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Migration behaviour of alkali and alkaline-earth metal ion–EDTA complexes and quantitative analysis of magnesium in real samples by capillary electrophoresis with indirect ultraviolet detection

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Abstract

A capillary electrophoretic (CE) method was developed for the separation of some common alkali and alkaline-earth metal ions using EDTA as complexing agent and pyridine as UV chromophore for indirect detection at pH 5.00. Effects of pH and concentration of complexing agent on the differences in the effective mobilities between two ions were considered and equations derived were used to deduce the optimum conditions for their separation. Baseline separation of a group of metal ions, including K, Na, Li, Mg, Sr and Ba, was achieved in less than 4 min. The calibration range for magnesium was found to be linear up to 1.00 μg/ml when samples were prepared in the running buffer while a hyperbolic calibration curve was obtained when prepared in water. Application of the method to the analysis of magnesium in river water, urine and a solid sample of calcium carbonate was demonstrated. Magnesium in those samples was determined to be 812 μg/ml, 78.0 μg/ml and 0.023% (w/w), respectively, with reproducibilities between 5–9% R.S.D. in terms of peak height depending on sample matrices.

1. Introduction

Capillary electrophoresis (CE) separates components on the basis of their differences in migration velocity in a suitable electrophoretic medium under the influence of an electric field of high strength [1–3]. Applications of CE have been found in many diverse fields, such as large biomolecules [4–6], pharmaceuticals [7], organic compounds [8] and inorganic anions/cations [9–12].

For metal cations there used to be two main factors which hamper their analysis by CE [10]. One was the poor detectability and the other the insufficient difference in their mobilities. Introducing complexing agents to enlarge the effective mobility differences between the ions and adopting indirect UV or fluorescence detection are common ways to overcome the above problems. The number of applications of capillary electrophoresis to the separation and determination of metal cations has rapidly increased [9–23].

Many of the papers published so far on the separation of metal cations were focused on separation strategies. A few published papers dealt with quantitation of metal ions in real

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samples [10,12,14–16,18,21,22]. In most of the reported CE methods for separation and determination of alkali and alkaline-earth metal ions, the calcium peak appeared before and very close to the magnesium peak in the electropherograms [12,14,15,18–23]. Some difficulties may arise when such methods are applied to the quantification of small amounts of magnesium in the presence of very large amounts of calcium, such as magnesium impurities in a calcium carbonate sample. Thus, there is a need to develop methods for the determination of magnesium in samples where considerable amounts of other cations which are likely to cause interference in the other methods commonly used for determination, such as spectrometric methods [24,25], are expected to be present.

In this paper a CE method was developed for the separation of some alkali and alkaline-earth metal ions using chemicals readily available, i.e. EDTA as a complexing agent, and pyridine as a UV chromophore for indirect detection at pH 5.00. The migration behaviour of alkali and alkaline-earth metal ion–EDTA complexes was studied. Guidelines were worked out for optimization of CE conditions, such as pH and the concentration of complexing agent in buffer, based on theoretical considerations. Effects of pH, concentration of EDTA and sample preparation procedures on separation and quantitation were experimentally investigated. The CE method was successfully applied to the determination of magnesium in real samples with relatively complex matrices.

2. Experimental

2.1. Chemicals

All metal ion solutions were prepared from nitrate salts. They were prepared as stock solutions of 1000 μg/ml (metal ion concentration). Metal ion solutions of other concentrations were prepared by appropriately diluting portions of the above stock solutions. Ethylenediaminetetraacetic acid disodium salt (EDTA) was a product of J.T. Baker (J.T. Baker, Phillipsburg, NJ, USA). Pyridine of analytical grade was purchased from Fluka (Fluka Chemie, Switzerland). Perchloric acid (60%) was also of analytical grade. Benzyl alcohol of analytical grade was used as neutral marker to measure electroosmotic flow (EOF). Deionized water used throughout the experiments was prepared with a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Buffers and pH adjustment

The running buffer contained 10 m*M* pyridine, which served both as the carrier electrolyte and background absorber for indirect UV detection. The adjustment of pH was accomplished by adding perchloric acid solution. The concentration of the complexing agent, EDTA, was set to 0.8 m*M* unless otherwise stated.

2.3. Sample preparation

Water samples and urine samples were first diluted with deionized water and then mixed with buffer to ensure that the differences in ionic strength, conductivity, and pH between samples and the running buffer were negligible and that peak height was in the linear range of the calibration curve for magnesium. Calcium carbonate (ca. 0.15 g) was accurately weighted into a beaker. A few drops of deionized water were added to wet the sample. Perchloric acid (60%) was added dropwise until calcium carbonate was completely dissolved (N.B., to avoid vigorous or explosive reactions one must be sure there is no oxidizable matter in the samples before adding the perchloric acid). During dissolution the beaker was covered with a watch glass to avoid any loss of the sample. The solution was quantitatively transferred from the beaker into a 10-ml volumetric flask and deionized water was added to the mark. Subsequent procedures for sample preparation were the same as those mentioned above for the liquid samples. Conditions will be specified where appropriate if different from those described above.

2.4. Apparatus

CE was performed with a laboratory built capillary electrophoresis system, equipped with a positive power supply (Spellman, Plainview, NY, USA) and a Linear UVIS 200 detector (Linear Instruments Corp., Reno, NV, USA). Electropherograms were recorded with a HP 3394A integrator (Hewlett-Packard, Avondale, PA, USA) connected with a switch for changing the polarity of the input signal. Polyimide-coated fused-silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) used were 39.5 cm long with an inner diameter (I.D.) of 75 μm and an outer diameter (O.D.) of 362 μm. An on-column detection window was created at 30 cm from the injection end and indirect UV detection was conducted at 254 nm. A hydrostatic sample injection mode was employed for sample introduction into the capillary at the anodic side. The field strength applied for separation was 190 V/cm and the voltage was 7500 V. Atomic absorption measurements were performed with an AA-670 atomic absorption/flame emission spectrophotometer (Shimadzu Corp., Kyoto, Japan).

3. Theory

In this section, equations for calculating the effective mobility differences between pairs of 1:1 metal ion–ligand complexes are derived. It is assumed that there are two kinds of metal ions, M and N, with identical mobilities U_M and U_N in free solution and that both M and N can form 1:1 complexes (ML and NL) with ligand L and the complexes, ML and NL, have identical mobilities U_{ML} and U_{NL}. It is also assumed that $K_{NL} > K_{ML}$. The effective mobilities of the metal ions will be the weighted sum of the mobilities of the free ions, U_f, and the mobilities of the complexes, U_c [26].

$$U_M^{eff} = (U_f + K_{ML}[L]U_c)(1 + K_{ML}[L])^{-1} \quad (1)$$

$$U_N^{eff} = (U_f + K_{NL}[L]U_c)(1 + K_{NL}[L])^{-1} \quad (2)$$

Although $U_M = U_N$ and $U_{ML} = U_{NL}$, U_M^{eff} and U_N^{eff} can be different from each other due to the difference in their capabilities to form complexes and the difference between U_f and U_c.

If the side-reaction of L with H^+ is the only one needed to be taken into account, the apparent stability constants K'_{ML} and K'_{NL} [27], can be used instead of K_{ML} and K_{NL} and the difference in effective mobilities becomes:

$$U_M^{eff} - U_N^{eff} = (K'_{NL} - K'_{ML})(U_f - U_c)[L'] \times \{(1 + K'_{ML}[L'])(1 + K'_{NL}[L'])\}^{-1} \quad (3)$$

and

$$a_{L(H)} = [L']/[L] \quad (4)$$

Rearranging Eq. 3 gives

$$U_M^{eff} - U_N^{eff} = (K_{NL} - K_{ML})(U_f - U_c)[L'] \times \{a_{L(H)}(1 + K'_{ML}[L'])(1 + K'_{NL}[L'])\}^{-1} \quad (5)$$

To determine the optimum concentration of the complexing agent for obtaining high resolution, one can differentiate Eq. 3 with respect to [L'] twice to obtain

$$(U_M^{eff} - U_N^{eff})_{max} = (K_{NL}K_{ML})^{1/2}(K_{NL} - K_{ML}) \times (U_f - U_c)\{[(K_{NL}K_{ML})^{1/2} + K_{ML}] \times [(K_{NL}K_{ML})^{1/2} + K_{NL}]\}^{-1} \quad (6)$$

When

$$[L'] = (K'_{ML}K'_{NL})^{-1/2} \quad (7)$$

Eq. 6 indicates the existence of the maximum difference in effective mobilities of ions M and N, which can be theoretically estimated.

It should also be recognized that there are practical limitations, which will be discussed later on, in the use of the concentration of complexing agent as a parameter for the optimization of the separation as calculated on the basis of Eq. 7.

4. Results and discussion

4.1. Effect of pH on separation and detection

To predict the effect of pH on separation, plots of the terms on the right hand side of Eq. 5

with omission of the factor $(U_f - U_c)$ (because of the lack of data on U_c) vs. pH in a broad range were constructed as shown in Fig. 1. Literature values of K'_{CaY}, K'_{MgY}, K'_{SrY}, K'_{BaY} and the dissociation constants of EDTA were used [27] and the assumption was made that $[Y'] = 0.8$ mM. It shows that separation of alkaline-earth metal ions may be achieved within a pH range of 4 to 7, where the values of the term, $(U_M^{eff} - U_N^{eff})/(U_f - U_c)$, are $6.7 \cdot 10^{-4}$ for curve 1 and $2.1 \cdot 10^{-4}$ for curve 2 at pH 4, and $1.6 \cdot 10^{-3}$ for curve 2 and $6.2 \cdot 10^{-3}$ for curve 3 at pH 7, respectively. It also illustrates that the peak pair of Sr–Mg will be the most difficult one of the three peak pairs (Ba–Sr, Sr–Mg and Mg–Ca) to separate in a pH range 4–7.

To examine the effect of pH on separation and detection, all other experimental conditions were kept constant except for the different amounts of perchloric acid used to adjust the pH of the buffer. At pH 5.00, the peaks for all the ions tested were baseline separated in 4 min with a low noise level and high detectability. Baseline separation of K, Na, Li, Mg, Sr and Ba was achieved. Under the proposed conditions the effective mobility of calcium was so low that the calcium peak eluted much later than the peaks of interest in the electropherogram and hence caused no interference in the analysis of the other cations. Many other metal ions, which form even more stable complexes with EDTA, could also be well resolved from the cations of interest. At pH 4.00, fractions of divalent cations forming complexes were smaller due to the side-reaction of Y with H^+. Furthermore, divalent cations exhibited effective mobilities which were higher than those at pH 5.00. Differences in the effective mobilities of Ba, Sr and Mg were so

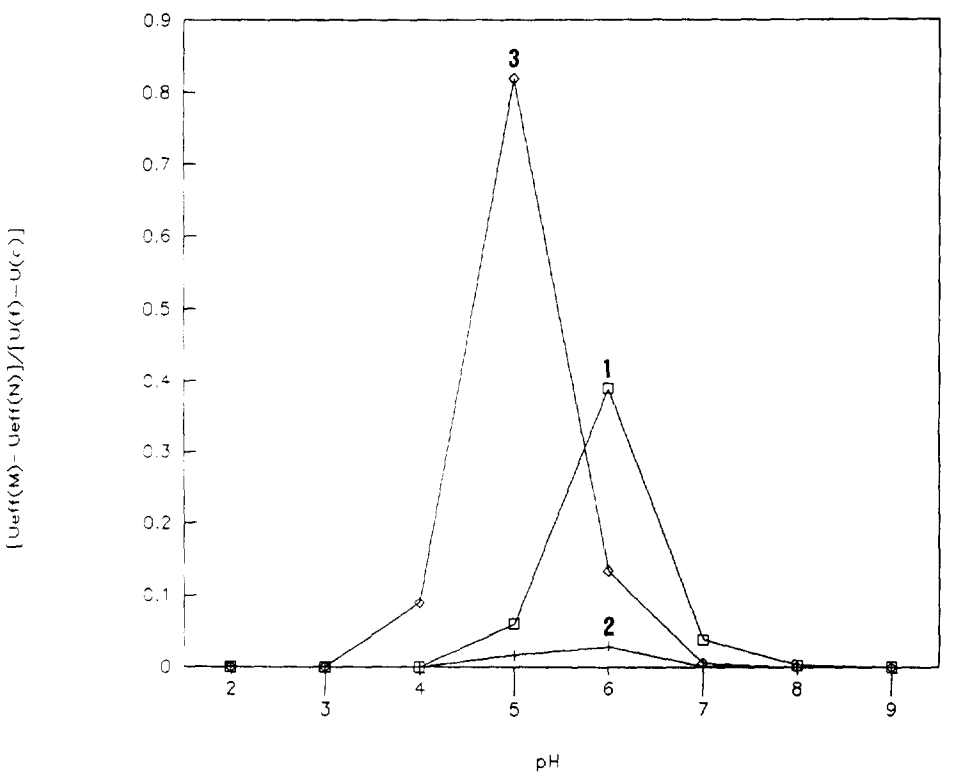

Fig. 1. Theoretical prediction of the effect of pH on the differences in effective mobilities of common alkaline earth metal ions in the presence of 0.8 mM EDTA. Ordinate is value of the terms on right hand side of Eq. 5 with omission of the factor of $(U_f - U_c)$. $1 = (U_{Ba}^{eff} - U_{Sr}^{eff})$; $2 = (U_{Sr}^{eff} - U_{Mg}^{eff})$; $3 = (U_{Mg}^{eff} - U_{Ca}^{eff})$.

small that separation of those peaks could not be achieved. The current was 11 μA, which is 1.5 times higher than that at pH 5.00. It was observed that a significantly more noisy baseline was obtained under these conditions. Possible reasons for the noisy baseline might be attributable to the effect of Joule heating [28] or the lack of buffering action. At pH 6.00, the migration times of monovalent metal ions, i.e. potassium, sodium, and lithium, were less than 3 min. With a run-time up to 10 min, which was three times longer than the migration time of the neutral marker, no peaks of divalent ions were observed. The reason why no peaks for the divalent metal ions appeared is not clear at present. One possible explanation is that the formation of a large portion of complexes of the divalent cations with EDTA reduced the effective mobilities of the divalent metal ions greatly as the apparent stability constants of the complexes increased with pH and made these ions less detectable. Another possible explanation is that at pH 6.00 pyridine existed mainly as the neutral molecule rather than in the pyridinium ion form since the pK_a value of the pyridinium ion is 5.2 [29]. This might lower the sensitivity of detection for the divalent metal ions as displacement of pyridinium by the metal ions would be masked by strong background absorbance from neutral pyridine molecules. Thus, although the difference in the effective mobilities of the divalent metal ions was theoretically predicted to be large at pH 6.00, this pH was not a favourable condition for CE analysis of the divalent ions in terms of detectability and separation time. Another observation is that since only a very small amount of perchloric acid was introduced to the buffer to adjust its pH to 6.00, the conductivity and ionic strength of the buffer were rather low. Consequently, a relatively low current of 3 μA was observed at this pH.

At pH 4.00, 5.00 and 6.00, the EOF measured with benzyl alcohol was found to be $3.1 \cdot 10^{-4}$ $cm^2/V\,s$, $5.8 \cdot 10^{-4}$ $cm^2/V\,s$, and $8.9 \cdot 10^{-4}$ $cm^2/V\,s$, respectively. The EOF increased almost linearly with pH in the pH range 4.00–6.00. Suppression of dissociation of silanol groups on the capillary wall lead to lowering of the charge density in the double layer. Consequently, a lower EOF was observed at lower pH [28]. Since both the EOF and complexation were affected by pH changes, resolution depended on the combined effects of the two parameters. Increase in the differences in effective mobilities resulting from increasing complexation with increase of pH resulted in enhanced resolution, but the large EOF at high pH had an adverse effect on resolution in the case of EOF and solutes moving in the same direction [1,2].

A more detailed study was performed on the effect of pH on the effective mobilities of Ba, Sr and Mg over the pH range 4.50–5.10. This pH range was chosen based on the facts that a lower pH led to merging of the peaks of Ba, Sr and Mg and that a higher pH caused the Mg peak to migrate slower than the water peak and hence became difficult to detect. In Fig. 2a, curves 1, 2 and 3 are plots of the experimental effective mobilities of Ba, Sr and Mg, i.e. U_{Ba}^{eff}, U_{Sr}^{eff} and U_{Mg}^{eff}, respectively. Effective mobilities were calculated by

$$U_M^{eff} = (L_t L_c / V)[(1/t_M) - (1/t_B)] \quad (8)$$

where L_t and L_c are the total length of the capillary and the effective length of the capillary, i.e., from the injection end of the capillary to the detection window, respectively; V is the applied voltage for separation; t_M and t_B are the migration times of metal ions and the neutral marker benzyl alcohol, respectively. Curves 4 and 5 are their differences, i.e. $U_{Ba}^{eff} - U_{Sr}^{eff}$ and $U_{Sr}^{eff} - U_{Mg}^{eff}$. Good agreement was obtained for the trend exhibited by the experimentally obtained curves 4 and 5 in Fig. 2a and the theoretically predicted curves 1 and 2 based on Eq. 5 as shown in Fig. 2b, although an exact comparison was not possible due to a lack of data for U_c. In the examined pH range of 4.50 to 5.10, $U_{Ba}^{eff} - U_{Sr}^{eff}$ increased much faster than $U_{Sr}^{eff} - U_{Mg}^{eff}$ with the increase of pH.

The UV chromophore, as a co-ion in the CE buffer, should have both a strong absorption at the detection wavelength and an ionic mobility similar to that of the solutes being detected [16,30]. Imidazole and pyridine were shown to

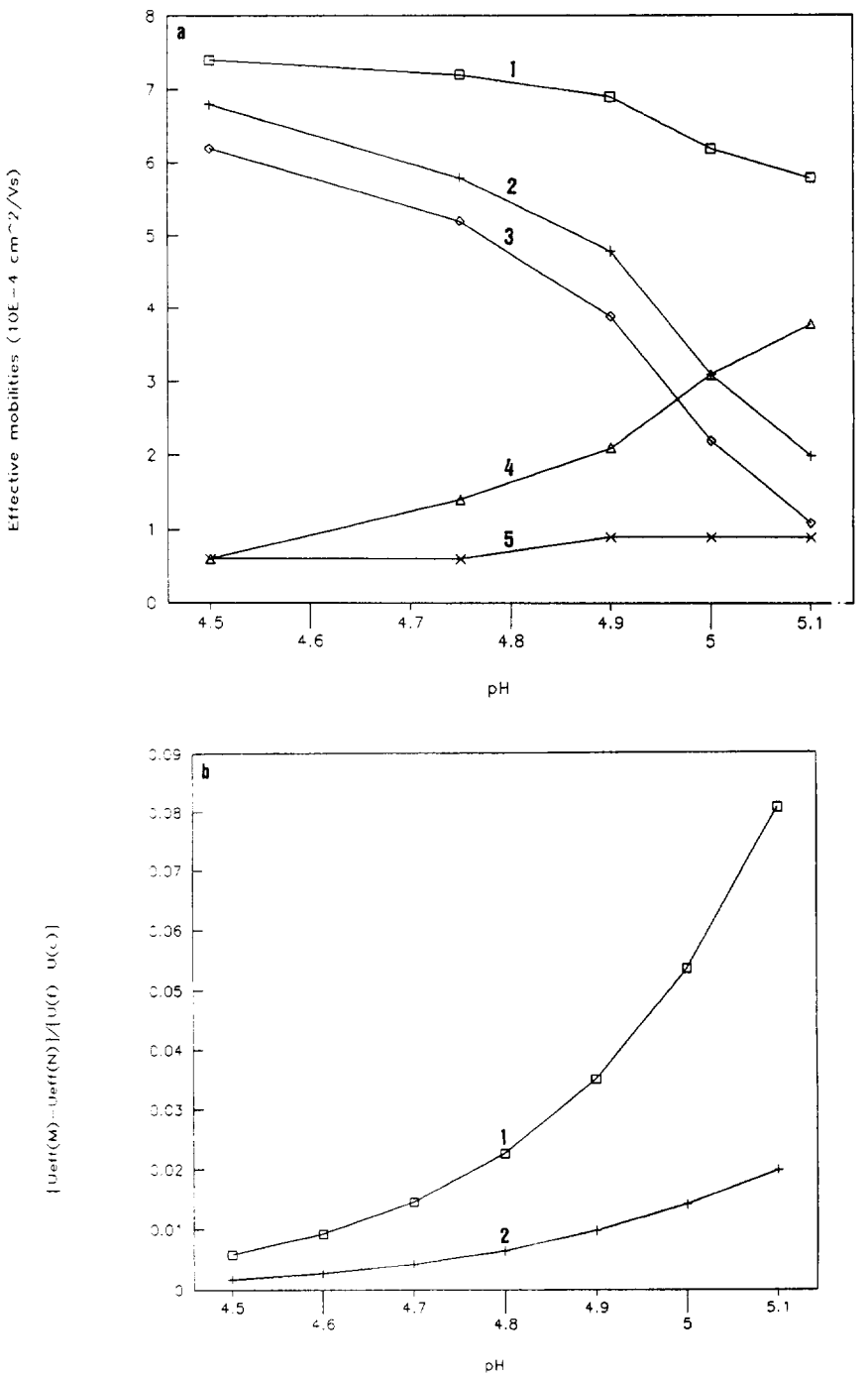

Fig. 2. Effect of pH on the effective mobilities of Ba, Sr and Mg in buffers containing 0.8 m*M* EDTA. (a) Experimental results. Curves 1, 2 and 3 represent the effective mobilities of Ba, Sr and Mg, respectively. Curves 4 and 5 show the differences in effective mobility ($4 = U_{Ba}^{eff} - U_{Sr}^{eff}$; $5 = U_{Sr}^{eff} - U_{Mg}^{eff}$). (b) Theoretical prediction of the effective mobility differences in Ba, Sr and Mg with omission of the factor of $(U_t - U_c)$ ($1 = U_{Ba}^{eff} - U_{Sr}^{eff}$; $2 = U_{Sr}^{eff} - U_{Mg}^{eff}$).

be appropriate as UV chromophores for indirect detection of common alkali and alkaline-earth metal ions [16]. The maximum absorption wavelength of imidazole is 214 nm where the complexing agent EDTA has a significant absorption and hence a high background which lowers the sensitivity. Pyridine has a maximum absorption wavelength of 254 nm where EDTA has only negligible absorption. Therefore pyridine was employed as UV chromophore in the present work.

In terms of sensitivity, a buffer of pH higher than 5.2 is unfavourable because in such cases a large fraction of pyridine exists as neutral molecules which can not be displaced by the metal ions of interest and will serve as UV absorbing species resulting in high UV background and low sensitivity.

4.2. Effect of EDTA concentration on separation

The first step in the optimization of the EDTA concentration was to decide on the concentration range of EDTA to be experimentally tested. Several criteria have been considered. The first is that the resolution should be as high as possible. From Eq. 7, it was calculated that at pH 5.00, to achieve the highest resolution between calcium and magnesium, magnesium and strontium, and strontium and barium, concentrations of EDTA should be 0.79 m*M*, 8.9 m*M* and 22 m*M*, respectively. Secondly, excessively high concentrations of EDTA should be avoided. Otherwise migration times of alkaline-earth metal ion peaks would be too long and the limits of detection would be high. Moreover, significant Joule heating may occur. Finally, extremely low concentrations of EDTA should not be used because in that case the migration times of the alkaline-earth metal ions would be highly sensitive to variations in their concentration and the concentrations of other ions in the sample which may also form complexes with EDTA.

Fig. 3 shows electropherograms obtained with different concentrations of EDTA. In all three electropherograms, calcium, magnesium, strontium and barium were well separated as expected. As a large portion of the calcium ions existed in the negatively charged complex form and the effective mobility of calcium was very low, no calcium peak did appear in the electropherograms. At 0.8 m*M* EDTA, the barium peak occurred between but well resolved from the sodium peak and the lithium peak. At lower concentration of EDTA, the effective mobility of the barium ions increased and the barium peak shifted forward closer to the sodium peak. At higher concentration of EDTA, the effective mobility of the barium ions decreased and the barium peak shifted backward closer to the lithium peak. Therefore, the subsequent experiments were conducted under the condition of 0.8 m*M* EDTA and 10 m*M* pyridine at pH 5.00.

4.3. Effect of sample preparation procedures on detection and quantitation

Sample preparation affected both detectability and linearity. Dissolving samples in water resulted in good detectability and poor linearity, but dissolving samples in running buffer had the opposite effect. With an injection time of 15 s at a height difference of 4.0 cm between the liquid levels of the sample vial and the buffer reservoir at the grounded electrode, the limit of detection (LOD) for magnesium (signal-to-noise ratio >2) was 75 ng/ml when samples were prepared in deionized water and 150 ng/ml when prepared in the running buffer. Such a difference might result from the sample stacking effect [31]. The LOD decreased down to 20 ng/ml when samples were prepared in deionized water and injections were made in 40 s with 6.5 cm difference in height. No further improvement in LOD was obtained when conditions for injection were set to 60 s and 6.5 cm. Although a slightly lower LOD (ca. 10 ng/ml) was obtained [32] with an extended path length capillary, i.e. with an "egg-shaped cell", the present method has the advantage that it uses conventional capillaries and thus would be compatible with most of the commercial detector designs. In addition, the method also has the advantages that it requires only readily available chemicals and that the resolution between the magnesium and calcium peaks

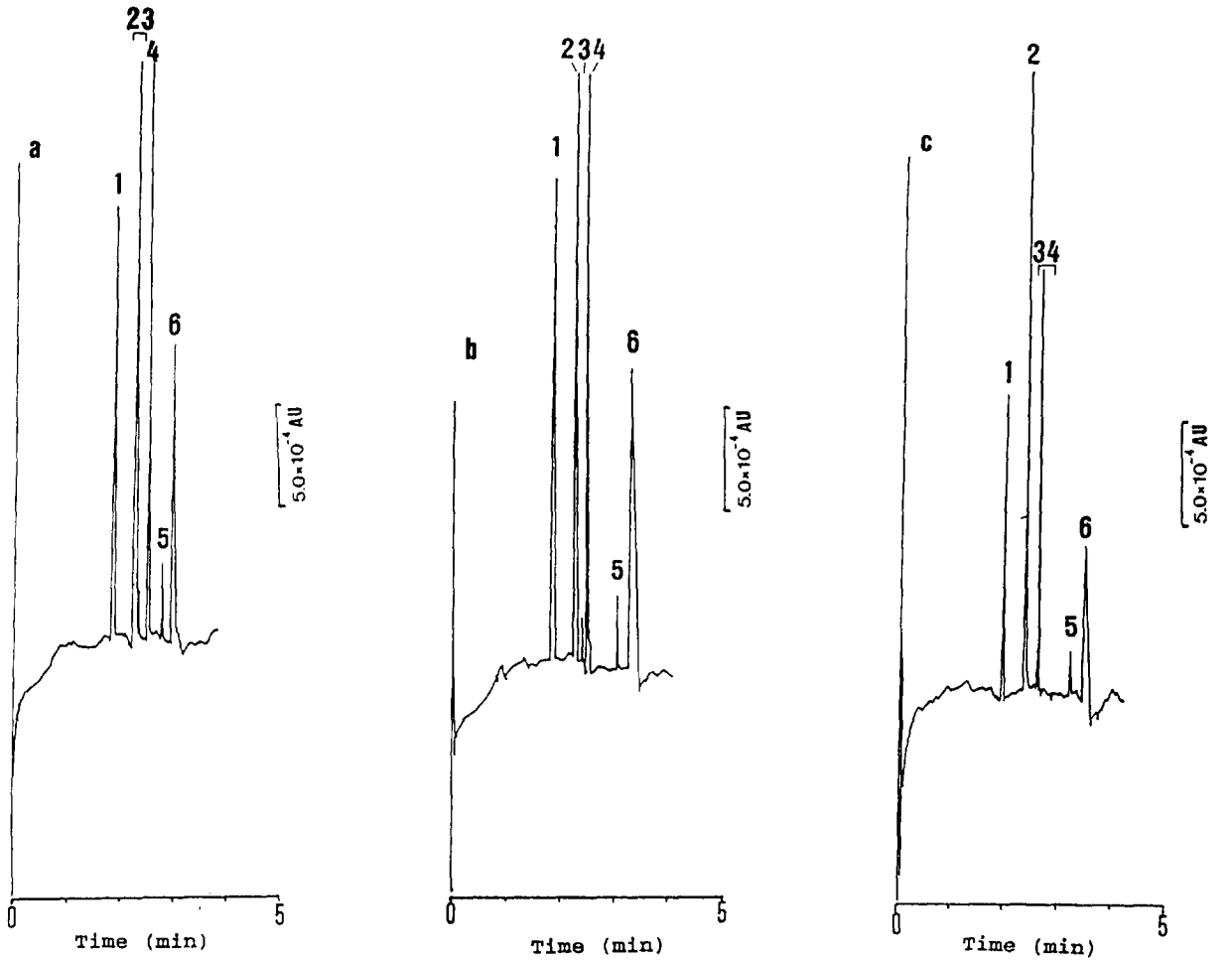

Fig. 3. Effect of concentration of EDTA on the separation of the metal ions. Conditions: L_{total} = 39.5 cm, $L_{effective}$ = 30.0 cm; pH 5.00; 10 m*M* pyridine; hydrostatic injection for 15 s with 4.0 cm height difference. (a) 0.6 m*M* EDTA; (b) 0.8 m*M* EDTA; (c) 1.0 m*M* EDTA. Peaks: 1 = K, 2 = Na, 3 = Ba, 4 = Li, 5 = Sr, 6 = Mg, and 7 = Ca. Sample concentration: K, Na, Ba, Li, Sr, Mg and Ca 1 μg/ml each in deionized water.

is so large that trace amounts of magnesium in the presence of large amounts of calcium can be separated and analyzed.

In order to maximize the dynamic detection range in the indirect UV detection mode, the absorbance of the UV-absorbing species in the running buffer was selected to be close to the upper limit of the detector linearity [10]. The running buffer used in the present experiments had an absorbance of 0.10 AU. The noise level of the baseline was lower than $2 \cdot 10^{-4}$ AU. Based on these considerations, linearity could be expected over at least two orders of the concentration range of the solute. However, the calibration graph for magnesium expressed as peak hight vs. concentration in the concentration range of 0.10–1.00 μg/ml showed a hyperbolic curve when standard solutions were prepared in deionized water. Nevertheless, with standard solutions prepared in the running buffer linearity between peak height and concentration was improved although the linear range was still limited. This non-linearity problem was previously reported by other researchers [16,18] in capillary electrophoresis of metal ions in the presence of complexing agents with indirect UV

detection. Full understanding of the reason for the non-linearity of the calibration curves has not yet been achieved.

A calibration graph for magnesium was constructed with the standard solutions prepared in running buffer and was found to be linear up to 1.00 μg/ml. The regression equation for the calibration graph was $y = 11.2 + 12822.8x$ with $r^2 = 0.9995$. Subsequent determinations were based on samples prepared in buffer solution in spite of the fact that the detection limit was lower when the samples were prepared in deionized water.

4.4. Application to the determination of magnesium in real samples

The method developed was applied to the determination of magnesium in river water, urine and a solid calcium carbonate sample. Table 1 gives the CE results for the above samples. Good agreement was obtained between the results obtained by the CE method and those obtained by atomic absorption spectrometry. Fig. 4 shows electropherograms obtained for the above samples. It was noted that even when the concentration of calcium in a sample was 1000 times higher than that of magnesium, these peaks were still well separated (see Fig. 4a). It was noted that the calcium peak was right next to the magnesium peak in Fig. 4a, which was not the case in other electropherograms. This was possibly due to the fact that the concentration of calcium ions was very high in this sample. Therefore a large portion of the calcium ions was not in the complexed form which had a lower mobility than the free ions. Consequently, a significant increase in the effective mobility of calcium was observed in Fig. 4a. Reproducibility of the CE results was in a range of 5–9% R.S.D. in terms of peak height, depending on sample matrices.

5. Conclusions

The migration behaviour of the metal ion–EDTA complexes was investigated. Equations were derived to represent the effects of pH and concentration of complexing agent on the difference in the effective mobilities. The differences in effective mobilities calculated using those equations were used for the optimization of the CE separation of metal ions with similar mobilities. K, Na, Ba, Li, Sr, and Mg could be well separated in less than 4 min by the method described in this paper. Sample preparation affected both linearity and detectability. Dissolving samples in water resulted in good detectability and poor linearity, but dissolving samples in running buffer had the opposite effect. Feasibility of the proposed method for application to real sample separation and quantitation was verified by the determination of magnesium in real samples. The method showed a reproducibility of 5–9% R.S.D. in terms of peak height, depending on sample matrices.

Table 1
Determination of magnesium in real samples

Sample	Result	
	CE	AA
Calcium carbonate[a] (% w/w)	0.023 (9.0, $n = 5$)[d]	0.021 (1.0, $n = 6$)
River water[b] (μg/ml)	812 (5.5, $n = 5$)	773 (1.4, $n = 10$)
Urine[c] (μg/ml)	78.0 (6.1, $n = 3$)	75.4 (0.4, $n = 3$)

[a] A solution of 1.50 mg sample in 1 ml buffer was injected.
[b] River water was diluted 1000 times with buffer before injection.
[c] Freshly collected urine was diluted 100 times with buffer.
[d] The values in parentheses are the relative standard deviations (%) in terms of peak height and the number of replicates.

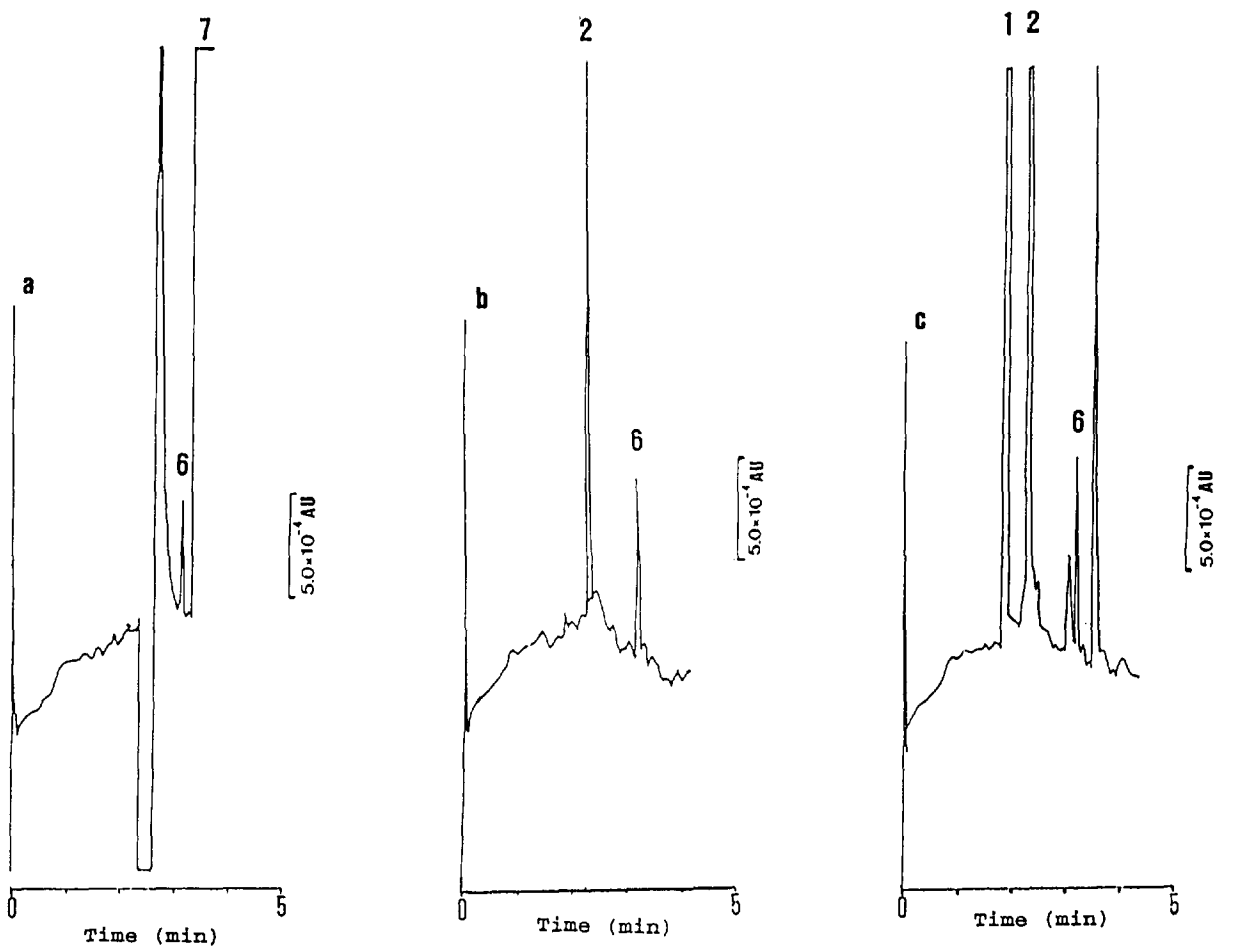

Fig. 4. Electropherograms obtained with some real samples. (a) Calcium carbonate sample, (b) river water, (c) urine. For sample preparation procedures see Table 1. Other conditions and peak identifications are the same as those in Fig. 3b.

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