Simultaneous determination of inorganic anions, organic acids and metal cations by capillary electrophoresis

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Abstract

A capillary electrophoresis method for the simultaneous analysis of inorganic anions, organic acids and metal cations was developed. 2,6-Pyridinedicarboxylic acid (PDC) was used as the background electrolyte to permit indirect UV detection of anions. The PDC also worked to confer a negative charge on metal cations via PDC-complex formation. In order to detect both anions and metal–PDC complexes simultaneously, the electroosmotic flow was reversed by adding cetyltrimethyl-ammonium hydroxide. In the method detection of anions was carried out with indirect UV detection, whereas metal cations were detected directly. Thirteen anions and three metal cations were completely separated at the operating buffer, pH 5.7. The R.S.D. ($n=6$) values of the method were better than 0.2% for migration time and between 1.1% and 3.9% for peak area. Calibration graphs were linear with correlation coefficients better than 0.9992. The minimum detectable levels ranged from 0.2 mg l^{-1} to 1.9 mg l^{-1} with 300 mbar pressure injection (6 nl) at a signal-to-noise ratio of 3. This method is simple, rapid and reproducible and could be readily applied to the simultaneous determination of anions and metal cations in a plating bath sample. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Background electrolyte composition; Inorganic anions; Organic acids; Metal cations; Pyridinedicarboxylic acid

1. Introduction

The analysis of inorganic anions, organic acids and cations is of interest in many fields, thus the demand for a simple and reliable method for the simultaneous determination of anions and cations has increased. Ion chromatography (IC) is a popular analytical technique for ion analysis. There are some chromatographic papers treating simultaneous separations of anions and cations, e.g., ethylenediamine-tetraacetic acid (EDTA) complexation method reported by Yamamoto et al. [1], ODS-adsorbing zwitterionic surfactants reported by Hu et al. [2]. However, they are impractical for real samples because the former method needs to form metal–

EDTA complexes prior to injection, and the latter's retention times and peak shapes are easily affected by counter ions. Therefore for anion and cation analysis different analytical methods, e.g., anion-exchange and cation-exchange chromatography, are generally used in IC.

Capillary electrophoresis (CE) is a powerful separation technique and is used more and more as a standard analytical tool for many ionic compounds [3–7]. Recently a couple of CE methods for simultaneous analysis of anions and cations have been described [8,9]. Padarauskas et al. [8] reported a unique method. The sample was injected from both ends of the capillary and after applying voltage both anions and cations migrated in opposite directions from different capillary ends and ions were detected at the detector window placed in the middle of the

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capillary. In the method detection was carried out by indirect UV detection with a two background electrolyte (BGE) system using imidazole and copper. Kuban and Karlberg [9] also described the separation of 22 anions and cations by using the method based on the sample injection from both ends of the capillary with two BGEs.

In this paper, we propose a new CE method for simultaneous analysis of inorganic anions, organic acids and metal cations by using 2,6-pyridinedicarboxylic acid (PDC) as not only a BGE but also a complexing agent. The method was optimized and then applied to the simultaneous determination of anions and metal cations in a nickel plating bath solution.

2. Experimental

2.1. Chemicals

Inorganic and organic anion standards were prepared from their sodium salts or free acids. The iron(II) standard was constructed from iron(II) ammonium sulfate and iron(III) from iron(III) sulfate· 12H$_2$O. The other metal cations were prepared from their chloride, nitrate and sulfate salts. Cetyltrimethylammonium hydroxide (CTAH) solution (25% in methanol) was purchased from Tokyo Kasei Kogyo (Tokyo, Japan). All other reagents were obtained from Wako (Osaka, Japan). The chemicals used were of analytical or reagent grade. Water was purified with a Milli-Q purification system (Millipore, Bedford, MA, USA).

2.2. Apparatus

All CE experiments were performed using a HP ^{3D}capillary electrophoresis system from Hewlett-Packard (Waldbronn, Germany). The system comprises a CE unit with built-in diode array detector and an HP^{3D}CE ChemStation for system control, data collection and data analysis. Separations were carried out on fused-silica capillaries of 112.5 cm (104 cm effective length)×50 μm I.D.

2.3. Electrophoretic procedures

The electrolyte solution was prepared containing 20 m*M* PDC and 0.5 m*M* CTAH which was used to reverse the direction of electroosmotic flow (EOF) [10]. The electrolyte pH was adjusted to 5.7 with 1 *M* NaOH.

Prior to first use, a new capillary was pretreated with the run electrolyte for 20 min. Before each injection, the capillary was preconditioned for 4 min by flushing with the run electrolyte. Sample was injected with a pressure of 50 mbar for 6.0 s. The applied voltage was set at −30 kV and the capillary temperature was thermostatted to 15°C. Detection was carried out using a UV diode array detector and the signal wavelength was set at 350 nm with a reference at 230 nm.

3. Results and discussion

3.1. Choice of PDC

In CE, anions and cations migrate in opposite directions. Consequently, simultaneous determination of high-mobility inorganic anions and cations in a single run has been difficult especially with low EOF. The problem can be overcome by transforming cations into negatively charged complexes. Several papers reported CE methods for cation analysis by adding complexing agent, e.g., EDTA [11] or nitrilotriacetic acid (NTA) [12] to the electrolyte. In these methods cations were negatively charged by forming complexes with these agents, thus they migrated toward the positive electrode. As we reported previously [13], PDC also exhibited high stability constants for metal cations and the PDC electrolyte demonstrated the excellent separation and reproducibility for inorganic and organic anion analysis.

In this work, we investigated a new CE approach for a simultaneous determination of anions and cations by using a PDC electrolyte. Fig. 1 shows a comparison of the electropherogram of three inorganic anions, four organic acids and two metal cations obtained using PDC and phthalate, which is popular for anion analysis [3], as the electrolyte. Although the cations were detected as negative peak,
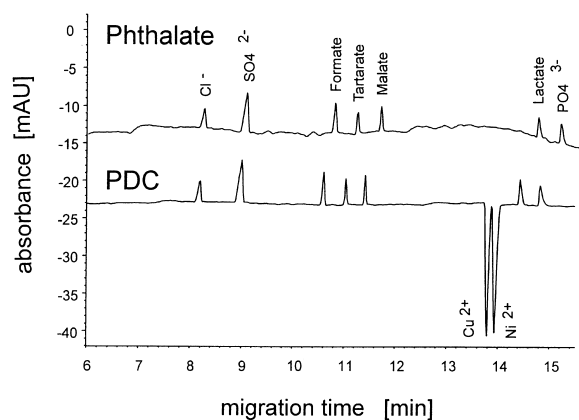
Fig. 1. Effect of BGEs complexing ability on metal cation separation.

the PDC provided a complete separation of all nine components. When using the phthalate, however, neither Cu^{2+} nor Ni^{2+} could be observed. Also an increase in baseline noise was obtained with the phthalate. In this method indirect UV detection using a signal wavelength of 350 nm with reference at 230 nm was employed to visualize anions which have little or no UV chromophore. This arrangement of signal and reference wavelengths are used so that the negative peaks associated with indirect detection are recorded as positive peaks. A decrease of absorption at 230 nm produced by the presence of inorganic and organic anions is recorded as a relative increase of the signal at 350 nm since the 230 nm signal is used as the reference wavelength. On the other hand the determined metal cations have UV absorbance at 230 nm, therefore a increase of absorption at the 230 nm was recorded as a relative decrease of the signal at 350 nm which is called negative peak. Table 1 listed stability constants for metal complexes with both

PDC and phthalate. PDC shows much higher stability constants for these cations than phthalate. In addition PDC exhibits high log K_2 values which mean the second cumulative formation constants. These data explain why PDC makes complexes with metals as divalent ligands. We presumed that PDC was able to make negative complexes with metal cations, so that they migrated toward the positive electrode, whereas metal–phthalate complexes were rare or did not charge negatively, so they could not be observed. Therefore PDC was selected as the most suitable electrolyte for simultaneous analysis of anions and metal cations.

3.2. Choice of buffer concentration and pH

We previously used 5 mM PDC electrolyte with 0.5 mM cetyltrimethylammonium bromide (CTAB) for inorganic anion and organic acid analysis [13]. However, in this work 20 mM PDC was chosen to improve resolution of the analytes. As our paper described, an increase in baseline noise was observed at the higher concentration of 7 mM with a 75 μm I.D. capillary, therefore a 50 μm I.D. capillary was selected to reduce the baseline noise. Instead of CTAB, CTAH was added to the electrolyte as an EOF reversing agent to improve the peak shape of Cl^{-1}.

Separations of six inorganic anions (Cl^-, NO_3^-, SO_4^{2-}, PO_2^{3-}, PO_3^{3-}, PO_4^{3-}), eight organic acids (oxalate, formate, tartarate, malate, citrate, succinate, acetate, lactate) and six metal cations (Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Pd^{2+}, Fe^{3+}) were studied over the pH range 3.6–6.4. The effect of changing the pH on the ions effective mobilities is shown in Fig. 2.

The effective mobility, μ_e, for each anion was calculated using the following equation

Table 1
Stability constants for metal complexes

	PDC			Phthalate		
	Log K_1	Log K_2	Log K_3	Log K_1	Log K_2	Log K_3
Cu^{2+}	9.14	16.52		3.46	4.83	
Ni^{2+}	6.95	13.50		2.14		
Fe^{2+}	5.71	10.36				
Fe^{3+}	10.91	17.13				
Co^{2+}	7.0	12.5		1.81	4.51	

From Ref. [14].

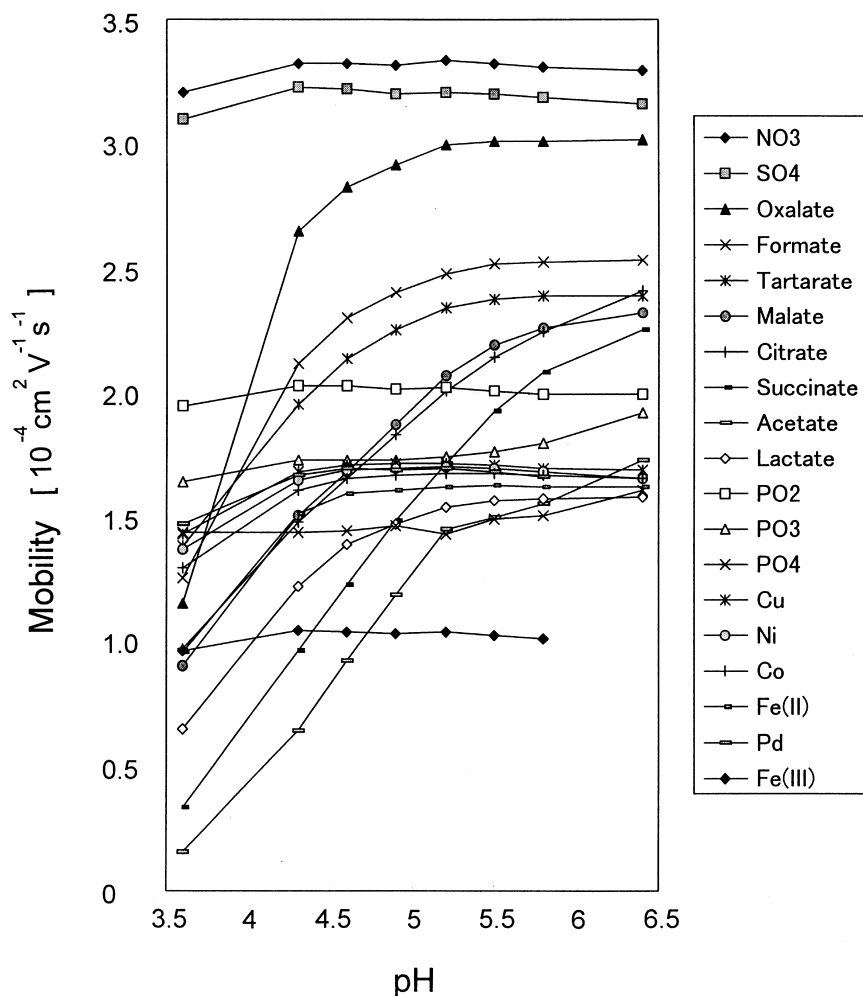Fig. 2. Effect of electrolyte pH on anion and metal cation separation.

$$\mu_e = lL/t_aV - lL/t_{EOF}V \quad (cm^2V^{-1}s^{-1})$$

where l and L are the length of the capillary to the detector and the total length of the capillary, respectively, V is the applied potential, t_a is the migration time of the anion and t_{EOF} is the migration time of a neutral marker.

As listed in Table 2, no inorganic anions have pK_a values in the pH 3.6 to pH 6.4 range thus their mobilities were nearly constant. On the other hand, most organic acids have pK_a values in this pH range, therefore mobility changes of the organic acids were most pronounced between pH 3.6 and 5.8 due to ionization changes of the anions at their pK_a values.

Although a few metal cations could not be separated at the pH, the optimum separation was obtained at pH 5.7.

3.3. Method validation

Fig. 3 shows an electropherogram of anion and cation standards at the operating pH 5.7, demonstrating that six inorganic, seven organic acids and three metal cations were well resolved in 15 min. The reproducibility, linearity and sensitivity of the method were tested. Table 3 shows the excellent reproducibilities obtained for migration time and peak area as reflected by the relative standard

Table 2
pK_a values of inorganic and organic anions

Anion	pK_{a1}	pK_{a2}	pK_{a3}
Chloride	−6.1		
Nitrate	−1.34		
Sulfate	−3.00	1.92	
Oxalate	1.27	4.27	
Formate	3.75		
Tartarate	3.04	4.37	
Malate	3.40	5.05	
Citrate	3.13	4.76	6.40
Succinate	4.21	5.64	
Hypophosphite	1.23		
Phosphite	1.30	6.6	
Lactate	3.86		
Phosphate	2.12	7.20	12.36

From Ref. [14].

Table 3
Reproducibility

Compound	R.S.D. ($n = 6$) (%)	
	Migration time	Peak area
Chloride	0.12	2.5
Nitrate	0.12	1.6
Sulfate	0.12	1.9
Oxalate	0.12	1.6
Formate	0.13	2.1
Malate	0.13	1.9
Citrate	0.13	1.4
Succinate	0.14	1.1
Hypophosphite	0.14	2.0
Phosphite	0.15	2.9
Copper(II)	0.16	3.1
Nickel(II)	0.16	1.4
Iron(II)	0.16	3.9
Lactate	0.16	3.1
Phosphate	0.15	2.9

deviation (R.S.D.) ($n = 6$). Only Fe^{2+} showed decreasing peak areas during the runs because it is easily oxidized. The calibration curves for both anions and cations were linear over the range 10 to 100 mg l^{-1} with correlation coefficients better than 0.9992. The detection limits for inorganic and organic anions were in the range from 0.8 to 1.9 mg l^{-1}, while metal cations were around 0.2 mg l^{-1} with 300 mbar s pressure injection (6 nl) at a signal-to-noise ratio of 3. This sensitive difference between anions and cations reflects the different detection techniques anions were detected with indirect UV detection, whereas metal cations were directly detected.

At a buffer of pH 5.7, resolution of metal cations was unsatisfactory. With respect only to metal cations, resolution was improved by decreasing pH to 3.8. Fig. 4 shows an electropherogram of 50 mg l^{-1} of five metal cation standards. In this method direct UV detection was carried out at 230 nm.

Determination of other cations including alkaline and alkaline earth metals was also studied, however,
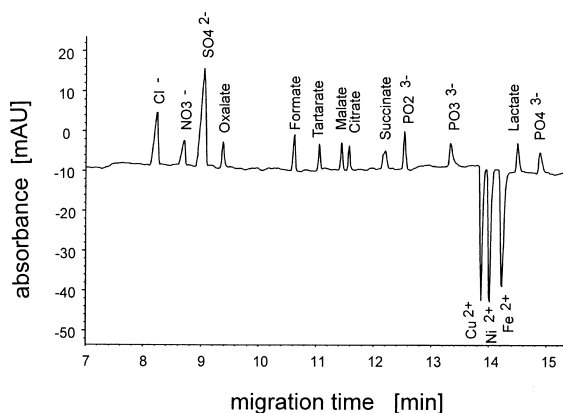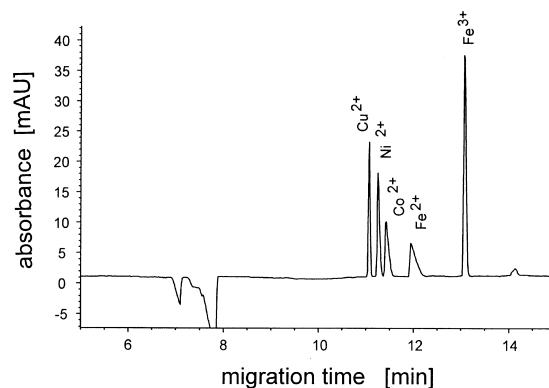

Fig. 3. Electropherogram of inorganic anion, organic acid and metal cation standard mixture. Concentrations: chloride, 71; nitrate, 62; sulfate, 63; copper(II), 20; nickel(II), 20; iron(II), 20; others, 30 mg l^{-1} each, Experimental conditions: capillary, fused-silica capillary 112.5 cm (effective length 104 cm)×50 μm; electrolyte, 20 mM PDC, 0.5 mM CTAH, pH 5.7; applied potential, −30 kV; injection, pressure, 6 s at 50 mbar; capillary temperature, 15°C; detection, signal = 350 nm, reference = 230 nm.

Fig. 4. Electropherogram of 50 mg l^{-1} each of metal cation standard mixture. Experimental conditions: electrolyte, 20 mM PDC, 0.5 mM CTAH, pH 3.8; detection, signal = 230 nm, reference = off. Other conditions as in Fig. 3.

no peaks were detected. This is because there is no change UV absorbance between these cation–PDC complexes and the PDC electrolyte. Therefore although these cations might make negative complexes with PDC they could not be observed. These results indicate this method is useful for metal cations which have UV absorbance.

3.4. Simultaneous anion and metal cation analysis in plating bath

The developed method was applied to the simultaneous determination of inorganic, organic anions and metals in an electroless plating bath sample. In electroless plating, the bath solutions contain several kinds of additives besides the plating metal salt [15]. An excess of a reducing agent, for example hypophosphite (PO_2^{3-}), must be added to the bath solution because the plating reaction terminates when the reducing agent is exhausted. Organic acids like acetate, lactate and citrate are added to the baths to provide both buffering of the bath solution and to prevent metal salt precipitation. The concentrations of these additives have a significant effect on the quality and effectiveness of the plating and may vary during the operation. Fig. 5 shows a typical result of the simultaneous anion and metal cation analysis in an electroless nickel plating bath solution. Since the bath solution contains high levels of additives,
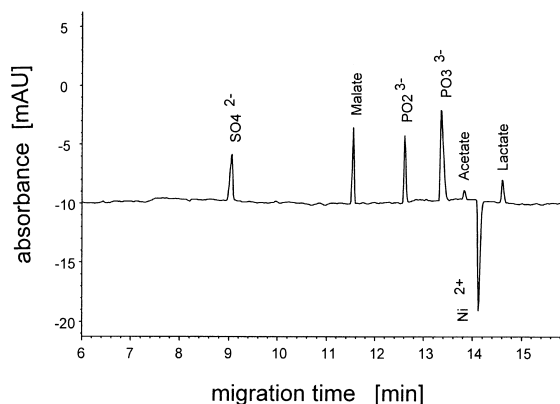
typically in g l^{-1} it was diluted 1:1000 with Milli-Q water prior to injection.

A well-defined electropherogram was obtained without interference from other matrix compounds. Peaks were identified by their migration times and the concentrations of sulfate, malate, hypophosphite, phosphite, acetate, nickel and lactate were calculated as 22, 21, 16, 33, 2.2, 4.5 and 6.6 g l^{-1}, respectively. Satisfactory reproducibilities were obtained for all ions with R.S.D. values ($n = 5$) for migration times better than 0.03% and for peak areas between 1.4 and 3.2%.

4. Conclusions

A reliable and simple CE method for the simultaneous determination of inorganic anions, organic acids and metal cations has been developed. PDC was used as the BGE not only to visualize ions which have little or no UV absorbance but also to make negatively charged complexes with metal cations. This method enabled simultaneous separation of both anions and metal cations in less than 15 min and provides excellent reproducibility, good linearity and appropriate sensitivity. Its utility was demonstrated in the analysis of inorganic anions, organic acids and metal cations in a plating bath sample. These results indicate that the proposed method can be useful for anion and metal cation analysis in many application areas.

Fig. 5. Electropherogram of inorganic anions, organic acids and metal cations in plating bath solution. Experimental conditions as in Fig. 3.

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