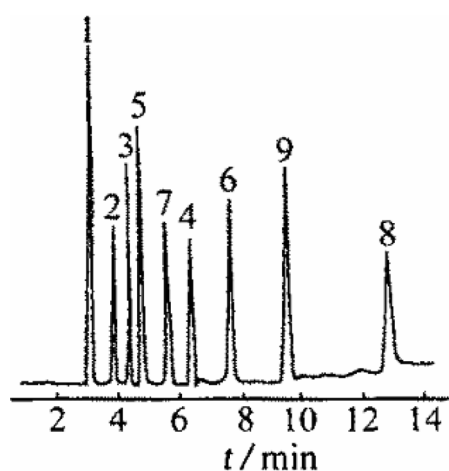


Fig. 1. Separation of anilines in MECC system (numbers same as in Table 1).

Table 1
Structural formula and pK values of 9 anilines


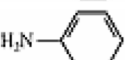


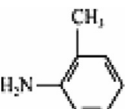
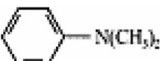
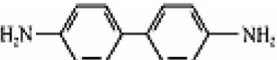
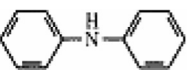
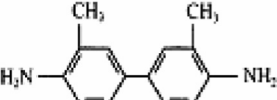
Serial no.	Name of compound	Empirical formula	Structural formula	pK _a	pK _b
1	<i>P</i> -amino-benzene-sulfonamide	C ₆ H ₆ N ₂ O ₂ S		10.5	–
2	Aniline	C ₆ H ₇ N		–	9.39
3	<i>P</i> -nitroaniline	C ₆ H ₇ N ₂ O ₂		–	13.01
4	<i>P</i> -amino-benzene-sulfonic	C ₆ H ₇ NO ₂ S		3.22	–
5	<i>O</i> -toluidine	C ₇ H ₃ N		–	9.56
6	<i>N,N</i> -dimethylaniline	C ₈ H ₁₁ N		–	8.85
7	Benzidine	C ₁₂ H ₁₂ N ₂		–	pK _{b1} –9.32 pK _{b2} –10.37
8	Diphenylamine	C ₁₂ H ₁₁ N		–	13.15
9	<i>O</i> -tolidine	C ₁₄ H ₁₆ N ₂		–	pK _{b1} –8.21 pK _{b2} –9.54

Table 2
Range of linearity, detection limit and separation efficiency of the nine kinds of aromatic amines

No.	Compound	Linear range (c/mol L ⁻¹)	Correlation coefficient	Detection limit (c/mol L ⁻¹) (n = 10) (S/N = 3)	Separation efficiency (N/m)
1	<i>P</i> -aminobenzenesulfonamide	2.9 × 10 ⁻⁴ ~1.3 × 10 ⁻³	0.9991	1.7 × 10 ⁻⁴	6.5 × 10 ⁵
2	Aniline	8.1 × 10 ⁻⁴ ~6.2 × 10 ⁻³	0.9983	4.5 × 10 ⁻⁴	8.0 × 10 ⁵
3	<i>P</i> -nitroaniline	9.8 × 10 ⁻⁵ ~5.6 × 10 ⁻⁴	0.9978	6.5 × 10 ⁻⁵	1.4 × 10 ⁶
4	<i>P</i> -aminobenzenesulfonic	1.7 × 10 ⁻⁴ ~8.9 × 10 ⁻⁴	0.9962	1.1 × 10 ⁻⁴	1.7 × 10 ⁶
5	<i>O</i> -toluidine	6 × 10 ⁻⁴ ~9.1 × 10 ⁻⁴	0.9970	9.6 × 10 ⁻⁵	1.0 × 10 ⁶
6	<i>N,N</i> -dimethylaniline	9.5 × 10 ⁻⁶ ~6.7 × 10 ⁻⁵	0.9988	6.7 × 10 ⁻⁶	2.8 × 10 ⁶
7	Benzidine	7.3 × 10 ⁻⁶ ~6.2 × 10 ⁻⁵	0.9968	2.9 × 10 ⁻⁶	1.5 × 10 ⁶
8	Diphenylamine	6.3 × 10 ⁻⁶ ~3.6 × 10 ⁻⁵	0.9965	5.3 × 10 ⁻⁶	5.0 × 10 ⁵
9	<i>O</i> -tolidine	9.3 × 10 ⁻⁶ ~7.5 × 10 ⁻⁵	0.9972	5.6 × 10 ⁻⁶	1.7 × 10 ⁶

Table 3
Recovery of nine kinds of aromatic amines in water samples

Compound	Added (mg/L)	Found (mg/L)	Recovery (%)	RSD (%) ($n = 10$)
<i>P</i> -aminobenzenesulfonamide	98.2	96.5	98.3	2.1
Aniline	105.1	102.3	97.3	2.3
<i>P</i> -nitroaniline	100.0	102.5	102.5	3.1
<i>P</i> -aminobenzenesulfonic	97.5	99.6	102.2	2.5
<i>O</i> -toluidine	100.0	97.6	97.6	2.2
<i>N,N</i> -dimethylaniline	100.0	103.9	103.9	2.0
Benzidine	100.0	102.2	102.2	1.8
Diphenylamine	100.0	97.0	97.0	1.6
<i>O</i> -tolidine	100.0	102.0	102.0	1.9

efficiency were within the range 5.0×10^5 – 2.8×10^6 N m⁻¹ for all the aromatic amines as shown in Table 2.

Experiments showed that for all the studied analytes, there were excellent linear relationship between the concentration and the peak height over the concentration range listed in the Table 2. The correlation coefficients were excellent with the R^2 values larger than 0.99 and detection limits ($S/N = 3$) were in the range of 2.9×10^{-6} – 4.5×10^{-4} mol L⁻¹ as shown in Table 2. Jeevan et al. [46] have developed a method for analysis of aromatic amines with MEKC after SPE and LLE, in which the detection levels were in the range of 0.227–7.801 $\mu\text{g mL}^{-1}$. Although the sample volume was smaller, the final detection level would be still much lower than that of this proposed method even if the difference of sample volume was considered. Therefore, this present method was very sensitive and would be able to analyze aromatic amines with a wide range.

3.7. Real sample analysis and recovery

Three real water samples including tap water, river water and water from the synthetic food colourants plant wastewater treatment were determined with the established method. The nine aromatic amines were found in water sample from the dyestuff plant wastewater. On the other

hand, as one important characteristic of a sample preparation methodology, recovery has the most flexible proof of what is acceptable. Therefore, the recoveries of aromatic amines in the real water samples were also examined with spiking standard solution with concentration as that of evaluating the repeatability. As shown in Table 3, satisfactory recoveries in the range of 97.0–103.9% and 1.6–3.1% RSD were obtained.

4. Conclusion

An analytical method based on combination β -CD with micellar electrokinetic capillary chromatography (MECC) to determine the levels of aromatic amines in the synthetic food colourants plant wastewater has been developed. The sample entered the capillary at the in positive electrode with lower β -CD concentration, the aromatic amines was detected at the negative electrode. The experiment revealed that the separation of aromatic amines increased quickly with a slight increase in β -CD concentration in MECC. Nine analytes reach the baseline separation in 13 min. The retention order of peaks of aromatic amines is related to the number of carbon atoms of the solute molecules and the numbers of amino. When the number of amino groups gets larger, the number of carbon atoms of the solute molecules becomes smaller, and the peaks elute earlier. It

combines the advantages of mixed micelle of MECC, of conventional SDS micelle and rapid separation of CE. This method showed excellent recoveries, repeatability and detection limits. In view of simplicity, sensitivity, quantitiveness, and being environment-friendly, the method is an excellent method for aromatic amines analysis.

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