

SEPARATION AND DETERMINATION OF SIX METAL CATIONS BY CAPILLARY ZONE ELECTROPHORESIS

JINZHANG GAO*, XIANGLI SUN, WU YANG, HAIFENG FAN, CHONGYANG LI AND XUEFENG MAO

(Chemistry & Chemical Engineering College, Northwest Normal University, Lanzhou 730070, P. R. China)

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ABSTRACT

A rapid, simple and reliable method was devised for separation and determination of six metal cations, based on the capillary zone electrophoresis. The results showed that the complete separation of K^+ , Cu^{2+} , Zn^{2+} , Mn^{2+} , Pb^{2+} and Cd^{2+} can be achieved within 5 min. A new electrolyte system containing 15 mmol·L⁻¹ imidazole as a background absorbance reference and 8 mmol·L⁻¹ malonic acid, 2 mmol·L⁻¹ 18-crown-6 ether as the complexing agents, 10% methanol as an organic modifier, by using acetic acid to adjust the pH=4.40 was developed. The applied voltage was 20 kV at 25 °C. Under the optimum conditions, 6 ions were separated and determined with the correlation coefficient of 0.9984-0.9993. The detection limits (S/N=3) from 0.05 (K^+) to 0.75 (Zn^{2+}) mg·L⁻¹. The repeatability of migration times was less than 0.60% and of peak area ranged from 3.4 to 5.6% (n=6). The results were compared with AAS for analyzing the real samples of waste-water and snow water.

Keywords: Electrolyte composition; metal cations; capillary zone electrophoresis

INTRODUCTION

As a separation technique the capillary electrophoresis (CE) is extremely useful in organic analysis and has been used successfully in many areas. In marked contrast to the extensive studies of organic compounds, very few works of inorganic ions have been reported. The first paper concerning the indirection detection of inorganic ions by using CE was reported by Hjerten [1] in 1967. Since then, the application to the separation and determination of inorganic substances has developed rapidly and many papers have been published [2-3], in which the capillary zone electrophoresis (CZE) is one of the widely used capillary electrophoresis techniques, and some of critical reviews have been summarized [4-7]. The use of capillary zone electrophoresis for the analysis of cations in water samples has been studied [8-12]. In recent years, although many instrumental analysis have been used in environmental water samples, such as ion chromatography (IC) [13], atomic absorption spectroscopy (AAS) [14], as well as inductively coupled plasma combined with mass spectrometry (ICP-MS) [15], the capillary zone electrophoresis holds the promise of even better separations and lower sample consumption [16]. Simultaneous determination of copper, cobalt and cadmium, manganese and lead were found to be influenced by the derivative spectrophotometry [17]. For the purpose, in this paper a new electrolyte system contained 15 mmol·L⁻¹ imidazole as background absorbance reference, 8 mmol·L⁻¹ malonic acid and 2 mmol·L⁻¹ 18-crown-6 ether as the complexing agents, 10% methanol as an organic modifier, pH adjusted by acetic acid (50%, V/V) to 4.40 was developed. The satisfactory results indicated that the proposed method could be used in water analysis.

EXPERIMENTAL

2.1. Instrumentation

Separation was performed on a P/ACE 5510 apparatus (Beckman Instruments, USA) equipped with a UV detector and wavelength filters (190, 200, 214, 254 and 280 nm). A fused silica capillary (total length 47 cm, 75 µm i.d.; Yongnian Fiber Optic Factory, China) was used. The distance from the point of injection to the detection window was 40 cm. Gold software System was used for data acquisition. A mode 211 pH-meter (HANNA, Italy) was used. Electromigration injection was carried out by using a voltage of 5 kV for 5 s. The separation temperature of 25 °C and the applied separation voltage of 20 kV were used, respectively.

2.2. Reagents and solutions

All reagents were of analytical grade and used as received from Tianjin Chemical Reagent Factory, China. Imidazole and 18-crown-6 ether were obtained from Sigma (Sigma Chemical Co., St. Louis, MO, USA). All solutions and electrolytes were prepared with ultra-pure water from a Milli-Q system (Millipore, Germany). Stock standard solutions of various metal cations (1g·L⁻¹) were obtained by dissolving their corresponding inorganic salts (nitrates, sulfates or chlorides), and stored in refrigerator prior to use.

2.3. Procedures

Before the use, the capillary was rinsed with 0.1 mol·L⁻¹ NaOH and ultra-pure water for 5 min, followed by the used carrier electrolyte for 10 min. The capillary was rinsed for 2 min with carrier electrolyte between runs. All electrolytes and samples were filtered through a 0.45 µm membrane filter and degassed by ultrasonication prior to analysis.

RESULTS AND DISCUSSION

In general, most inorganic anions and cations have no strong absorption in UV-visible spectral region. For improving the sensitivity, complex reactions are commonly used, that is, adding some complexing agent (such as α-hydroxyisobutyric acid (HIBA), citrate, EDTA and acetic acid) into the electrolytic solution. If so, some factors in operation, e.g., the composition and concentration of buffer, pH adjustment as well as voltage and temperature, should be optimized in advance.

3.1. Optimization of the running buffer

The running buffer composition and concentration affect basically the sensitivity and selectivity. Padaruskas et al. [18] pointed out that the separation efficiency was proportional to running buffer concentration. The larger running buffer concentration, the higher separation efficiency. In this study, we use imidazole in buffer as the background absorption at 214 nm to examine the operation conditions. The influence of imidazole concentration was studied from 5 to 18 mmol·L⁻¹ while the background electrolyte (BGE) was at pH=4.40. Too low concentration may broaden the cation peak to cause difficult in separation. With increasing the concentrations of electrolyte, a better resolution was observed. However, when the concentration of imidazole was over 15 mmol·L⁻¹, the large Joule heat would produce to make the baseline excursion. Thereby the suitable concentration of 15 mmol·L⁻¹ was chosen.

Generally, most of single cations are difficult to separate directly by CE, as their migration velocities are very close to each other. The use of some weak complexing agents, such as HIBA, malic, glycolic, tartaric and malonic, can improve the separation efficiency. In this study, malonic acid of 8 mmol·L⁻¹ was used for separating 6 cations, just showing in Figure 1.

Fig 1 shows that K^+ and Mn^{2+} cannot be complete baseline separation by using malonic acid only. Some papers reported [16,19,20] that the addition of crown ether (18-crown-6 ether) could improve the selectivity. For improving the separation between K^+ and Mn^{2+} ions we investigated the effect of 18-crown-6 ether on the separation showing in Figure 2. Results indicated that adding 2 mmol·L⁻¹ of 18-crown-6 ether in the electrolyte makes a good baseline separation for 6 cations within 5 min.

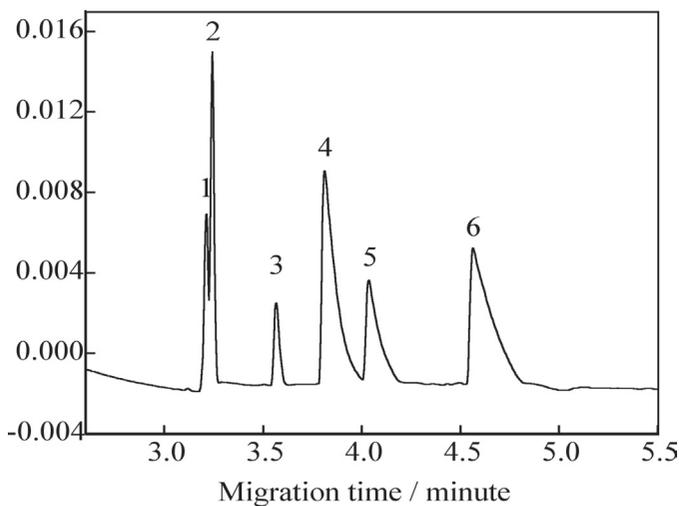


Figure 1. Electropherogram separation for 6 cations. Electrolyte: 15 mmol·L⁻¹ imidazole, 8 mmol·L⁻¹ malonic acid, pH 4.40. Injection conditions: electromigration injection; 5 kV, 5 S. Separation voltage: 20 kV. Temperature: 25 °C. Indirect UV detection at 214 nm. 1. K⁺; 2. Mn²⁺; 3. Pb²⁺; 4. Cd²⁺; 5. Zn²⁺; 6. Cu²⁺

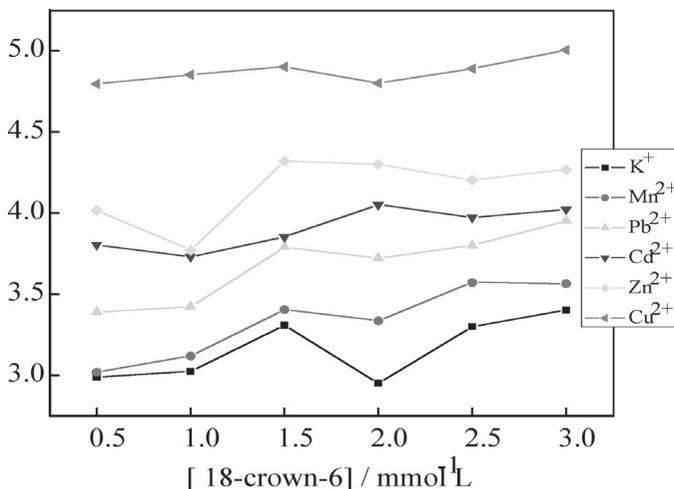


Figure 2. Effect of 18-crown-6 ether concentrations on the migration time of six metal cations. Electrolyte: 15 mmol·L⁻¹ imidazole, 8 mmol·L⁻¹ malonic acid, 10% methanol, pH 4.40. Injection conditions and time as same in Figure 1.

In the pre-experimental, the addition of methanol was found to improve the property of electrolyte solution. In this study, 10% of methanol was suitable. More or less than the value would decrease the separation efficiency.

3.2. pH of the running buffer

The separation of metal cations should carry out in acidic media, due to the precipitation of heavy metal ions being formed in basic solutions [12]. Moreover, the electroosmotic flow (EOF) can be affected by the pH of running buffer. In the experimental, the effect of pH on the sensitivity was studied in the range of 3.80-4.80. If the pH were less than 3.80, the separation between Pb²⁺ and Cd²⁺ would be difficult; more than pH 4.40, the migration time would be prolonged and the noise dramatically increased. As shown in Figure 3, the optimum condition was chosen at pH = 4.40.

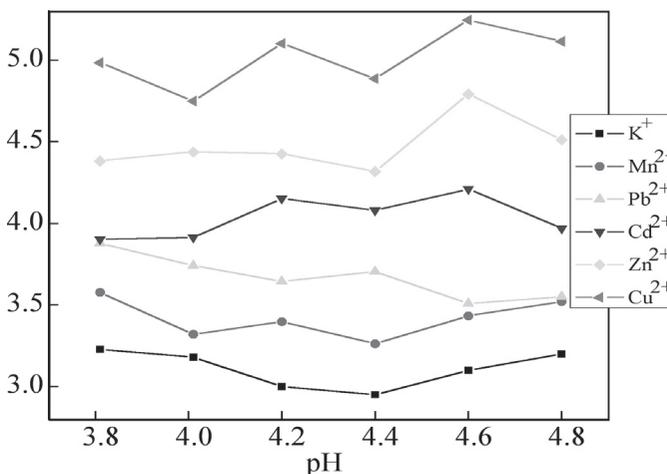


Fig.3. Effect of electrolyte pH on the migration time of six cations. Electrolyte: 15 mmol·L⁻¹ imidazole, 8 mmol·L⁻¹ malonic acid, 2 mmol·L⁻¹ 18-crown-6 ether 10% methanol, pH 4.40. Injection conditions and time, the same as in Figure 1.

3.3. Choice of voltage and temperature

Generally, both applied voltage and temperature affect migration time of ions in electrolyte. With increasing the applied voltage the migration time of ions shortens; the higher temperature could also cause the migration time to be short. That is to say, under higher voltage and temperature the speed of ions would be faster. However, high voltage can cause the Joule-heat formed to raise temperature, and higher temperature gives a bad repeatability. A suitable way (20 kV at 25 °C) in the study was adopted. As shown in Figure 4, under the chosen conditions, a complete baseline separation for 6 ions (K⁺, Cu²⁺, Zn²⁺, Mn²⁺, Pb²⁺ and Cd²⁺ with 10 mg·L⁻¹) was done within 5 min.

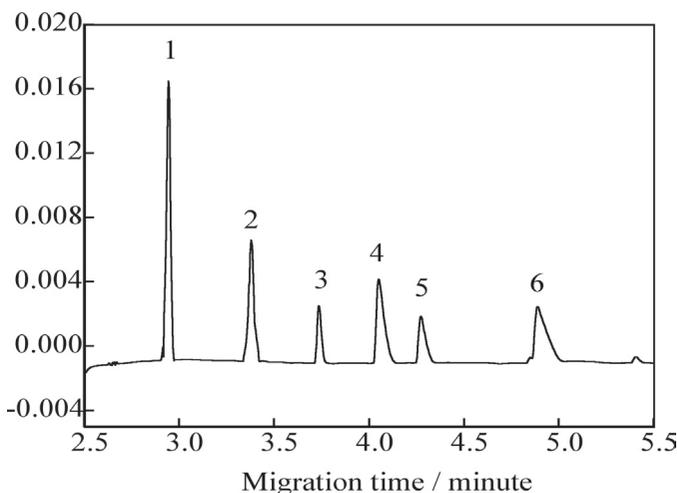


Figure 4. Separation of a standard cations mixture. Electrolyte: 15 mmol·L⁻¹ imidazole, 8 mmol·L⁻¹ malonic acid, 2 mmol·L⁻¹ 18-crown-6 ether and 10% (V/V) methanol; pH 4.40; Voltage: +20 kV; Temperature: 25 °C; electromigration injection (5 kV, 5 S); indirect UV detection at 214 nm. 1.K⁺; 2.Mn²⁺; 3.Pb²⁺; 4.Cd²⁺; 5.Zn²⁺; 6.Cu²⁺

3.4. Quantitative analysis

Under the proposed conditions, a mixture containing 6 metal ions was detected. The linear range, detection limit and correlation coefficient are listed in Table 1. To ensure the corrected data mentioned above, each point was detected in triplicate. The correlation coefficients were limited from 0.9984 to 0.9993. Limit of detection (LOD) was defined as the analyte concentrations corresponding to a signal equal to three times the background noise (S/N=3), which were found to be from 0.05 to 0.75 mg·L⁻¹.

Table 1.- Determination limit (LOD) and correlation coefficient (r) of cations analyses

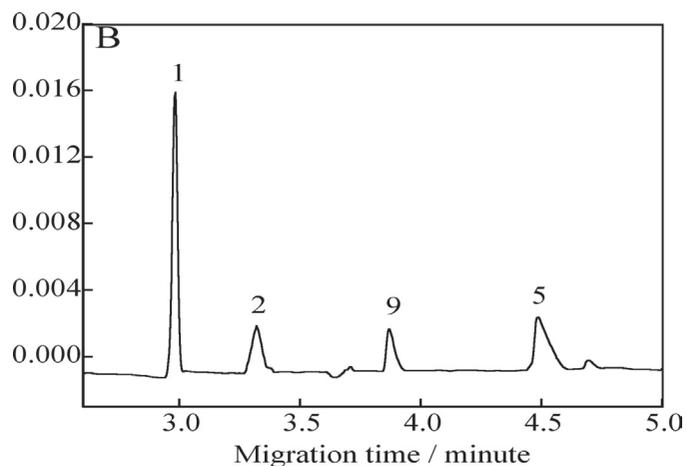
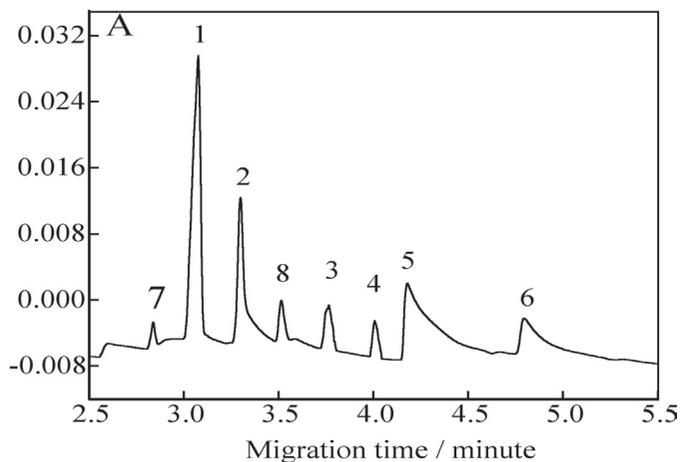
Analytes	Limit of detection (LOD) (mg·L ⁻¹)	Linear range (mg·L ⁻¹)	Correlation coefficient (r)
K ⁺	0.05	0.5-30	0.9986
Cu ²⁺	0.05	0.2-30	0.9993
Zn ²⁺	0.75	1-30	0.9991
Mn ²⁺	0.1	0.2-30	0.9987
Cd ²⁺	0.1	1-32	0.9984
Pb ²⁺	0.1	0.5-20	0.9989

The repeatability of the proposed method was evaluated by a standard solution containing 6 ions with 5 mg·L⁻¹; which was determined repeatedly for 8 times. Table 2 indicated that the relative standard deviation (RSD) of peak area was ranged from 3.4% to 5.6%.

Table 2.- Relative standard deviations (RSD) of Migration times and Peak area (n=8).

Analytes	Migration time (RSD, %)	Peak area (RSD, %)
K ⁺	0.33	4.8
Cu ²⁺	0.42	5.6
Zn ²⁺	0.55	3.9
Mn ²⁺	0.36	3.7
Cd ²⁺	0.39	3.4
Pb ²⁺	0.47	4.4

Under the optimum conditions, some of real samples, such as wastewater and snow water, were examined by the proposed method. The data obtained by CZE are in good agreement with those detected by atomic absorption spectrometry (AAS). Moreover, the recovery test was also carried out with the satisfactory results. All results are given in Figure 5, Table 3 and Table 4.

**Figure 5.** Electropherogram of the cations in (A) waste water and (B) snow water samples with proposed method. Experimental conditions: the same as in Fig. 4.

1. K⁺; 2. Mn²⁺; 3. Pb²⁺; 4. Cd²⁺; 5. Zn²⁺; 6. Cu²⁺; 7. NH₄⁺; 8. Ni²⁺; 9. Co²⁺;

Table 3: Analytic results of six metal cations in the water samples. (Unit: mg·L⁻¹)

Samples	Element	Found by CZE	Found by AAS
Waste water	K ⁺	7.96	7.92
	Cu ²⁺	2.21	2.27
	Zn ²⁺	3.46	3.40
	Mn ²⁺	0.88	0.91
	Cd ²⁺	1.12	1.07
	Pb ²⁺	1.51	1.58
	NH ₄ ⁺	0.23	
	Ni ²⁺	0.66	
	Snow water	K ⁺	8.80
	Cu ²⁺	ND	0.12
	Zn ²⁺	1.08	1.13
	Mn ²⁺	0.34	0.30
	Cd ²⁺	ND	ND
	Pb ²⁺	ND	ND
	Co ²⁺	0.10	

*: semi-quantive; ND means that this ion has not been found by using CZE and/or AAS techniques.

Table 4.- Recoveries (%) obtained by the method of standard additions for analyzed cations in snow water.

Cations	Added amount (mg·L ⁻¹)	Found amount (mg·L ⁻¹)	Recovery (%)
K ⁺	5.00	13.52	94.4
Cu ²⁺	5.00	4.92	98.4
Zn ²⁺	5.00	6.10	100.4
Mn ²⁺	5.00	5.33	99.8
Cd ²⁺	5.00	4.88	97.6
Pb ²⁺	5.00	5.04	100.8

4. CONCLUSIONS

Although capillary zone electrophoresis is used to determining the organic compounds, the application to inorganic ions is quite successful, too. In this paper, we studied the separation of 6 ions by CZE. The background electrolyte consists of 15 mmol·L⁻¹ imidazole, 8 mmol·L⁻¹ malonic acid, 2 mmol·L⁻¹ 18-crown-6 ether, and 10% methanol. The pH of solution was 4.40 at 25 °C and applied voltage 20 kV. Under conditions, 6 metal-ions in real samples were separated and detected successfully within 5 min. The proposed method can be used in environmental analysis.

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