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Quantitative determination of inorganic minor cations in sodium-, calcium-, magnesium-matrix simulated samples by capillary electrophoresis

X. Cahours, Ph. Morin*, M. Dreux

Institut de Chimie Organique et Analytique, CNRS UPRES-A 6005, B.P. 6759, 45 067 Orléans Cedex 2, France

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Abstract

The analysis of ammonium, alkali and alkaline-earth trace cations (0.5 ppm) in samples with a calcium, sodium or magnesium matrix (500 ppm) has been achieved using 10 m*M* imidazole (pH 4.5) electrolyte to which a complexing agent (15-crown-5, oxalic acid or dipicolinic acid) has been specifically added in order to decrease the electrophoretic mobility of the matrix cation and thus to allow the separation of higher mobility cations at sub-ppm concentrations. The influence of several experimental parameters (complexing agent concentration, buffer pH and temperature) have been studied in order to optimize the separation. The complexing agent concentration appears to be the main parameter governing the selectivity of the cations during the analysis of matrix samples. In optimized conditions, we have checked that the separation between minor inorganic cations is not significantly altered by an increase in the matrix cation concentration. As the concentration of the matrix cation increases, the migration times of minor cations remain unchanged even for a 1000 ppm concentration of the matrix cation. Finally, these optimized buffers allow the quantitation of minor cations down to 0.05% (w/w) for calcium- or magnesium- matrix simulated samples and 0.2% (w/w) for sodium-matrix simulated samples.

Keywords: Inorganic cations

1. Introduction

The analysis and quantitation of inorganic cations have become necessary in various fields, such as in the manufacture of cosmetics or food technology and in the pharmaceutical industry. Inorganic cations can be analysed by various analytical techniques, including atomic spectroscopy, electrochemistry, ion chromatography, and capillary electrophoresis [1,2]. In the last five years, capillary electrophoresis (CE) has been increasingly used. This technique allows the routine analysis of ionic samples whose concentrations are in the same order of magnitude [3–6]. However, the determination of minor cations in the presence of a high concentration cation is extremely difficult due to peak overlapping of the major cation which prevents the minor cation detection (Fig. 1). In order to improve the analyses of ionic matrix samples, it seems necessary to introduce a supplementary separation mechanism, based upon the selective complexation of the matrix cation. Indeed, the addition of a specific complexing agent to the background electrolyte induces a decrease in the electrophoretic mobility of the matrix cation [7–11].

*Corresponding author.

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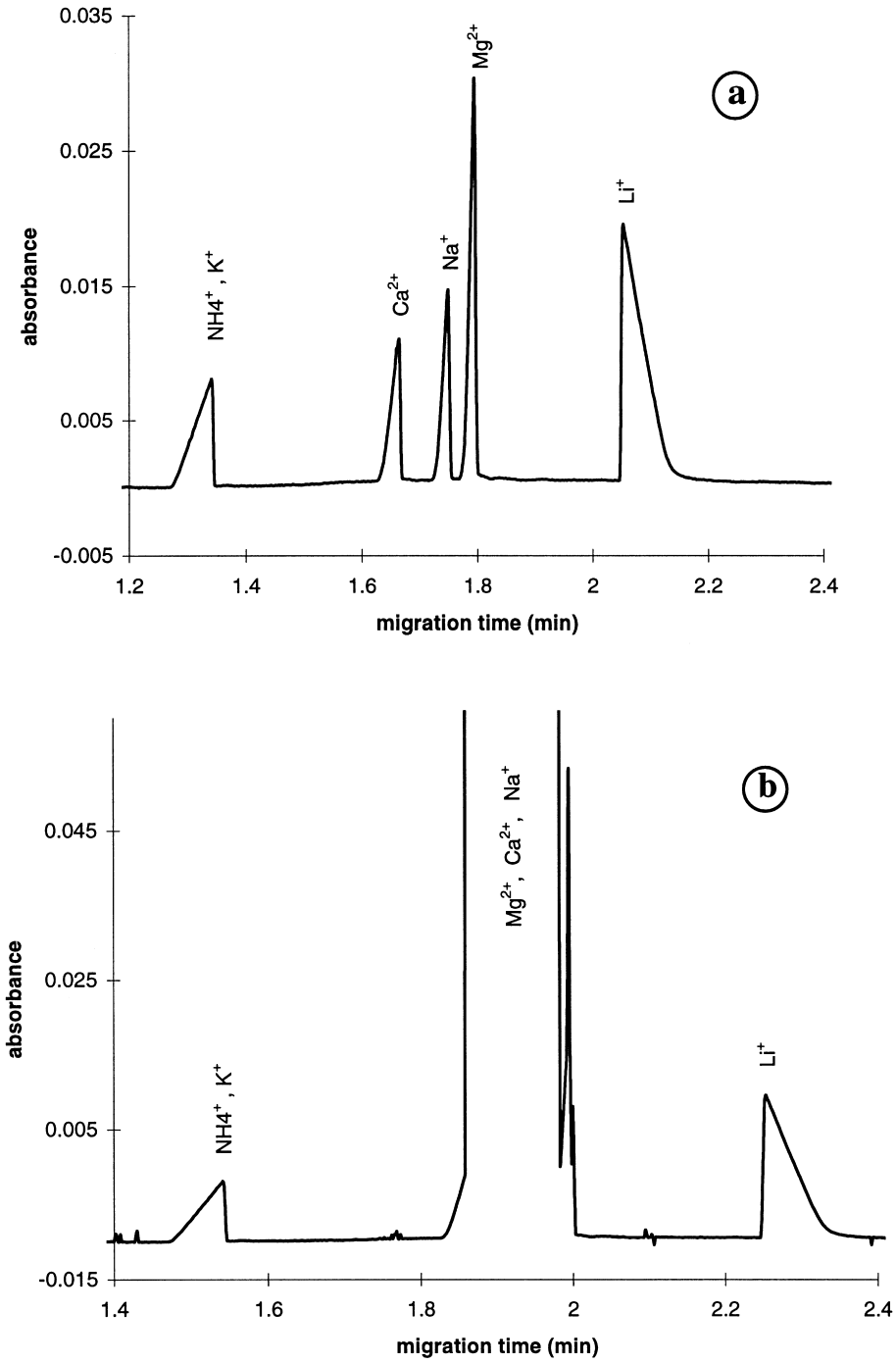

Fig. 1. Separation of a mixture of inorganic cations by capillary electrophoresis. (a) At the same concentration, (b) in a sodium matrix simulated sample. Fused-silica capillary dimensions: 47 cm (40 cm to detector)×75 μm I.D., 100 μm×800 μm aperture; electrolyte, 10 m*M* imidazole, pH 4.5; indirect UV detection at 214 nm; applied voltage: +30 kV; temperature: 25°C; hydrodynamic injection: 5 s; cation concentration: (a) 10 mg l^{-1}; (b) 10 mg l^{-1} except for Na^+ 500 mg l^{-1}.

The purpose of this study was to develop a procedure by capillary electrophoresis for the simultaneous analysis of minor inorganic cations in sodium-calcium-magnesium matrix simulated samples. Several complexing agents of inorganic cations were tested such as 15-crown-5 for sodium [12], oxalic acid for magnesium [13] and dipicolinic acid for calcium cations. The following physico-chemical parameters (complexing agent concentration, buffer pH, temperature, applied voltage) were optimized in order to achieve the quantitation of minor inorganic cations.

2. Experimental

2.1. Apparatus

Capillary electrophoresis separation was carried out on a P/ACE 2210 apparatus (Beckman Instrument, Fullerton, CA, USA), using a fused-silica capillary of 47 cm×75 μm I.D×375 μm O.D, with a length from injection to detection of 40 cm. The solutes were injected at the anode end of the capillary in the hydrodynamic mode under nitrogen superpressure (0.5 p.s.i). Separations were made at constant temperature by immersion of the capillary in a cooling liquid circulating in the cartridge. Indirect UV detection was performed at 214 nm (maximum absorbance wavenumber of the imidazole buffer). The detection window was set at 7 cm from the end of the capillary and the detection aperture dimensions were 100 μm×800 μm. Detector time constant was 1 s. and the data acquisition rate was 20 Hz. An IBM PS/2 computer and System Gold software version 7.11 (Beckman) were used for instrument control and for data collecting and processing.

The pH of each solution was checked on a Beckman pH meter (Model ϕ 10, Fullerton, CA, USA).

The capillary was conditioned daily by rinsing with 1 *M* sodium hydroxide (10 min), then water (5 min) and finally with electrophoretic buffer (10 min). Between two consecutive injections, the capillary was equilibrated with the electrolyte buffer for 5 min. Linear regression was done by using the software Regrelis (Logedic, Vesoul, France).

Buffers have been prepared with the help of Phoebus software (Sedere Co, Franklin MA, USA).

2.2. Chemicals

Imidazole (99% purity) was obtained from Sigma (St. Louis, MO, USA) while 15-crown-5 (99%), oxalic acid (99%) and dipicolinic acid (2,6-pyridinedicarboxylic acid (99%)) were purchased from Aldrich (Milwaukee, WI, USA). The water used for the preparation of electrolytes was of HPLC quality obtained from Elgastat UHQ II system (Villeurbanne, France). The electrolyte pH was adjusted by adding either 1 *M* acetic acid stock solution (Carlo Erba, Milan, Italy) for pH values higher than 4.5, or by adding 17 *M* formic acid solution (Aldrich) for pH values smaller than 4.5. All buffers and rinsing solutions were filtered before use through a membrane filter of 25 mm diameter and 0.2 μm porosity (Whatman, Maidstone, UK).

3. Results and discussion

During the separation of inorganic cations by CE with an indirect detection, the electrophoretic buffer must contain a chromophore co-ion with an electrophoretic mobility close to that of the analytes in order to minimize the electromigration dispersion and to obtain symmetrical and efficient electrophoretic peaks. Beck and Engelhardt [3] were the first to use imidazole ($pK_{a_1}=6.9$ and $pK_{a_2}=14.5$) as co-ion whose UV spectrum has a maximum absorption at 211 nm ($\varepsilon=4770\ l\,mol^{-1}\,cm^{-1}$). The heterocyclic imidazolium cation has an electrophoretic mobility of $45.8\cdot10^{-5}\ cm^2\,V^{-1}\,cm^{-1}$ (measured in 10 m*M* sodium acetate at pH 4.5) close to that of magnesium and sodium cations (46.3 and $48.1\cdot10^{-5}\ cm^2\,V^{-1}\,cm^{-1}$, respectively, measured in 10 m*M* imidazole electrolyte at pH 4.5 [7]).

3.1. Influence of the concentration of complexing agent added to the imidazole electrolyte

François et al. [7] have studied the complete separation of ammonium, alkali and alkaline earth cations by CE, and optimized the composition of

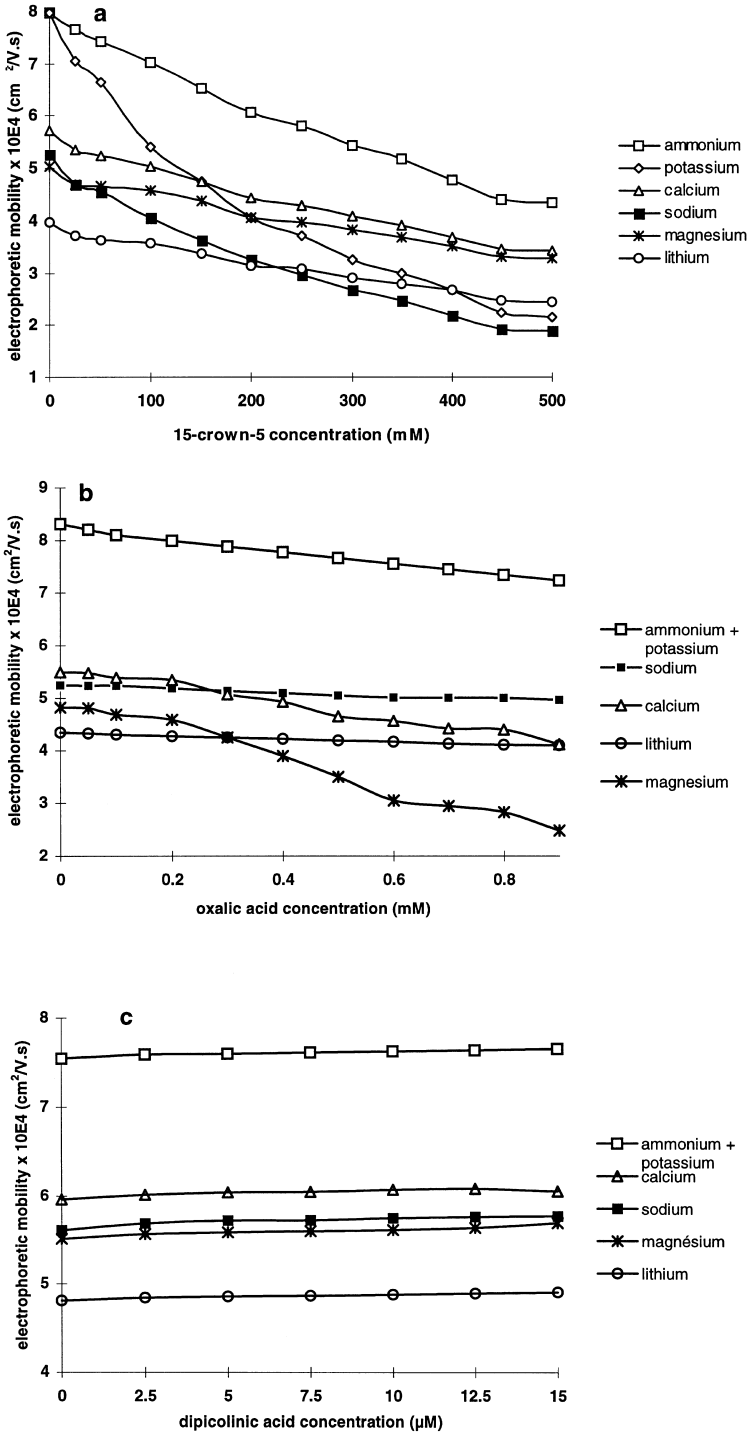

Fig. 2. Influence of complexing agent concentration on the electrophoretic mobility of several inorganic cations. Fused-silica capillary dimensions: 47 cm (40 cm to detector)×75 μm I.D., 100 μm×800 μm aperture; indirect UV detection at 214 nm; applied voltage: +30 kV; temperature: 25°C; hydrodynamic injection: 5 s; cation concentration 10 mg l^{-1}. Electrolyte: (a) 10 m*M* imidazole, 15-crown-5, pH 4.5, (b) 10 m*M* imidazole, oxalic acid, pH 4.5, (c) 10 m*M* imidazole, dipicolinic acid, pH 4.5.

Table 1
Influence of 15-crown-5 concentration on the electrophoretic resolution of Li^+/K^+ and K^+/Na^+ couples

15-Crown-5 concentration (m*M*)	R_s (lithium-potassium)	R_s (potassium-sodium)
400	0	2.1
450	0.8	1.8
500	1.5	1.7
550	2.9	0.2

Experimental conditions as in Fig. 2a.

18-crown-6-imidazole buffer. According to these authors, the migration order of these inorganic cations mainly depends on the concentration of 18-crown-6.

In our study, a complexing agent (15-crown-5, oxalic acid or dipicolinic acid) has been added to the imidazole buffer (10 m*M*, pH 4.5). Then, the electrophoretic mobility of each inorganic cation has been determined and plotted versus the complexing agent concentration (Fig. 2). The shape of the electrophoretic mobility-complexing agent concentration curves differ depending on the complexation degree of the cation:

- for a non-complexed cation, its electrophoretic mobility remains either unchanged by a variation in the complexing agent concentration, because the buffer viscosity is constant (for example, sodium and lithium with oxalic acid, or cations with dipicolinic acid), or decreases due to an increase of the buffer viscosity (for example, lithium, calcium and magnesium with 15-crown-5).
- for a complexed cation, an increase in the complexing agent concentration induces a weaker electrophoretic mobility (for example, sodium and potassium cations with 15-crown-5, or magnesium and calcium with oxalic acid).

Oehrle [12] compared different crown-ethers for the separation of inorganic cations. It can clearly be seen that 15-crown-5 is a specific complexing agent of sodium cation, but also of potassium cation. Indeed, the stability constant of the complex between an inorganic cation and a crown-ether molecule depends on the diameters of the crown-ether cavity and of the inorganic cation. Table 1 reports the resolution between Li^+ and K^+ cations and, also between K^+ and Na^+ cations, when 15-crown-5 was added to the imidazole buffer (10 m*M*, pH 4.5). In order to determine the cationic composition of a sodium-matrix simulated sample by CE, the imidazole buffer (10 m*M*, pH 4.5) must contain 15-crown-5 at 500 m*M*.

Likewise, when oxalic acid is added to the imidazole buffer (10 m*M*, pH 4.5), the magnesium cation migrates more slowly due to its complexation with the oxalate anion. The migration order between calcium and sodium cations was reversed as the electrolyte contains more than 0.3 m*M* oxalic acid. These preferential complexations between divalent cations and oxalate anion agree with results reported by Lin et al. [13]. Table 2 reports the variation of resolution between Ca^{2+} and Li^+ cations, and also between Li^+ and Mg^{2+} cations when various concentrations of oxalic acid were added to this imidazole buffer. So, the analysis of inorganic cations can

Table 2
Influence of oxalic acid concentration on the electrophoretic resolution of Ca^{2+}/Li^+ and Li^+/Mg^{2+} couples

Oxalic acid concentration (m*M*)	R_s (calcium-lithium)	R_s (lithium-magnesium)
0.50	2.9	3.6
0.60	2.0	5.7
0.65	1.9	5.8
0.70	1.8	6.2
0.75	1.8	6.6
0.80	1.6	7.3
0.90	0.3	9.7

Experimental conditions as in Fig. 2b.

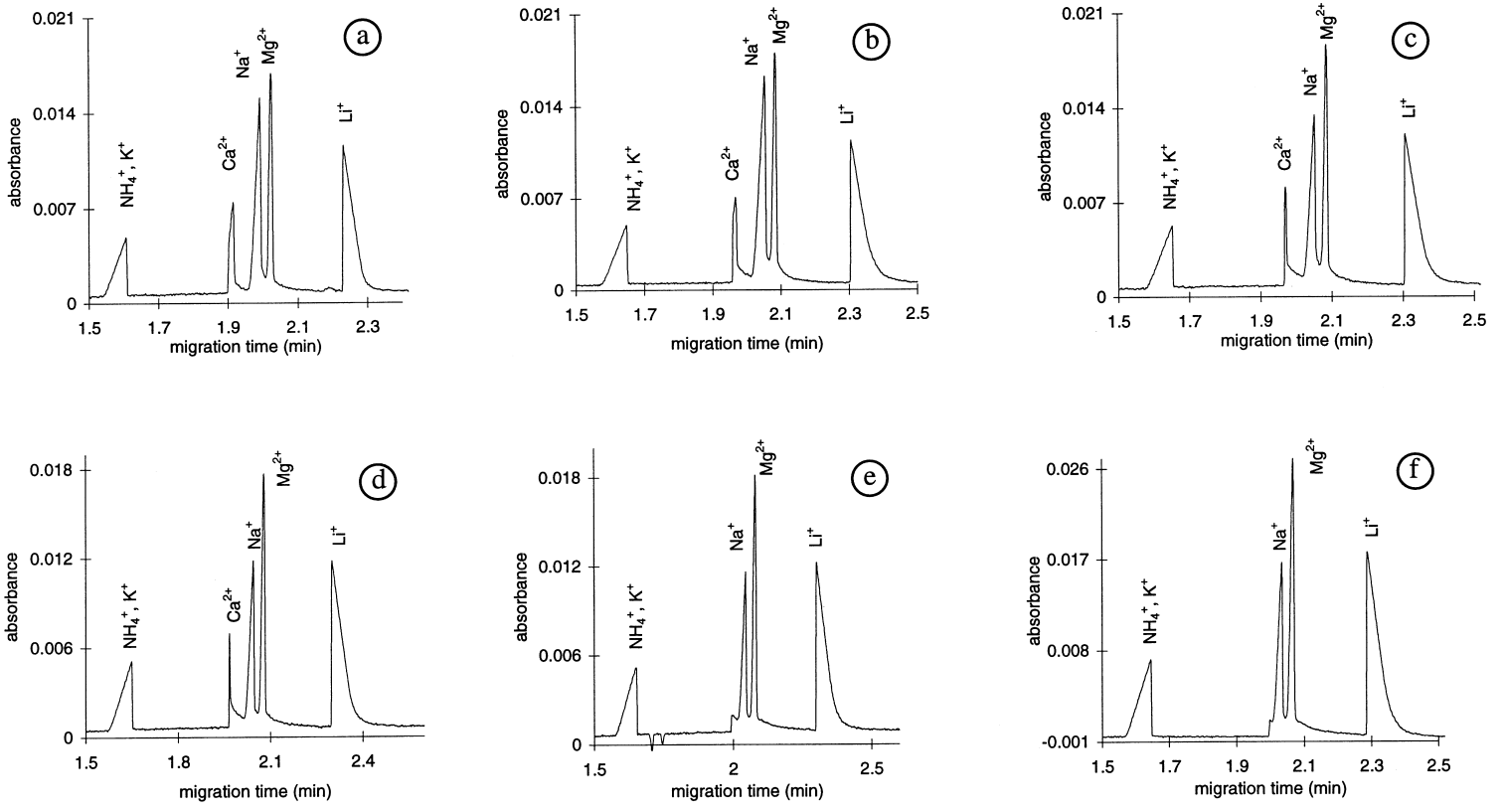

Fig. 3. Influence of dipicolinic acid concentration added to imidazole electrolyte on the cation migration order. Fused-silica capillary dimensions: 47 cm (40 cm to detector)×75 μm I.D., 100 μm×800 μm aperture; electrolyte, 10 m*M* imidazole, dipicolinic acid, pH 4.5; indirect UV detection at 214 nm; applied voltage: +30 kV; temperature: 25°C; hydrodynamic injection: 5 s; cation concentration 10 mg l^{-1}. Dipicolinic acid concentration (μ*M*): (a) 2.5; (b) 5; (c) 7.5; (d) 10; (e) 12.5; (f) 15.

Table 3
Influence of buffer pH on resolution between inorganic cations

pH	R_s (ammonium–calcium)	R_s (calcium–magnesium)	R_s (magnesium–lithium)	R_s (lithium–potassium)	R_s (potassium–sodium)
3.5	7.06	2.24	4.57	1.16	2.37
4.0	6.67	2.01	4.26	1.58	2.19
4.5	6.54	1.95	4.02	1.90	2.08
5.0	4.74	1.34	3.61	1.77	1.86

Fused-silica capillary dimensions: 47 cm (40 cm to detector)×75 μm I.D., 100 μm×800 μm aperture; electrolyte: 10 m*M* imidazole, 500 m*M* 15-crown-5; indirect UV detection at 214 nm; applied voltage: +30 kV; temperature: 20°C; hydrodynamic injection; 5 s; cation concentration: 10 mg l^{-1}.

be successfully achieved by employing the imidazole buffer (10 m*M*, pH 4.5) to which 0.5 m*M* oxalic acid has been added. In the case of a magnesium-matrix sample, a nice separation has been obtained at 0.75 m*M* oxalic acid.

Finally, dipicolinic acid is known to form a neutral and strong complex with calcium cation and may offer an efficient way to analyze calcium-matrix samples. Variable concentrations of dipicolinic acid was added to the imidazole buffer (10 m*M*, pH 4.5). In the 2.5–15 μ*M* range, the electrophoretic mobilities of inorganic cations remain constant, but the peak area of the calcium cation decreases (Fig. 3). As the concentration of dipicolinic acid is equal to 12.5 μ*M*, the calcium peak disappears from the electropherogram.

3.2. Effect of electrolyte pH

The influence of electrolyte pH has been studied by using 10 m*M* imidazole and 500 m*M* of 15-crown-5 electrolyte at different pH values (Table 3). Going from pH 3.5 up to pH 5.0 increases the electroosmotic flow (by five times), but induces smaller resolution between two consecutive cations (except for the Li^+/K^+ couple). For example, the K^+/Na^+ resolution increases from 1.86 at pH 5 to 2.37 at pH 3.5. The best compromise between Li^+/K^+ and K^+/Na^+ resolutions occurs at pH 4.5.

3.3. Effect of temperature

The influence of temperature on the separation of these inorganic cations has been carried out with 500 m*M* 15-crown-5, 10 m*M* imidazole buffer (pH 4.5) in the 20–35°C range. Table 4 reports the values of peak efficiencies of six cations and resolutions between five couples of cations at four temperatures (20, 25, 30, 35°C). Temperature variation affects

Table 4
Influence of temperature on peak efficiency (*N*) and resolution (R_s)

Temperature (°C)	*N* (ammonium)	*N* (calcium)	*N* (magnesium)	*N* (lithium)	*N* (potassium)	*N* (sodium)
20	37 000	168 800	208 400	15 700	33 500	27 000
25	32 400	147 800	219 800	13 800	31 800	24 300
30	27 800	113 200	187 800	11 200	27 200	21 100
35	21 300	98 900	132 700	11 800	26 100	18 900
	R_s (ammonium–calcium)	R_s (calcium–magnesium)	R_s (magnesium–lithium)	R_s (lithium–potassium)	R_s (potassium–sodium)	
20	6.25	2.08	3.98	1.91	2.03	
25	5.60	1.72	3.01	1.46	1.72	
30	5.02	1.51	2.72	1.00	1.54	
35	4.48	1.38	2.39	0.79	1.10	

Fused-silica capillary dimensions: 47 cm (40 cm to detector)×75 μm I.D., 100 μm×800 μm aperture; electrolyte: 10 m*M* imidazole, 500 m*M* 15-crown-5, pH 4.5; indirect UV detection at 214 nm; applied voltage: +30 kV; temperature: 25°C; hydrodynamic injection: 5 s; cation concentration: 10 mg l^{-1}.

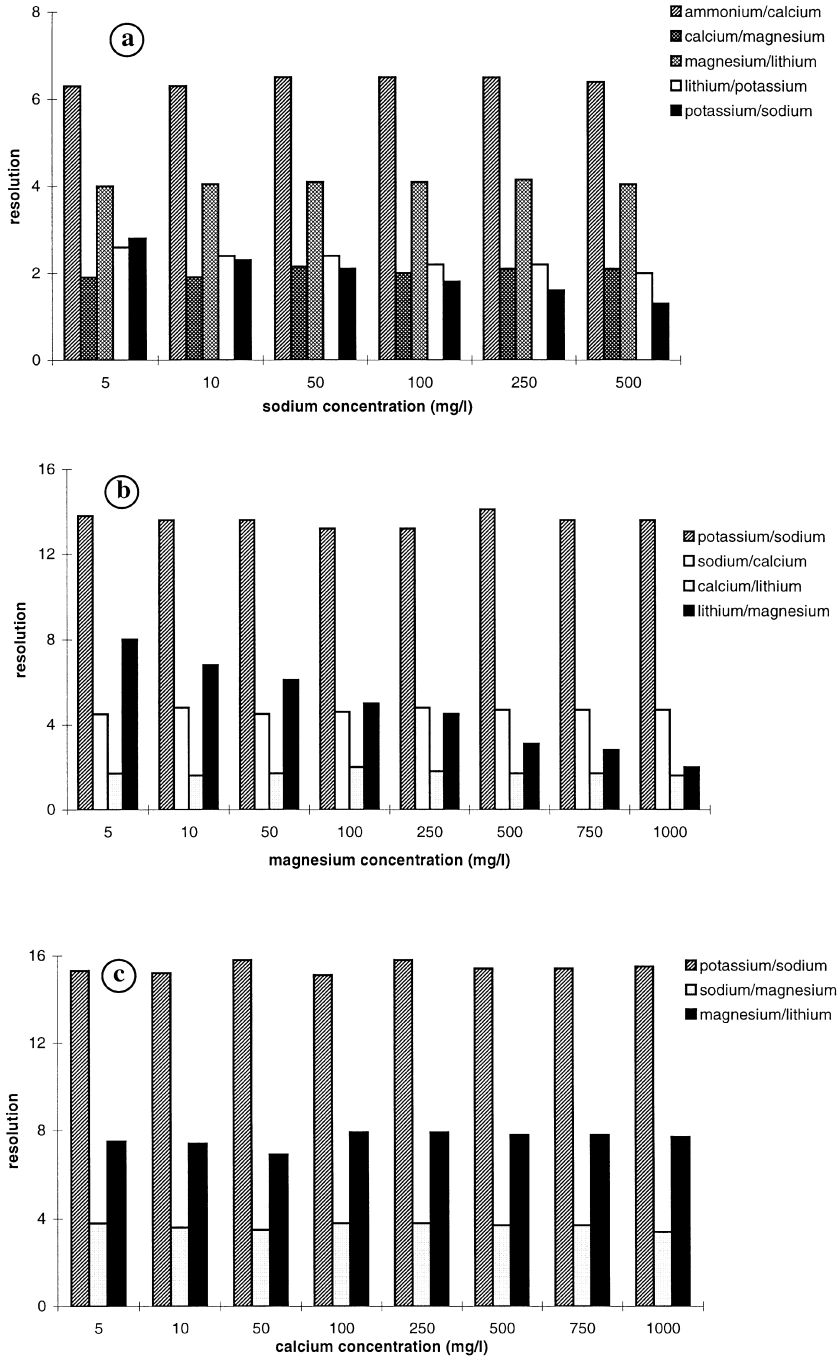

Fig. 4. Influence of matrix cation concentration on the resolution between minor inorganic cations of the sample. Fused-silica capillary dimensions: 47 cm (40 cm to detector)×75 μm I.D., 100 μm×800 μm aperture; electrolyte: (a) 10 m*M* imidazole, 500 m*M* 15-crown-5, pH 4.5, (b) 10 m*M* imidazole, 0.75 m*M* oxalic acid, pH 4.5, (c) 10 m*M* imidazole, 200 μ*M* dipicolinic acid, pH 4.5; indirect UV detection at 214 nm; applied voltage: +30 kV; hydrodynamic injection: (a) 5 s, (b) 1 s, (c) 5 s; temperature: (a) 20°C, (b) 25°C, (c) 25°C. Cation concentration: (a) 10 mg l^{-1} for NH_4^+, K^+, Mg^{2+}, Li^+, Ca^{2+} and from 1 to 500 mg l^{-1} for Na^+, (b) 10 mg l^{-1} for NH_4^+, K^+, Li^+, Ca^{2+}, Na^+ and from 1 to 1000 mg l^{-1} for Mg^{2+}, (c) 10 mg l^{-1} for NH_4^+, K^+, Mg^{2+}, Li^+, Na^+ and from 1 to 1000 mg l^{-1} for Ca^{2+}.

numerous physical parameters of the buffer (viscosity, dielectric constant, pH) and, the electroosmotic flow and the electrophoretic mobilities of the analytes are modified. Increasing temperature induces higher electrophoretic mobility, but does not significantly alter at pH 4.5 the selectivity of the separation. However, peak efficiencies are slightly better at lower temperature due to a reduced axial diffusion. Thus, it seems more interesting to work at 20°C rather than at 35°C due to a noticeable increase in resolution between Li^+ and K^+ cations (0.79 to 1.91), and, between K^+ and Na^+ cations (1.10 to 2.03).

3.4. Influence of the matrix cation concentration on separation

The influence of the concentration of the matrix cation (Na^+, Mg^{2+} or Ca^{2+}) on the separation of inorganic cation mixture has been investigated with the optimized buffers. The concentration of complexing agent added to the imidazole buffer (10 m*M*) was equal to 500 m*M* for 15-crown-5 and 0.75 m*M* for oxalic acid. For dipicolinic acid, its concentration depends on calcium concentration (12.5 μ*M* dipicolinic acid for 10 mg l^{-1} calcium cation and 200 μ*M* dipicolinic acid for 1000 mg l^{-1} calcium cation).

The resolution between minor cations (10 mg l^{-1} concentration) has been determined at different matrix cation concentrations (1–500 mg l^{-1} range for sodium matrix and 1–1000 mg l^{-1} range for magnesium and calcium matrix). The resolution between minor inorganic cations is not significantly altered by an increase in matrix cation concentration (Fig. 4). Obviously, an increasing matrix cation concentration modified the resolution between the matrix cation and its neighbouring cation (for instance, K^+ and Na^+ cations with 15-crown-5-imidazole buffer, or Li^+ and Mg^{2+} cations with oxalic acid-imidazole buffer).

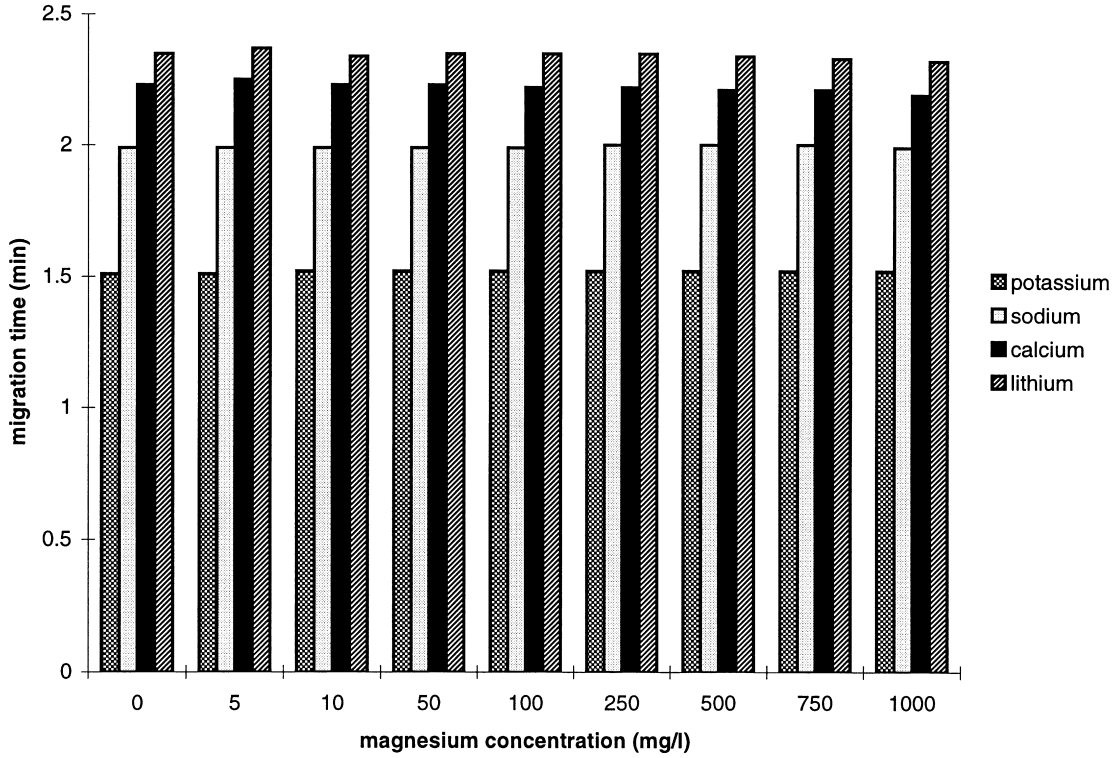

Fig. 5. Influence of matrix cation concentration (magnesium) on the migration times of minor inorganic cations. Experimental conditions as in Fig. 4b.

Table 5
Quantitative analysis of inorganic trace level cations in sodium-, magnesium- or calcium-matrix simulated samples

	Matrix cation	Minor cation	Slope	*y*-Intercept	Correlation coefficient (*r*)
a	Sodium (500 mg l^{-1})	Calcium	0.0618	0.0973	0.9915
		Magnesium	0.1185	−0.0204	0.9961
		Ammonium	0.131	−0.0185	0.9987
		Lithium	0.2454	−0.0533	0.9984
b	Magnesium (1000 mg l^{-1})	Potassium	0.1238	−0.0131	0.9991
		Calcium	0.0894	0.2547	0.9999
		Sodium	0.0807	0.1746	0.9956
		Lithium	0.3378	−0.0254	0.9994
c	Calcium	Potassium	0.1002	−0.0574	0.9977
	Calcium	Magnesium	0.1273	0.0198	0.9974
		Sodium	0.0337	−0.4508	0.9918
		Lithium	0.2505	−0.0077	0.9989

Fused-silica capillary dimensions: 47 cm (40 cm to detector)×75 μm I.D., 100 μm×800 μm aperture; electrolyte: (a) 10 m*M* imidazole, 500 m*M* 15-crown-5, pH 4.5, (b) 10 m*M* imidazole, 0.75 m*M* oxalic acid, pH 4.5, (c) 10 m*M* imidazole, 200 μ*M* dipicolinic acid, pH 4.5; indirect UV detection at 214 nm; applied voltage: +30 kV; hydrodynamic injection: (a) 5 s, (b) 1 s, (c) 5 s; temperature: (a) 20°C, (b) 25°C, (c) 25°C. Cation concentration: (a) 1–30 mg l^{-1} for NH_4^+, K^+, Mg^{2+}, Li^+, Ca^{2+} and 500 mg l^{-1} for Na^+, (b) 0.5–50 mg l^{-1} for NH_4^+, K^+, Li^+, Ca^{2+}, Na^+ and 1000 mg l^{-1} for Mg^{2+}, (c) 0.5–50 mg l^{-1} for NH_4^+, K^+, Mg^{2+}, Li^+, Na^+ and 1000 mg l^{-1} for Ca^{2+}.

At last, the influence of magnesium concentration on the migration time of several minor cations (potassium, calcium, sodium and lithium) with optimized oxalic acid–imidazole buffer is shown in Fig. 5. It has been reported numerous times in the literature that migration times of minor cations are strongly modified by an increase in the matrix cation concentration. Using oxalic acid–imidazole buffer, the migration times of minor cations remain unchanged when the concentration of matrix cation becomes higher.

3.5. Quantitative analysis

Calibration curves have been determined for minor cations, either in the 1–30 mg l^{-1} concentration range with 500 mg l^{-1} sodium-matrix, or in the 0.5–50 mg l^{-1} concentration range with 1000 mg l^{-1} magnesium- or 1000 mg l^{-1} calcium-matrix. These experiments were carried out by using 10 m*M* imidazole-based electrolytes containing either 15-crown-5 (500 m*M*), oxalic acid (0.75 m*M*) or dipicolinic acid (200 μ*M*), as complexing agent according to the ionic nature of the sample matrix. For all analysed inorganic cations, the linear correlation coefficients were greater than 0.991 (Table 5). However, the quantification of potassium cation in a 500 mg l^{-1} sodium-matrix cannot be performed by using 10 m*M* imidazole, 500 m*M* 15-crown-5, pH 4.5 buffer because the asymmetry of the sodium peak does not allow an accurate quantitation of minor potassium cation.

Finally, Fig. 6. reports the optimized CE analysis of several minor inorganic cations in sodium-, magnesium- or calcium-matrix simulated samples by using 10 m*M* imidazole buffer (pH 4.5) to which a complexing agent (15-crown-5, oxalic acid or dipicolinic acid) has been added. The separation and quantitation of minor cations has been achieved at low level (0.05%, w/w, in calcium- or magnesium-matrix simulated samples and 0.2%, w/w, in sodium-matrix simulated sample).

4. Conclusion

The separation of inorganic minor cations in sodium-, magnesium- or calcium-matrix simulated samples can be achieved by capillary electrophoresis with a modified imidazole buffer (10 m*M*) to which a complexing agent of the matrix cation (15-crown-5, oxalic acid, dipicolinic acid) is added. The selectivity of the separation is generally managed by varying the concentration of the complexing agent, and, also the buffer pH and the temperature.

Using these modified imidazole buffers, the

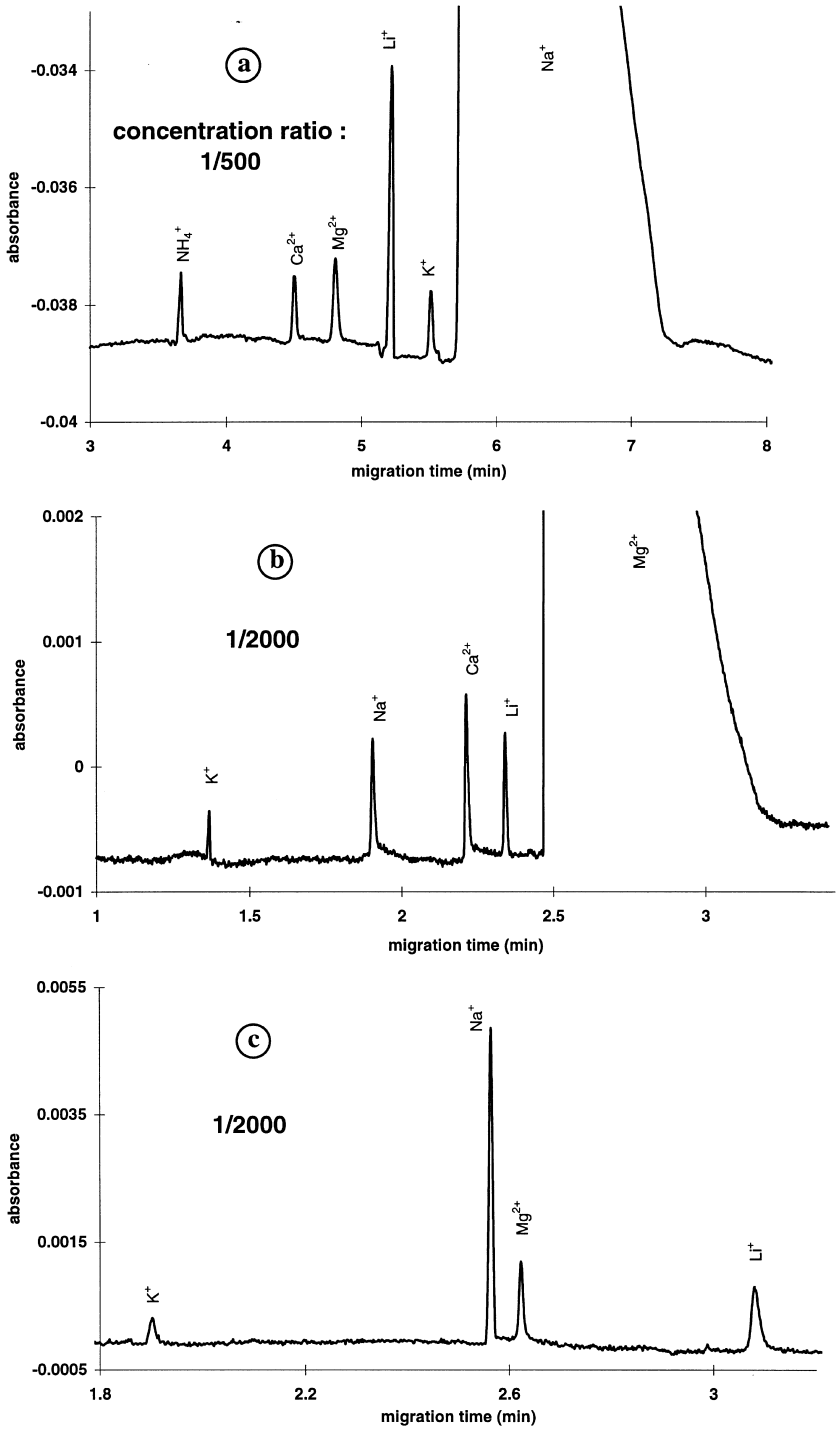

Fig. 6. Optimized separations of inorganic minor cations in an ionic-matrix simulated sample by capillary electrophoresis. Experimental conditions as in Fig. 4, except: Cation concentration: (a) 1 mg l^{-1} for NH_4^+, K^+, Mg^{2+}, Li^+, Ca^{2+} and 500 mg l^{-1} for Na^+, (b) 0.5 mg l^{-1} for NH_4^+, K^+, Li^+, Ca^{2+}, Na^+ and 1000 mg l^{-1} for Mg^{2+}, (c) 0.5 mg l^{-1} for NH_4^+, K^+, Mg^{2+}, Li^+, Na^+ and 1000 mg l^{-1} for Ca^{2+}.

quantitation of minor cations has been achieved with contents as low as 0.05% (w/w) in calcium-or magnesium-matrix and 0.2% (w/w) in sodium-matrix simulated samples.

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