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Original Article

Determination of transitions metal ions as complexes with 2, 6-pyridinedicarboxylic acid by capillary electrophoresis

Narumol Vachirapatama* and Nilnet Theerapittayatakul

Department of Chemistry, Faculty of Science and Technology,
Thammasat University, Rangsit, Pathum Thani, 12121 Thailand.

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Abstract

A capillary electrophoresis (CE) method for the simultaneous separation of transition metal ions was developed on a fused-silica column coated with poly(diallyldimethylammonium chloride) (PADDC). **2,6** -pyridine dicarboxylic acid (PDC) was used to form on-column complexation with metal ions and were detected at UV wavelength. Ten metal ions, Ni (II), Cu(II), Zn(II), Fe(II), Fe(III), Co(II), Cd(II), V(IV), Pb(II), and Mn(II), were studied using **5** mM **2,6-** pyridine dicarboxylic acid containing 4 mM tetrabutylammonium hydroxide at pH 4.0 as a background electrolyte. The external standard calibration curve exhibited good linearity (R^2 is 0.9927 to 0.9982) and the detection limits (determined at signal to noise ratio equal three) were 0.07-2.2 mg/L by using a 6 sec injection time, at 50 mbar and -20 kV power supply. The %-relative standard deviation (n=5) for migration time, peak area and peak height of ten metal ions were 0.52-0.95, 0.26-2.5, and 0.89-3.3, respectively. The developed capillary electrophoresis method was successfully applied to determine metal ions in the plating solution.

Keywords: transition metal ions, complexation, capillary electrophoresis, **2,**6-pyridine dicarboxylic acid**,** plating solution

1. Introduction

Transition metal concentration plays an important role in the environment, soil and water, and in industries, for example plating industries. Therefore, simple, sensitive, and rapid methods are required for the determination of transition metal ions in real samples. Currently, several methods are used for the determination of transition metal ions, such as atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), and ion chromatography (IC). However, simultaneous multi-element analysis for AAS is impossible, while ICP-AES and ICP-MS instruments are still expensive. The disadvantages of IC are its large consumption of effluent and high costs for the column.

Capillary zone electrophoresis (CZE) has rapidly developed over the past few years and became an alternative method for the analysis of transition metal ions because of its advantages in speed, resolution, and simplicity. The background electrolyte of the CZE for the separation of the transition metal ions was selected with its mobility similar to the analytes in order to avoid fronting or tailing of the peak at the optimal pH. To provide a greater difference in electrophoretic mobility, the addition of a complexing agent to the electrolyte in order to form metal complexes has been used (Qin and Li, 2004). **2,6** -pyridine dicarboxylic acid (PDC) was often selected as a ligand added into an electrolyte to form complexes with metal ions on a bare fused silica column with UV detection (Chen *et al.*, 2001; Chen *et al.*, 2002; Chen *et al.*, 2004; Soga *et al.*, 1999). The results showed that the PDC strongly formed anionic complexes with metal ions. However, a good peak shape and a low detection limit were the requirements to improve the analysis of cations in real samples. From previous works, many different ligands used as complexing

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* Corresponding author.
Email address: nvachira@yahoo.com

agents were added into the background electrolyte for the separation of alkali, alkali earth, and transition metal. For example, 4-aminopyridine-hydroxyisobutyric acid (HIBA) was used for the analysis of K^+, Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, and Cu^{2+} in water samples obtained from a river that was polluted by copper industry (Shakulashvili *et al.*, 2000). Imidazole-acetic acid was used for the analysis of K^+, Ba^{2+}, Ca^{2+}, Na^+, Mg^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Li^+, and Cu^{2+} in a grape and pineapple juice (Suarez-Luque *et al.*, 2006), while imidazole-HIBA electrolyte was used for separation of K^+, Ca^{2+}, Na^+, Mg^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Co^{+2}, and Zn^{2+} (Sze et al., 2007). N,N-dimethylbenzylamine-lactic acid-(18-crown-6 ether) was used for the analysis of Rb^+, NH_4^+, K^+, Na^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Fe^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} in orange juice and tea extract (Fung *et al.*, 2006). Furthermore, background electrolytes containing pyridine-glycolic-(18-crown-6 ether), imidazole-thiocyanate, HIBA-imidazole-(18-crown-6-ether)-acetonitrile, imidazole-acetic, and imidazole-HIBA-didodecyldimethylammonium bromide (DDAB)-(18-crown-6-ether) were used for the separation of alkali and alkali earth (NH_4^+, K^+, Ca^{2+}, Na^+, and Mg^{2+}) in natural water (Hiissa *et al.*, 1999), drinking water (Haumann *et al.*, 2000), standard cations (Johns *et al.*, 2004), biodiesel (Piovezan *et al.*, 2010) and explosive residue (Hopper *et al.*, 2005), respectively.

As to our knowledge, no previous paper has showed the simultaneous separation of Fe(II), Fe(III), V(IV) and Pb(II) by CE, the aims of this research were to develop a CE method for the simultaneous separation of Ni (II),Cu(II), Zn(II), Fe(II), Fe(III), Co(II), Cd(II),V(IV), Pb(II) and Mn(II) on a modified CE column. The separation conditions were optimized to obtain the highest sensitivity and the developed method was then applied to the determination of transition metal ions in plating solutions.

2. Experimental

2.1 Chemicals and samples

All water used was distilled and then deionised using an Elgastat (UHQ, PS, UK). Stock standard metal ions of 1,000 ppm (Ni(II),Cu(II), Zn(II), Fe(II), Fe(III), Co(II), Cd(II),V(IV), Pb(II) and Mn(II)) were prepared from AR grade chemicals (Aldrich, WI, USA), poly(diallyl dimethylammonium chloride) (20% w/v PDDAC with molecular weight of 400,000-500,000; Sigma-Aldrich, Steinheim, Germany), **2,6** pyridine dicarboxylic acid 99%, (PDC, Aldrich), tetrabutylammonium hydroxide (0.1 M TBAOH, Dionex, Sunnyvale, CA, U.S.A.), AR grade of sodium hydroxide, hydrochloric acid, nitric acid and HPLC grade methanol (Merck, Darmstadt, Germany) were used in this study. Nickel and copper plating solutions were obtained from the plating industry in Thailand.

2.2 Instrumentation and conditions

Separations were performed using a polyamide-coated, fused silica capillary (Polymicro technology (Phoenix, AZ, USA), coated with 0.5% PDDAC, 70 cm length with 75 mm I.D. and a distance of 61.5 cm from the point of injection to the detection window. The analytes were performed on an HP^{3D} CE (Agilent Technologies, Bracknell, UK), equipped with a negative power supply. The applied separation voltage was -20 kV. The temperature of the capillary tube during electrophoresis was maintained at 15 °C. Analyte injection was carried out under a 50 mbar pressure and injection time was 6 sec. The electrophoretic zones were detected at 214 nm with a photodiode array detector. The background electrolyte was a mixture of 5 mM PDC and 4 mM TBAOH at pH 4.0. Before operation, the capillary was pre-treated by flushing with an electrolyte for 4 min. The detection limits were determined for the metal concentration giving a signal-to-noise ratio of three.

2.3 Procedure

2.3.1 Sample preparation

Nickel plating and copper plating solutions were diluted 1:20,000 and 1:10,000, respectively, with deionized water prior to injection.

3. Results and Discussion

3.1 Choice of detection wavelength for metal- PDC complexes

In several previous papers, PDC was used as a background electrolyte for an indirect CE method because PDC exhibited high molar absorptivity (Soga *et al.*, 1997; Soga *et al.*, 1998; Soga *et al.*, 1999; Esteves *et al.*, 2004; Wu *et al.*, 2004). With a UV detector, the detection wavelength used for the separation of metal-PDC complexes was chosen from metal-PDC spectra. Figure 1 shows the absorption spectra

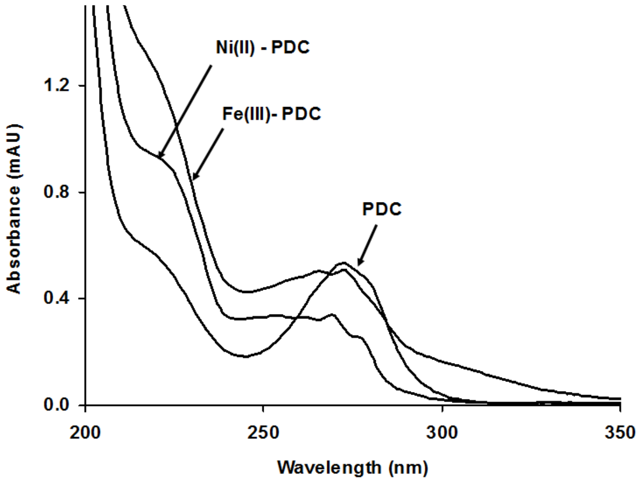

Figure 1. Absorption spectra of 0.08 mM of PDC at pH 4 and metal-PDC complex at pH 4 Conditions for metal complex preparation: [Ni(II)] = [Fe(III)] = 0.08 mM, [PDC] =0.08 mM).

of PDC, Ni(II)-PDC and Fe(III)-PDC complexes. From the absorbance comparison of PDC and metal-PDC complex spectra of Ni(II),Cu(II), Zn(II), Fe(II), Fe(III), Co(II), Cd(II), V(IV), Pb(II) and Mn(II), the optimal detection wavelength of metal-PDC complex for CE was selected at 214 nm due to provide the maximum absorbance for metal-PDC complexes.

3.2 Separation conditions

In this research, a developed CE method for the simultaneous separation of transition metal ions by using PDC as on column complexing agent was investigated. The conversion of metal ion to metal-PDC anionic complex on the CE column depended on pH and concentration of PDC. In previous work (Chen *et al.*, 2001), solutions of 10 mM of PDC containing different surfactants, such as CTAB, TTAB and TMAOH at pH 4, were used as a background electrolyte and the results showed the problem from the baseline drift and poor peak shape of metal-PDC complexes. In order to obtain good baseline and good peak shape including high sensitivity, the capillary wall of bared fuse silica was modified and the polymer consisted of 0.5% PDDAC, which was selected for coating the capillary column for 50 min. PADDC is a dynamically cationic polymer, which after coating on the capillary wall will reverse the direction of the EOF (Vachirapatama *et al.*, 2002).

The separation of the transition metal ions was started with the detection at the anodic end of the coated capillary. The preliminary experiments of the electrolyte composition were optimized for the separation of metal ions. First, the PDC concentration over the range 3-10 mM was investigated. The results showed that 5 mM PDC provided the highest peak height, therefore 5 mM was selected. Second, the pH of the electrolyte had a significant effect on conversion from metal ion to metal-PDC complex and the pH over the range 4-7 was investigated. It was found that the pH at 4 provided the highest peak height and peak area of the metal complexes. Using a pH that was beyond a pH of 4, the peak height and peak area of the complexes decreased and migration time also increased. Therefore, the optimum pH for the metal complex formation was selected at pH 4. Initial experiments with an electrolyte containing only PDC at pH 4 using coated fused silica capillary resulted in poor separation of metal complexes. Only two metal-PDC complexes of Pb(II) and Fe(III) were separated. The addition of 0.5-5 mM TBAOH, as the ion-pair reagent for anionic complex in the electrolyte, was determined. By increasing the concentration of TBAOH from 0.5 to 4 mM, TBAOH in the electrolyte increased the selectivity of the separation and migration time. After a metal–PDC complex formed an ion-pair with TBA^+ which resulted in the electrophoretic mobility of the metal –PDC complex decreased. The highest peak height and the best separation of six complexes of Cu(II), Cd(II), V(IV), Mn(II), Fe(III) and Pb(II) were obtained from 4 mM TBAOH. Therefore, 4 mM TBAOH was selected. Figure 2 shows an electropherogram of standard mixture of Cu(II), Cd(II), V(IV), Mn(II), Fe(III) and Pb(II) complexes under the optimized conditions. However, retention of Ni(II), Zn(II), Fe(II), Co(II) and Cu(II) complexes were co-eluted at this condition (see Table 1). In addition, the TBAOH added into the background electrolyte cannot resolve the overlapping peak of Ni-PDC and Cu-PDC complexes. But, after cetyltrimethylammonium hydroxide (CTAH) was added as an ion-pair reagent in the background electrolyte over the range 0.5-2 mM, the results showed 0.5 mM CTAH that provided a good separation of Ni-PDC and Cu-PDC (Figure 3). Finally, the applied voltage was investigated over the range -15 to -25 kV. Increasing the negative voltage resulted in decreasing the migration time and peak height. Thus, -20 kV was selected because it was the best condition for receiving short migration time and highest peak height.

3.3 Analytical performance characteristics

The detection limits of metal-PDC (determined at a signal to noise ratio of 3) were in the range from 0.07-1.11 mg/L by using a 6 sec injection time at 50 mbar,-20 kV power supply and 5 mM PDC containing 4 mM TBAOH at pH 4 as an electrolyte. The external calibration of metal complexes

Table 1. Performance characteristics of the proposed method for the determination of transition metal ions.

Metal ions	Detection limit (mg/L)	Migration time	% RSD (Intra-day, n=5)		%-RSD (Inter-day, n=5)		Regression equation	Correlation coefficient
			Migration time	Peak area	Migration time	Peak area		
Cu(II)	0.14	6.71	0.95	2.5	0.95	2.5	$y = 4.52x - 0.84$	0.9968
Ni(II)	0.07	6.73	0.83	1.4	0.89	1.5	$y = 4.75x - 6.47$	0.9982
Zn(II)	0.81	6.82	0.75	1.3	0.58	1.5	$y = 1.23x - 9.76$	0.9972
Fe(II)	0.20	6.85	0.57	0.4	0.65	0.9	$y = 5.46x - 30.12$	0.9972
Co(II)	0.17	6.91	0.85	0.3	0.85	0.3	$y = 6.34x - 24.8$	0.9968
Cd(II)	0.49	6.94	0.52	0.5	0.45	0.5	$y = 0.97x - 2.14$	0.9927
V(IV)	0.16	7.14	0.53	1.0	0.50	2.4	$y = 3.99x - 2.05$	0.9941
Mn(II)	0.18	7.53	0.53	1.1	0.54	1.2	$y = 5.50x - 0.49$	0.9934
Fe(III)	0.10	8.02	0.53	1.2	0.55	1.7	$y = 14.01x - 0.98$	0.9932
Pb(II)	1.11	8.41	0.54	0.8	0.55	1.0	$y = 1.08x + 7.63$	0.9935

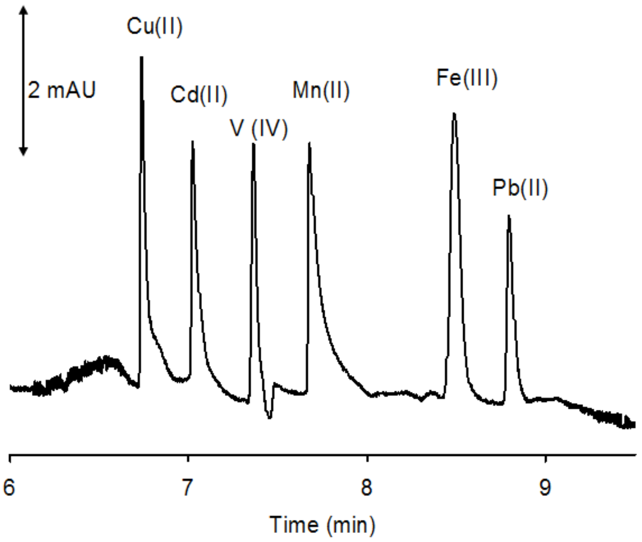

Figure 2. Electropherogram of standard Cu(II) (3 mg/L), Cd(II) (10 mg/L), V(IV) (5 mg/L), Mn(II) (5 mg/L), Fe(III) (3 mg/L) and Pb(II) (20 mg/L) ions. Conditions: 15°C, -20 kV, injection time: 6 s; electrolyte: 5 mM PDC and 4 mM TBAOH at pH 4.

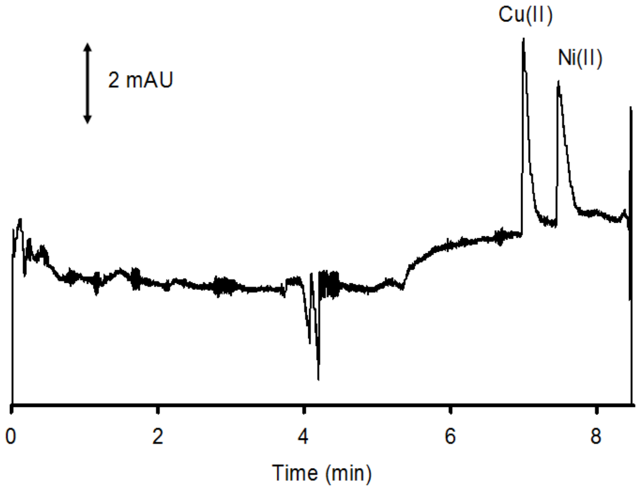

Figure 3. Electropherogram of standard Cu(II) (5 mg/L) and Ni(II) (5mg/L) complexes. Conditions: 15°C, -20 kV, injection time:6 sec; electrolyte: 5 mM PDC and 0.5 mM CTAH at pH 4.

exhibited good linearity over the range of 2-20 mg/L and R^2 ranged from 0.9927 to 0.998. The %-relative standard deviation (n=5) for migration time, peak area, and peak height of ten metal ions were 0.5235-0.9508, 0.2596-2.5110, and 0.8882-3.3116, respectively. However, the migration of metal-PDC complexes can change because the solution contained different matrix ions and several injections were done. Therefore, the coating of the capillary wall has to be repeated when the migration time changing was observed. The performance characteristics of the proposed method are summarized in Table 1.

3.4 Determination of transition metal ions in plating solutions

PADDC is a cationic polymer, after coating on the capillary wall will reverse the direction of EOF (Vachirapatama *et al.*, 2002). The coating capillary column provided higher sensitivity and better peak shape of metal ions than using an uncoated capillary column (Chen *et al.*, 2001). The developed method was applied to the determination of transition metal ions in a plating bath of nickel and copper. Figure 4 shows the electropherograms of nickel plating bath with and without a spike of standard Ni(II) and the electropherograms of copper plating bath with and without a spike of standard Cu(II) are shown in Figure 5. The spiking of the sample with standard ions was used to confirm peak identification of the

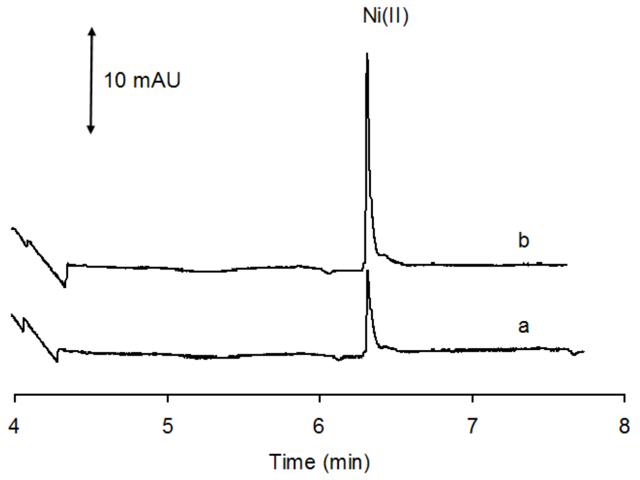

Figure 4. Electropherograms of (a) nickel plating bath, (b) nickel plating bath spiked with 5 mg/L Ni(II). Electropherographic conditions were identical to those outlined in Figure 2.

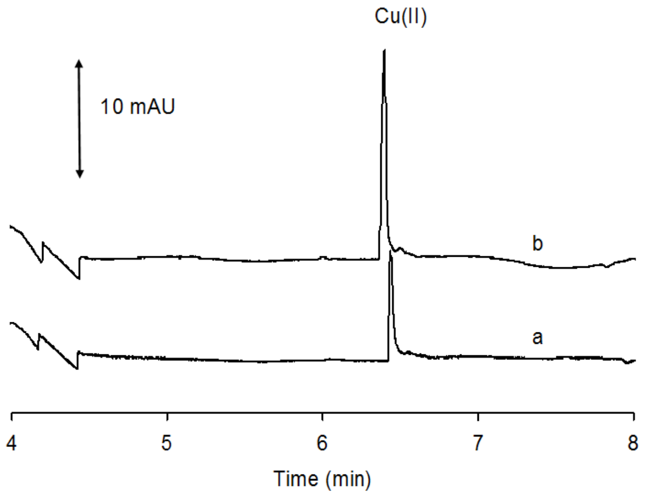

Figure 5. Electropherograms of (a) copper plating bath, (b) copper plating bath spiked with 5 mg/L Ni(II). Electropherographic conditions were identical to those outlined in Figure 2.

metal-PDC complex. After the standard of Ni and Cu was spiked in plating bath, the experiments showed that there was no matrix in the plating bath affecting the peak area and migration time of Ni(II)-PDC and Cu(II)-PDC complexes. The recoveries of standard metal ions in plating bath were over the range 99.5-100.5%. Therefore, an external calibration curve was used for the determination of metal ions in the plating bath. 9.25% Ni(II) and 4.66% Cu(II) were found in plating baths for three replicates. %-RSD for Ni(II) and Cu(II) were 2.2 and 3.1, respectively.

4. Conclusion

The simultaneous separation of transition metal ions as metal-PDC complexes by capillary electrophoresis was achieved successfully by using an electrolyte containing PDC and tetrabutylammonium hydroxide at pH 4. The capillary column coated with poly(diallyldimethylammonium chloride) provided high sensitivity, flat baseline and good peak shape of metal ions. The developed technique was applied successfully to determine the metal ions in plating bath.

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