Short communication

Simultaneous capillary electrophoretic separation of small anions and cations after complexation with ethylenediaminetetraacetic acid

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Abstract

A new approach for simultaneous separation of small inorganic and organic anions and metal cations by capillary electrophoresis is demonstrated. Metal cations in the sample are transformed into their chelates with EDTA and are separated together with the anions using an anionic separation mode. Simultaneous separation of 19 common anions and cations was achieved in about 6 min with the electrolyte containing 5 mM K_2CrO_4, 3 mM boric acid, 35 μM cetyltrimethylammonium bromide and 12 μM EDTA at pH 8. Limits of detection ($s/n=3$) were in the range from 4 ppb for Cl^- up to 1250 ppb for Cu–EDTA and RSDs of peak areas ranged from 1.4% for Cl^- up to 8.5% for Mn–EDTA chelate. The practical applicability of the method was demonstrated on the analysis of anions and cations in various water samples. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Metal chelates; Inorganic anions; Inorganic cations; Organic acids

1. Introduction

Separation of small ions by capillary electrophoresis (CE) has attained large attention in the recent years. High resolution, short analysis times and low electrolyte and sample consumption are the main advantages of CE technique compared to ion chromatography (IC).

Several research groups have shown the potential of capillary electrophoresis in the analysis of small anions [1,2] and cations [3–5]. The analysis of anions and cations is usually accomplished in separate CE systems using different background electrolytes.

The potential of CE for simultaneous determination of anionic and cationic compounds has been recognized by several authors. Large anions and cations with moderate migration velocity can be simultaneously separated in such an electrolyte system, where one class of analytes migrates in the same direction as the electroosmotic flow (EOF) whereas the other class migrates opposite to the direction of the EOF. Simultaneous separation of anions and cations can be achieved on condition that the migration velocity of the ions in the other class does not exceed the velocity of the EOF. Such separations have been demonstrated for instance by Jorgensson et al. [6] or Shamsi et al. [7]. Based on the same principle, slowly migrating organic anions and inorganic cations (Li^+, K^+) could be separated in a system with a high EOF [8]. Some small chloro anions and inorganic cations were simultaneously determined by Bächman et al. [9] using dual indirect fluorescence detection. The system employed one common background electrolyte but two capillaries and two detectors, making this approach experimentally complicated.

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Recently a new approach for simultaneous determination of small ions has been demonstrated by Kuban et al. [10]. Simultaneous separation of 22 small ions within 3 min has been accomplished by injecting the sample from both capillary ends. Cations and anions migrate towards the capillary center and are detected approximately in the middle of the separation capillary. Indirect UV detection at 254 nm was used with electrolyte consisting of 4-aminopyridine–H_2CrO_4. Independently Paradauskas et al. [11] showed the same principle for the separation of eight inorganic ions. They employed the electrolytes based on imidazole–HNO_3 or fumaric acid–HNO_3 and detection at 214 nm. In the last mentioned applications the electrolyte composition is rather critical and not universal, e.g. transition metal cations cannot be detected since they often precipitate by the electrolyte counterions or at high pH used.

An alternative approach for simultaneous separation of small inorganic and organic anions and some metal–ethylenediaminetetracetic acid (EDTA) chelates is presented in the following paper.

2. Experimental

2.1. Instrumentation

All separations were performed on a P/ACE 5010 CE system (Beckman Instruments, Fullerton, CA, USA). Polyimide coated capillaries (Polymicro Technologies, AZ, USA) of 50 µm I.D. were used. The total length of the capillary was 67 cm, with the detection window burned 7 cm from the capillary end. Separation potential of 25 kV was applied during all separations. Samples were introduced either by the hydrodynamic or electrokinetic injection mode. Indirect UV detection at 254 nm was used. The electropherograms were evaluated using System-Gold software system (Beckman Instruments).

2.2. Reagents and solutions

All chemicals were of reagent grade. Deionized water was used throughout. Inorganic anion stock solutions, 1000 mg/l, were prepared from the corresponding sodium salts. Organic anion stock solutions were prepared from their respective acids which

were neutralized by using sodium hydroxide. Stock solutions of cations, 1000 mg/l, were prepared from their inorganic salts (e.g. chloride, sulfate, nitrate, etc.). Metal–EDTA complexes were prepared by mixing the cation stock solutions with an excess of EDTA tetrasodium salt solution. The working electrolyte was prepared daily from the stock solutions containing 600 mM sodium chromate, 30 mM cetyltrimethylammonium bromide (CTAB) (5%, v/v ethanolic solution), 100 mM boric acid and 60 mM EDTA. The pH was adjusted by the addition of 100 mM NaOH. The electrolyte was filtered and degassed prior to use. Real samples were spiked with concentrated EDTA solution before introduction into the capillary electrophoresis system. Dilution due to the addition of EDTA solution was less than 1%.

3. Results and discussion

3.1. Electrolyte composition

EDTA is known to form 1:1 chelates with a large number of metal cations in the oxidation states II–IV. The chelates are usually non-absorbing at wavelengths higher than 220 nm and are stable in a broad range of pH. If EDTA tetrasodium salt is used for complexation with II- and III-valent cations, metal–EDTA chelates possess negative net charge and can be thus separated in anionic separation mode.

The use of chromate based electrolytes for the separation of small anions is advantageous due to the high molar absorptivity of the chromate anion as well as because of its high electrophoretic mobility. Separation of large anions having moderate mobility is still possible though in some cases unacceptable peak-broadening can be observed.

The parameters which influence the separation selectivity of metal–EDTA chelates were evaluated in respect to achieve the best separation. The concentrations of K_2CrO_4, boric acid, CTAB and pH were varied. It has been shown that the concentration of K_2CrO_4 and the pH are of major importance concerning the separation selectivity. In Table 1 the separation selectivity of 11 metal cations is demonstrated in electrolyte containing 3 mM and 5 mM K_2CrO_4. The separation selectivity changes for several metal–EDTA chelates can be observed.

Table 1
Migration times of metal–EDTA chelates observed in different electrolyte systems: 3 mM boric acid, 30 μM CTAB, pH 8.0 and 3 (electrolyte I) or 5 mM K$_2$CrO$_4$ (electrolyte II)

Ion	Migration time (min)	
	Electrolyte I	Electrolyte II
Cu^{2+}	5.18	5.24
Cd^{2+}	5.38	5.78
Pb^{2+}	5.39	5.35
Zn^{2+}	5.41	5.60
Co^{2+}	5.46	5.52
Mg^{2+}	5.77	5.91
Al^{3+}	5.81	5.46
Ca^{2+}	5.91	6.09
Ni^{2+}	5.91	5.56
Mn^{2+}	5.98	5.70
Fe^{3+}	6.91	6.67

3.2. Separation selectivity of Mg– and Ca–EDTA complexes

Analysis of water samples, especially mineral water, requires quantitative determination of rather high concentrations of Mg^{2+} and Ca^{2+} ions. Attention was paid to the optimization of the electrolyte composition for the separation of high concentrations (about 100 mg/l) of Mg^{2+} and Ca^{2+} ions.

CTAB concentration and pH value were found to be the main parameters influencing the resolution of Mg– and Ca–EDTA peaks. When using too low pH (<8) the Mg– and Ca–EDTA chelates could not be separated, on the other hand pH higher than 8.5 led to serious peak tailing and resolution was decreased. A similar relation was found also when varying the CTAB concentration. Low concentration of CTAB resulted in low EOF and though the resolution of Mg– and Ca–EDTA peaks was very good separation selectivity of other, especially anionic, constituents of the samples was influenced. On the contrary the resolution of Mg–/Ca–EDTA peaks was low when using high concentration of CTAB. Compromise electrolyte composition giving the best results was as follows: 5 mM K$_2$CrO$_4$, 3 mM boric acid, 35 μM CTAB, 12 μM EDTA, pH 8.2.

Addition of EDTA into the separation electrolyte improved the peak shape of several metal–EDTA complexes. Most probably the excess of EDTA in the electrolyte promotes the metal–EDTA equilibrium towards the negatively charged metal–EDTA
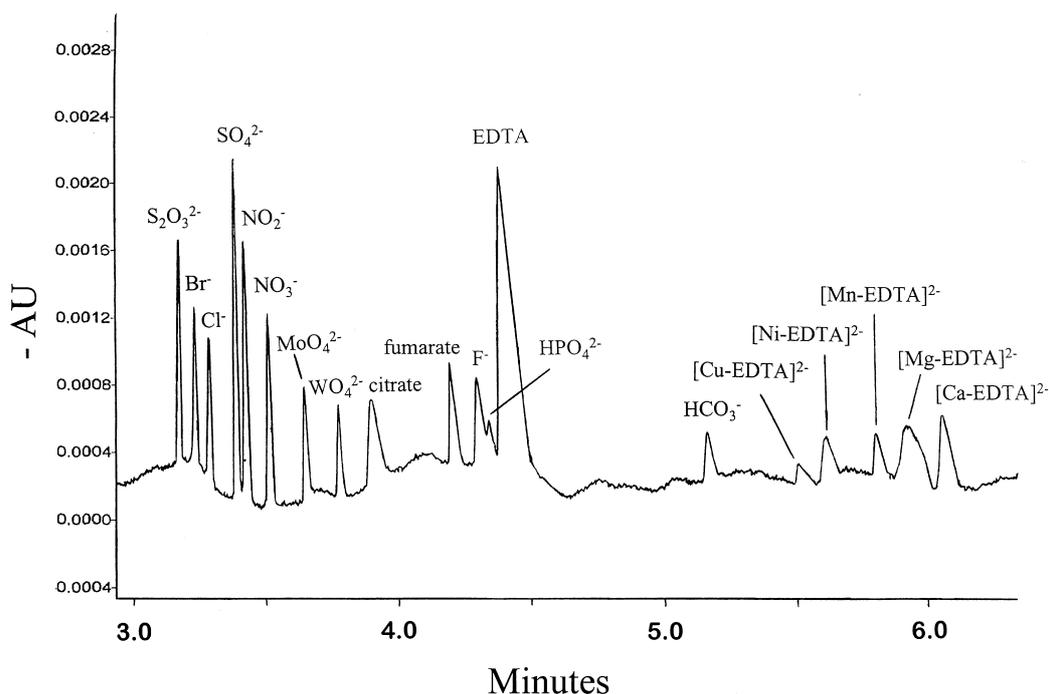
Fig. 1. Simultaneous separation of 19 anions and cations. Electrolyte: 5 mM K$_2$CrO$_4$, 3 mM boric acid, 35 μM CTAB, 12 μM EDTA at pH 8.2. CE conditions: high voltage 25 kV, hydrodynamic injection 2 s, indirect UV detection at 254 nm.
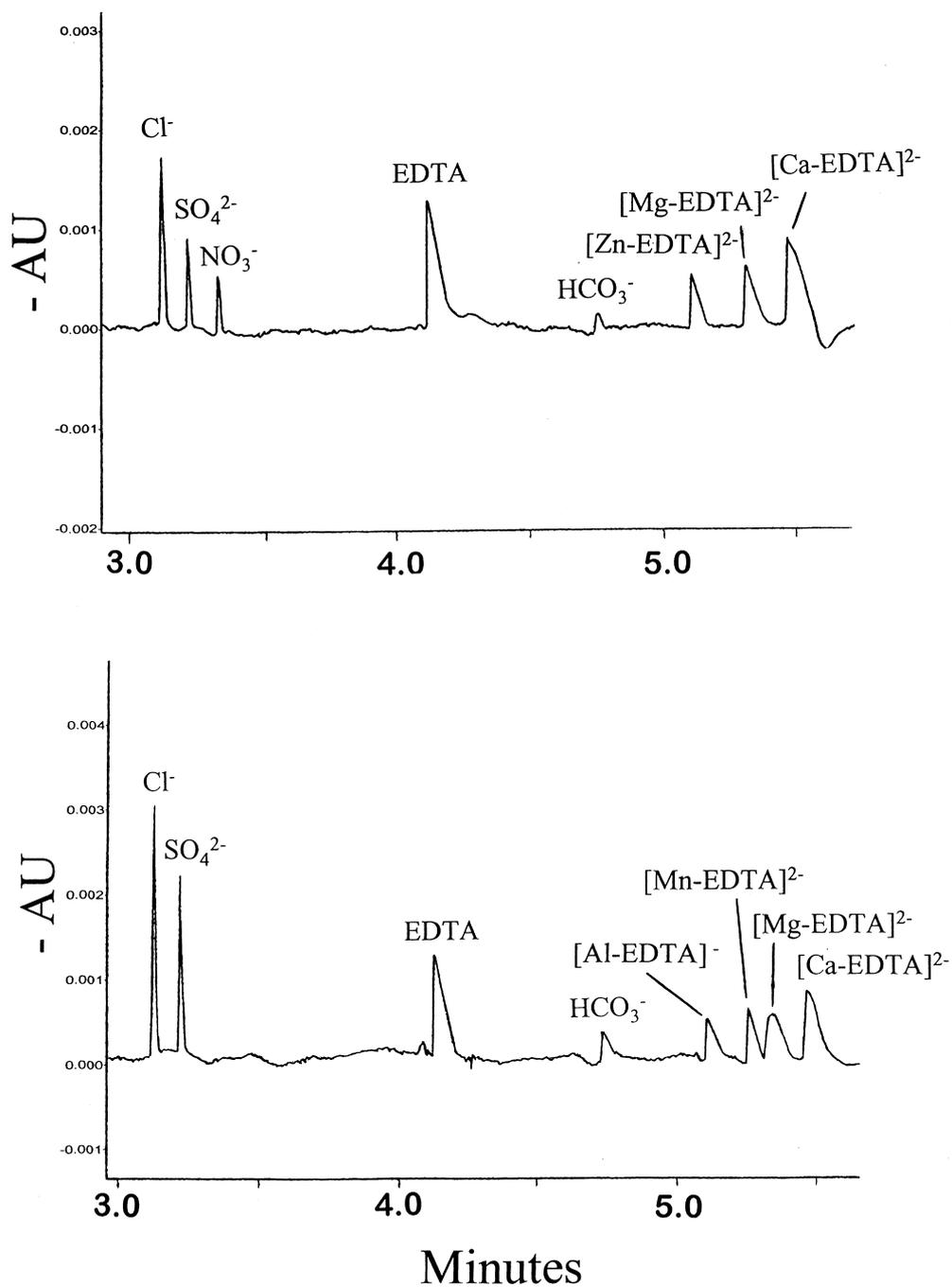
Fig. 2. Separation of some metal–EDTA chelates and inorganic anions. Conditions as in Fig. 1.

Table 2
Concentrations of anions and cations in mineral and tap water samples

Sample	Concentration (mg/l)						
	Cl^-	SO_4^{2-}	NO_3^-	F^-	HCO_3^-	Mg^{2+}	Ca^{2+}
Mineral water 1	3.1	3.1	1.2	0.4	1400	3.6	9.6
Mineral water 2	454.0	83.1	5.8	2.1	2650	20.5	37.8
Mineral water 3	16.2	39.6	ND[a]	1.4	4340	5.5	9.0
Tap water 1	22.1	26.4	16.7	ND[a]	182.0	3.2	101.5
Tap water 2	38.9	25.5	16.1	ND[a]	116.0	1.0	69.3

[a] Not detected.

chelate, thereby increasing its negative net charge.

An electropherogram which demonstrates the separation of 19 common anions and cation–EDTA complexes is shown in Fig. 1. Separation of several other metal–EDTA chelates and some inorganic anions is illustrated in Fig. 2.

3.3. Analysis of real samples

Samples of tap and mineral water were analyzed after spiking with an excess of concentrated EDTA solution. Table 2 summarizes the results of quantitative analysis of various tap and mineral water samples. The concentrations of ions were in good agreement with the concentrations given on the bottle labels (mineral water samples) except for the concentration of Mg^{2+} and Ca^{2+} which was lower than stated. This could be explained by precipitation of Mg^{2+} and Ca^{2+} during the storage by dissolved CO_2 present in the mineral water. Fig. 3 shows a
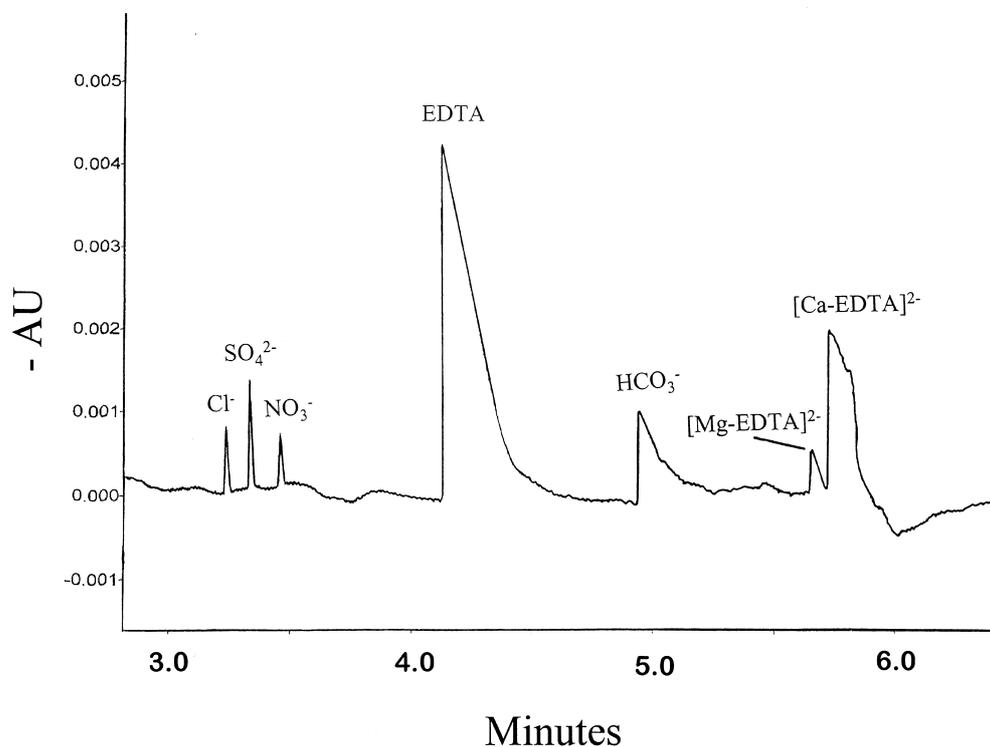
Fig. 3. Analysis of anions and cations in tap water sample. Conditions as in Fig. 1.

Table 3
Detection limits for different anions and metal–EDTA chelates (in ppb)

Ion	LOD (ppb)	Ion	LOD (ppb)	Ion	LOD (ppb)
$S_2O_3^{2-}$	250	Fumarate	60	Citrate	500
Br^-	125	F^-	250	$[Cu-EDTA]^{2-}$	1250
Cl^-	4	HPO_4^{2-}	250	$[Ni-EDTA]^{2-}$	150
SO_4^{2-}	30	HCO_3^-	250	$[Mn-EDTA]^{2-}$	150
NO_2^-	125	MoO_4^{2-}	250	$[Mg-EDTA]^{2-}$	150
NO_3^-	125	WO_4^{2-}	500	$[Ca-EDTA]^{2-}$	75

Electrolyte: 5 mM K_2CrO_4, 3 mM boric acid, 35 μM CTAB, 12 μM EDTA at pH 8.2. Conditions: high voltage 25 kV, hydrodynamic injection 7 s, indirect UV detection at 254 nm.

representative electropherogram of simultaneous determination of some anions and cations in the tap water sample.

4. Conclusions

In the present paper we have demonstrated that it is possible to separate simultaneously small anions and cations as anionic metal–EDTA chelates with LODs ranging from units to thousands of ppb (see Table 3) and RSDs between 1.4 and 8.5% ($n=5$). The ability of the method was demonstrated on the analysis of inorganic anions and cations in water samples. The main drawback of the method is that K^+, Na^+ and NH_4^+ cations cannot be determined since they do not form stable complexes with EDTA. By using the injection of the sample from the opposite capillary end determination of 1A-group cations (K^+, Na^+, Cs^+) and NH_4^+ could be accomplished. The work is in progress to evaluate the method for simultaneous analysis of some 1A-, 2A-group cations and transition metals.

Acknowledgements

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