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## Simultaneous determination of alkali, alkaline earth and transition metal ions by capillary electrophoresis with indirect UV detection

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### Abstract

Determination of metal ions in aqueous samples using capillary electrophoresis can be accomplished with indirect UV detection. For optimal determination of alkali, alkaline earth, and transition metal ions, several electrolyte systems were studied. Detection at 214 nm was performed with a background electrolyte containing reagents with inherent absorbance in the UV range: imidazole, 4-methylbenzylamine and 4-aminopyridine. Glycolic acid and  $\alpha$ -hydroxyisobutyric acid were used as complexing reagents. A mixture of 16 metal ions was successfully separated. The detection limits were between 92 ppb for Ca and 454 ppb for Cu with hydrostatic injection. All peaks were completely resolved and well separated. A separation efficiency of about 650 000 theoretical plates per meter was achieved for the Mg ion. The described methods can be used successfully in routine analysis of real samples. One of the methods was applied to an environmental water sample from the Georgian river Kasretula. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Water analysis; Environmental analysis; Background electrolyte composition; Complexation; Metal cations

### 1. Introduction

Determination of metal ions, including alkali, alkaline earth, and transition metal ions, is of great importance because of medical and environmental problems. Thus, sensitive and rapid methods are needed to determine the qualitative and quantitative composition of these possible metal contamination sources. The separation of alkali, alkaline earth, and transition metals with conventional ion-exchange chromatography still exhibits several disadvantages such as long analysis times and high costs for special column hardware.

After the introduction of capillary electrophoresis, determination of metal cations was achieved by Hjertén [1]. Conductivity detection of metal ions using CZE was performed [2], but the use of this method for routine analysis is problematic. After the utilization of the indirect UV detection method for the detection of lanthanide ions [3], it became more popular and even indispensable, especially for routine analyses. In recent years, a number of works have been dedicated to the problem of separating and detecting metal ions. Among them are investigations on the separation of alkali and alkaline earth metal ions, amines and amino alcohols using different background electrolytes (BGEs) [4] and on the determination of alkali and alkaline earth metals in environmental water samples and blood [5]; Cheng et al. [6] proposed several buffer systems for the separation of metal cations; Xiong and Li [7]

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described the relationship between the sensitivity and electrophoretic properties of background electrolytes for alkali metal ions; Lee and Lin [8] investigated the influence of different BGEs and complexing agents on the separation of metal ions; some physico-chemical parameters were optimized to achieve the quantitation of alkali and alkaline earth metal cations in the work of Cahours et al. [9].  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were determined in seawater and formation water using 4-methylbenzylamine as buffer component and  $\alpha$ -hydroxyisobutyric acid as a complexing reagent by Tangen et al. [10]. Weston et al. [11–13] investigated the influence of different BGEs and complexing reagents on the separation of alkali, alkaline earth and transition metals and lanthanide metals, and the detection sensitivity. New approaches for the simultaneous separation of inorganic anions and metal cations are described in original works of Padarauskas et al. [14] and Kubaň et al. [15].

In this paper we report on the optimization and utilization of a new background electrolyte which permits highly effective, selective and successful separation of a mixture of the cations K, Na, Ba, Sr, Ca, Mg, Mn, Li, Fe(II), Co, Cd, Ni, Zn, Pb, Cr and Cu. The migration behavior of complexes with respect to complexing reagent concentration is also discussed. In this work, we have included data on the qualitative and quantitative analysis of an environmental water sample, showing the possible application of these methods for the determination of metal ions in other environmental matrices.

## 2. Experimental

Experiments were performed with a Waters CIA system (Milford, MA, USA) equipped with a positive power supply. A voltage of 25 kV was applied for separation. Waters Millenium V2.10 software was used for the control of instrument settings, data acquisition and analysis. Indirect UV detection was achieved at 214 nm. Separations were made at a constant temperature of 25°C by automatic temperature control. Bare fused-silica capillaries [108 cm (100 cm effective length)  $\times$  75  $\mu\text{m}$  I.D.] were purchased from Polymicro Technologies (Phoenix, AZ, USA). New capillaries were conditioned by rinsing

with 0.1 M NaOH for 1 h, followed by a 30-min rinse with water and a 30-min rinse with the appropriate electrolyte; they were washed after every change of electrolyte with a 5-min rinse of 0.1 M NaOH and then with water and the appropriate electrolyte. The samples were introduced into the capillary by the hydrostatic injection mode: injection time 20 and 30 s with a height difference of 10 cm. The current was monitored for all evaluated BGEs and was in the range of 10 to 25  $\mu\text{A}$ .

All electrolytes were prepared daily using water from a Milli-Q unit (Millipore, Bedford, MA, USA) through dilution of an appropriate amount of the UV-absorbing buffer compound and the complexing reagent. Imidazole (Merck, Darmstadt, Germany), 4-methylbenzylamine (UV CAT-1; Fluka, Buchs, Switzerland) and 4-aminopyridine (Fluka) were used as UV-absorbing compounds and glycolic acid (Fluka) and  $\alpha$ -hydroxyisobutyric acid (HIBA, Fluka) were used as complexing reagents. Before use, all electrolytes were filtered through a 0.45  $\mu\text{m}$  membrane filter (Sartorius, Göttingen, Germany) and degassed in an ultrasonic bath. The pH was varied as indicated in the figures, adjusted by addition of the complexing reagent solution to the required value. Alkali and alkaline earth metal standard solutions were prepared from chloride and nitrate salts of analytical grade (Merck and Fluka). The transition metal standard solutions were prepared from chloride and nitrate salts by dilution of atomic absorption standards (Merck and Fluka). Metal cation standard solutions were prepared by dilution of appropriate weights of the above-mentioned salts to 1 mg/ml concentration and filtered through a 0.45  $\mu\text{m}$  membrane filter prior to use. The environmental water sample was collected from the River Kasretula located in the southeastern region of Georgia near a copper industry, filtered with the same filter and diluted 40-fold prior to injection.

## 3. Results and discussion

The most important optimization parameter for the separation of cationic compounds is the choice of a suitable cationic background electrolyte. In our in-

vestigations, we have used three BGEs: imidazole, UV CAT-1 and 4-aminopyridine.

A mixture of 14 metal ions could be separated using imidazole (Fig. 1). All peaks are completely resolved. Detection of Pb in this system was problematic because of the very small peak height. Strong peak distortion of the Cu peak is caused by the formation of a very stable complex with glycolic acid with only small mobility.

The detection sensitivity of Pb can be improved using UV CAT-1 as BGE (Fig. 2). Additionally the Cu peak shows a more symmetrical peak shape. Fe and Cr could not be resolved because of their similar mobility using  $\alpha$ -hydroxyisobutyric acid as a complexing reagent. Thus, this separation system can only be applied for mixtures without Fe or Cr.

The successful separation of 16 metal cations is depicted in Fig. 3. The migration order follows the

sequence K, Na, Ba, Sr, Ca, Mg, Mn, Li, Fe, Co, Cd, Ni, Zn, Pb, Cr, Cu. All peaks are completely baseline resolved. Comigration of Fe and Cr no longer occurs. Plate numbers achieved are listed in Table 1.

The buffer concentration has a great effect on the peak shape (in the case of a metal mixture it is very important for resolution). The peaks become more symmetrical with increasing concentration. The plate number increases together with buffer concentration. However, this optimization step is limited. A high buffer concentration causes an increase of noise, and temperature and, accordingly, Joule heating increase. We used 10 mM UV CAT-1 as a buffer component (Fig. 2) instead of 5 mM. If we compare the results with those achieved under the same conditions in previous studies, in spite of the use of a significantly longer capillary, the increase in buffer concentration causes much more symmetrical peaks. We believe

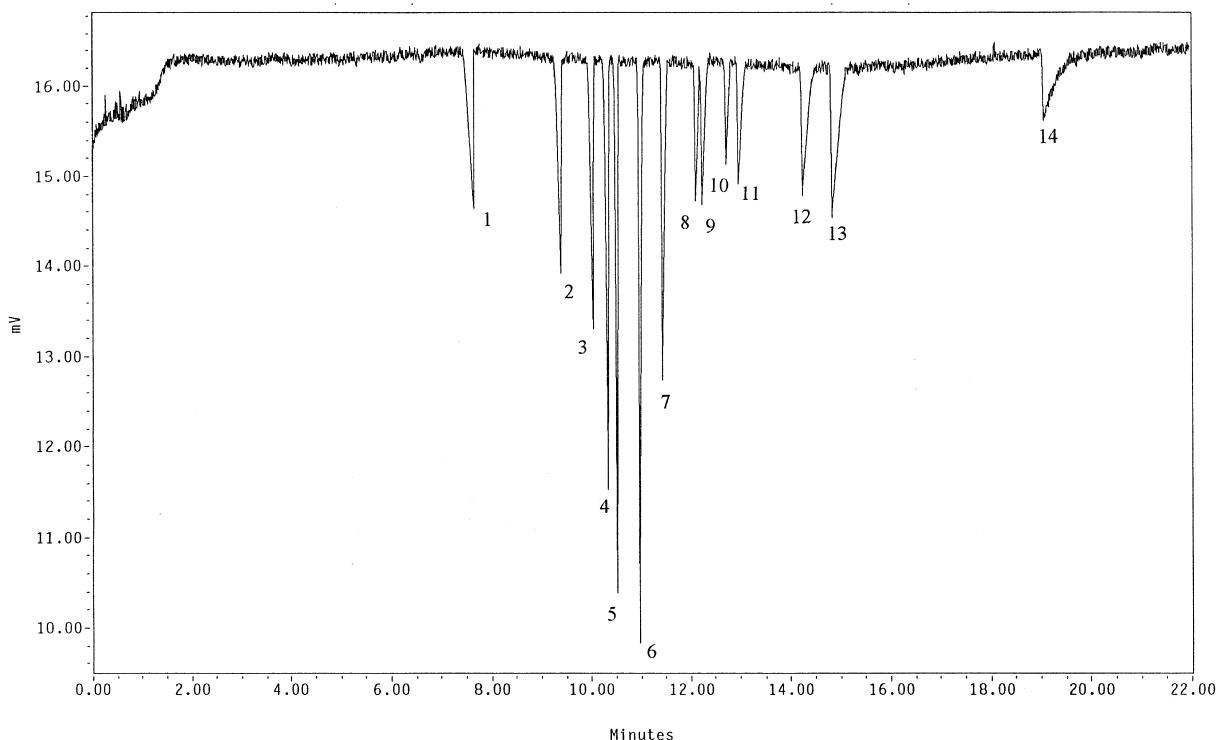


Fig. 1. Electrophoretic separation of 14 metal ions. Carrier electrolyte, 10 mM imidazole–13 mM glycolic acid (pH 4.32); hydrostatic injection, 20 s from 10 cm height; voltage, 25 kV. Peaks according to the sequence: 1=K (0.8 ppm), 2=Ba (1.8 ppm), 3=Sr (1.6 ppm), 4=Na (2.6 ppm), 5=Ca (2.4 ppm), 6=Mg (2.0 ppm), 7=Mn (2.1 ppm), 8=Fe (1.6 ppm), 9=Cd (1.6 ppm), 10=Li (1.0 ppm), 11=Co (1.0 ppm), 12=Ni (1.6 ppm), 13=Zn (1.8 ppm), 14=Cu (1.0 ppm).

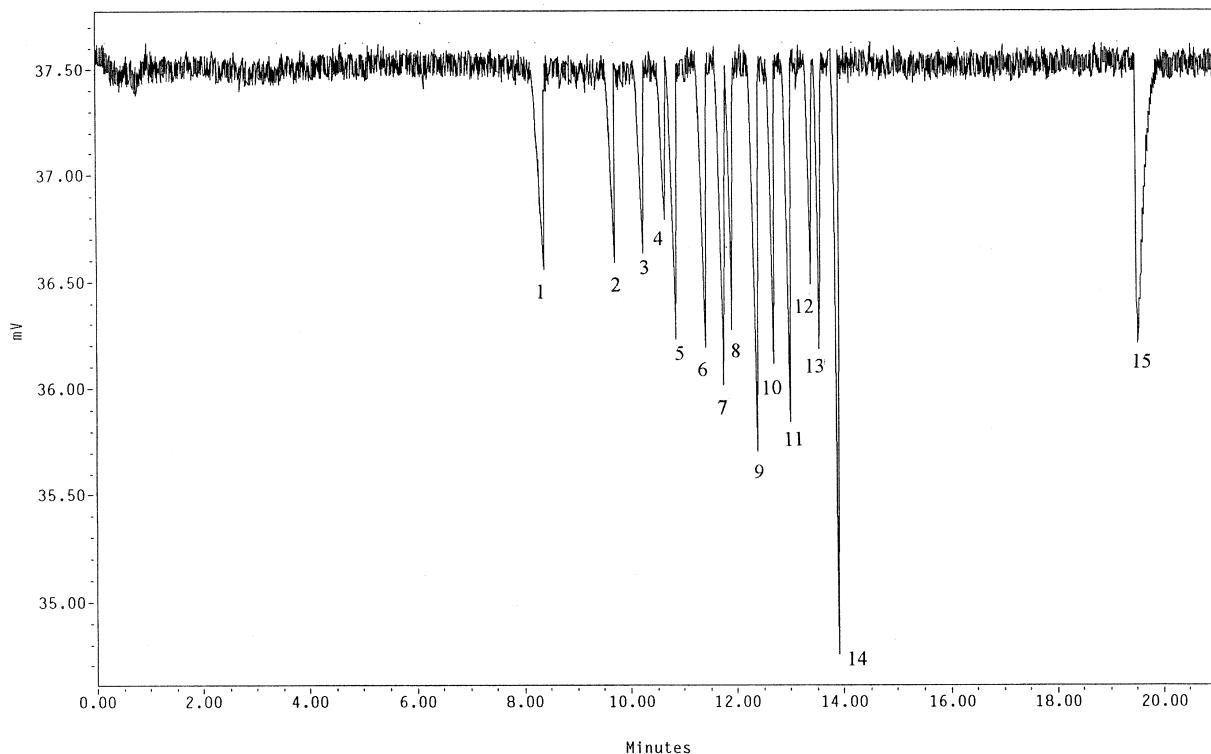


Fig. 2. Electrophoretic separation of 15 metal ions. Carrier electrolyte, 10 mM UV CAT-1–6.5 mM HIBA (pH 4.3); hydrostatic injection, 20 s from 10 cm height; voltage, 25 kV. Peaks according to the sequence: 1=K (0.4 ppm), 2=Ba (0.8 ppm), 3=Sr (0.8 ppm), 4=Ca (0.3 ppm), 5=Na (0.5 ppm), 6=Mg (0.6 ppm), 7=Mn (0.6 ppm), 8=Cd (0.8 ppm), 9=Cr (1.4 ppm), 10=Co (1.0 ppm), 11=Li (0.8 ppm), 12=Pb (0.8 ppm), 13=Ni (1.0 ppm), 14=Zn (1.8 ppm), 15=Cu (1.0 ppm).

that this can be explained by the very high level of sorption phenomena in the dispersion of migrating zones, as expected. The enhanced concentration of the buffer component appears to be successfully competing with metal cations (being in equilibrium with the complex form) for sorption centers on the capillary wall.

The migration orders of metal ions in UV CAT-1 and 4-aminopyridine buffers are not identical (Figs. 2 and 3), although the same complexing reagent ( $\alpha$ -hydroxyisobutyric acid) at the same concentration was used. This phenomenon is caused by the use of sulfuric acid to adjust the pH value in a system with 4-aminopyridine as a buffer component. Sulfuric acid acts as a complexing reagent for metal ions. Comparison of the migration order in all three cases shows that the presence of sulfuric acid as complexing reagent is more significant for transition metals

than for alkali and alkaline earth metals except Na, which migrate faster in the 4-aminopyridine system than in other systems. The comparatively small influence of different complexing reagents or mixtures upon the migration of alkali and alkaline earth metals seems to be conditioned by their high mobility in comparison with transition metals, independent of the complexing reagent. Thus, the use of a complexing reagent mixture can contribute to varying and improving the mobility and separation selectivity.

The influence of complexing reagent ( $\alpha$ -hydroxyisobutyric acid) concentration on the mobility of metal ions was investigated. As depicted in Fig. 4, Mn, Cd, and Ni ions are especially subject to alterations of the complexing reagent concentration. In the 5.75–6.5 mM range of complexing reagent, the migration order of Mn changes significantly and

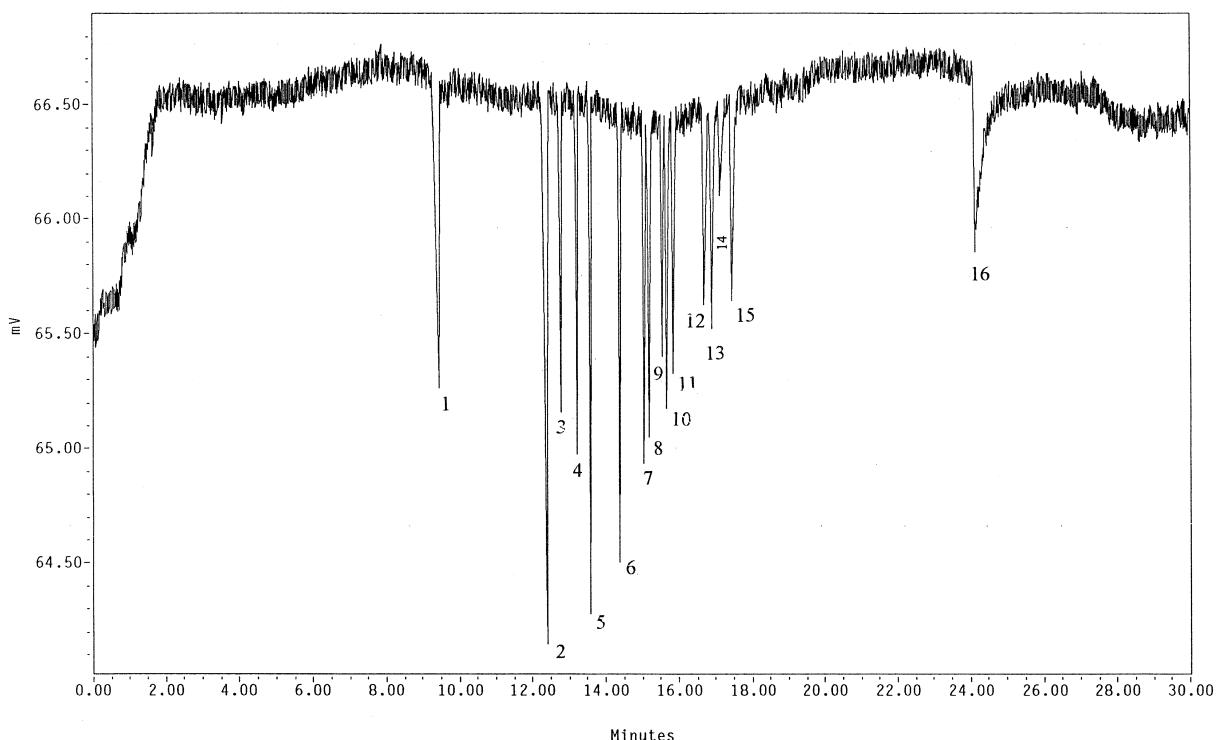


Fig. 3. Electrophoretic separation of 16 metal ions. Carrier electrolyte, 10 mM 4-aminopyridine–6.5 mM HIBA (pH 4.5 adjusted with sulfuric acid); hydrostatic injection, 20 s from 10 cm height; voltage, 25 kV. Peaks according to the sequence: 1=K (0.4 ppm), 2=Na (0.8 ppm), 3=Ba (1.2 ppm), 4=Sr (0.6 ppm), 5=Ca (0.6 ppm), 6=Mg (0.6 ppm), 7=Mn (0.6 ppm), 8=Li (0.4 ppm), 9=Fe (0.6 ppm), 10=Co (0.6 ppm), 11=Cd (0.6 ppm), 12=Ni (0.6 ppm), 13=Zn (0.6 ppm), 14=Pb (0.4 ppm), 15=Cr (0.8 ppm), 16=Cu (1.0 ppm).

it changes place with Li, which is apparently caused by the formation of a more stable complex with Li, depending on the increasing concentration of com-

Table 1  
Efficiency (plate number,  $N$ ) achieved for metal ions separated in the 4-aminopyridine–HIBA buffer system<sup>a</sup>

Cation	Plate number ( $m^{-1}$ )	Cation	Plate number ( $m^{-1}$ )
K	65 000	Fe	316 000
Na	164 000	Co	261 000
Ba	354 000	Cd	328 000
Sr	379 000	Ni	293 000
Ca	306 000	Zn	474 000
Mg	651 000	Pb	184 000
Mn	550 000	Cr	164 000
Li	302 000		

<sup>a</sup> Separation conditions as in Fig. 3.

plexing reagent. We can see this tendency by observing the Li curve in Fig. 4. The migration behavior of other metals does not change. The mobility of alkali and alkaline earth metals is less affected by changes in concentration. The influence on mobility and accordingly upon migration order of the above metal ions is most significant in the concentration range of about 5–7 mM of  $\alpha$ -hydroxyisobutyric acid. Thus, changing the complexing reagent concentration makes it possible in some cases to vary the mobility of metal ions and optimize their separation.

To confirm the potential of the described method (Fig. 3) for the routine analyses of environmental sample matrices, Fig. 5 shows the cation analysis of water from the River Kasretula (extensively polluted by a copper industry) and the quantitative results achieved are:  $K^+$   $12 \pm 0.17$  ppm,  $Na^+$   $10.3 \pm 0.12$  ppm,  $Ca^{2+}$   $137 \pm 2.7$  ppm,  $Mg^{2+}$   $183.2 \pm 3.1$  ppm,

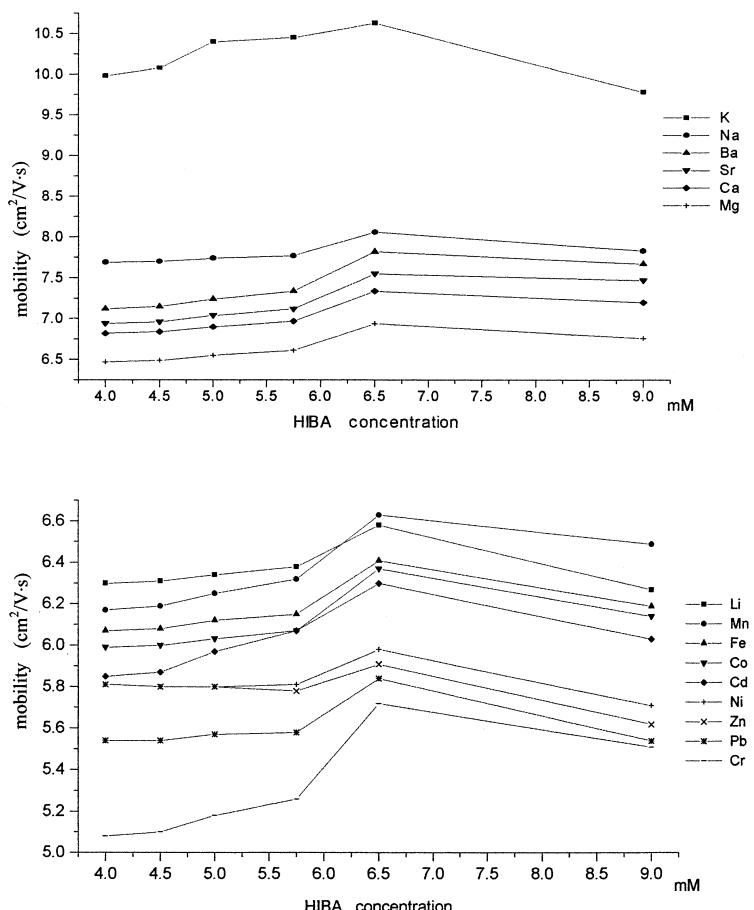


Fig. 4. Influence of complexing reagent concentration on the mobility of metal ions. Carrier electrolyte, 10 mM 4-aminopyridine–HIBA (pH 4.5 adjusted with sulfuric acid); hydrostatic injection, 20 s from 10 cm height; voltage, 25 kV; indirect UV detection at 214 nm.

$Mn^{2+}$  14±0.25 ppm,  $Zn^{2+}$  130±2.5 ppm,  $Cu^{2+}$  100±1.9 ppm (for five consequence runs).

Calibration curves were plotted with respect to peak areas normalized by migration time on metal concentrations. The linearity of calibration graphs was >0.998. The use of time-corrected peak areas provides a linear response for all elements found in the river water sample in the range 0.75–80 ppm. Identification of peaks was carried out in all cases in two ways, by comparing the migration time of known ions in a standard containing only a single metal ion with those in a metal mixture, and by a spike method — the addition of single metal species to a metal mixture and identification of the peak with increased height. The detection limit for metals,

based on a peak height three-fold the baseline noise, is listed in Table 2 for the electrophoretic system with 4-aminopyridine and HIBA at pH 4.5.

#### 4. Conclusions

A rapid and effective electrophoretic method with 4-aminopyridine as UV-absorbing compound and HIBA as complexing reagent (pH 4.5) has been developed for the successful determination of 16 metal ions. The potential of the method for quantitative and qualitative analysis of metal ions in complex matrix in environmental sample is presented. By

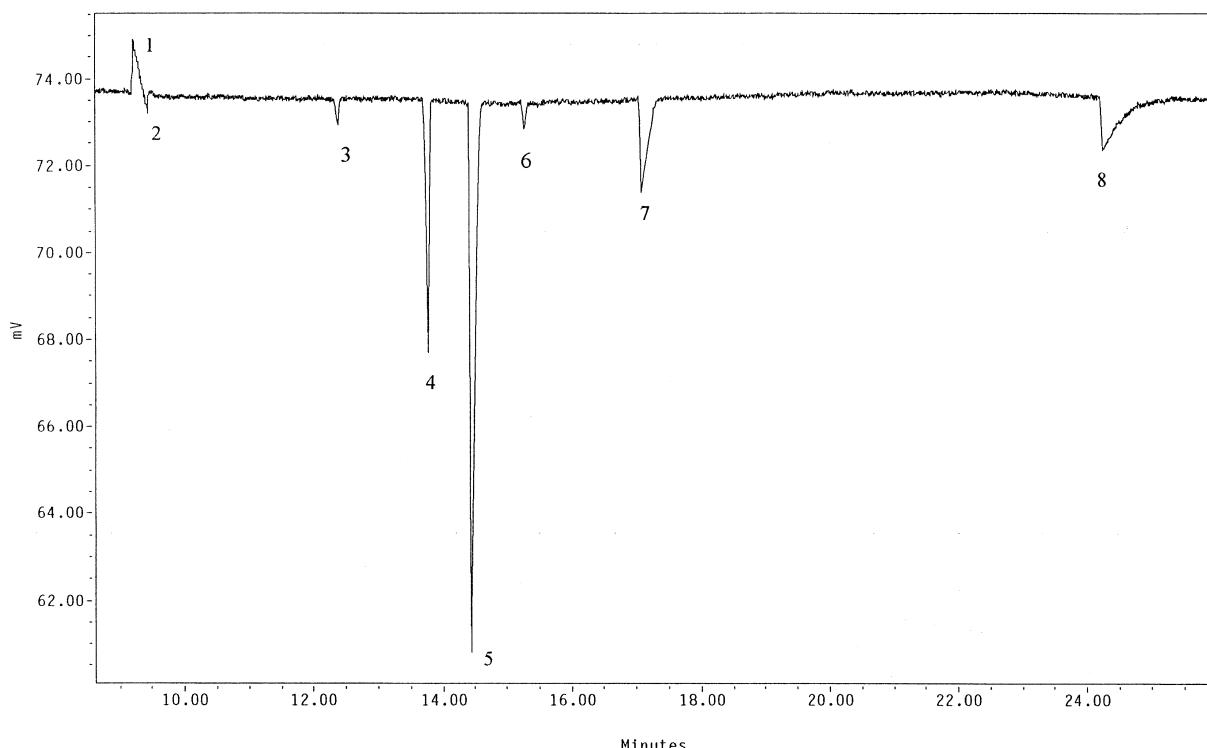


Fig. 5. Analysis of a water sample. Carrier electrolyte, 10 mM 4-aminopyridine–6.5 mM HIBA (pH 4.5 adjusted with sulfuric acid); hydrostatic injection, 30 s from 10 cm height; voltage, 25 kV. The sample was diluted 1:40 before injection. Peaks: 1=system peak, 2=potassium, 3=sodium, 4=calcium, 5=magnesium, 6=manganese, 7=zinc, 8=copper.

Table 2  
Detection limit of various metal ions<sup>a</sup>

Cation	Detection limit (ppb)	Cation	Detection limit (ppb)
K	100	Fe	200
Na	114	Co	162
Ba	300	Cd	182
Sr	133	Ni	261
Ca	92	Zn	222
Mg	105	Pb	364
Mn	139	Cr	320
Li	100	Cu	454

<sup>a</sup> Signal-to-noise ratio ~3; separation conditions as in Fig. 3.

varying the buffer concentration, the peak shape can be improved. Using complexing agents at various concentrations can change the migration order of metal ions and optimize their separation. Utilization of a complexing reagent mixture gives additional

possibilities to vary the mobility and select optimal conditions for separation.

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