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Capillary electrophoretic estimation of sulfate stability constants of metal ions and determination of alkali and alkaline earth metals in waters

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Abstract

We studied the influence of sulfate concentration on the effective mobilities of mono-, di- and trivalent ions and developed a method for the determination of sulfate stability constants. Relative migration times of several cations were determined. Capillary electrophoresis with indirect detection using 4 mmol/l copper(II) sulfate, 18-crown-6 and formic acid in background electrolyte was then applied to the determination of the metal ions in mineral and tap waters samples. The results were compared with those of ion chromatography. The CE detection limits were estimated [signal/noise ratio (S/N)=3] in the range from 0.59 (for Li) to 12.9 mg/l (for Ba).

Keywords: Water analysis; Stability constants; Buffer composition; Metal cations; Sulfate; Alkali metals; Alkaline earth metals

1. Introduction

Ion chromatography (IC) and increasingly capillary electrophoresis (CE) are the techniques most frequently used for the determination of ionized compounds. IC has been used with advantage for the determination of alkali and alkaline earth metals. However, to achieve simultaneous separation of mono- and divalent cations it is necessary to use either special cation exchangers [1–3] or gradient elution. Most frequently, the separated ions are detected by conductivity. Another popular detection technique is indirect photometry [4–6]. The latter technique is also utilized quite often in CE. The following compounds were previously described as UV absorbing components in CE electrolytes for indirect detection: aromatic amines, 4-aminopyridine,

imidazole [7–9], 1,1'-di-n-heptyl-4,4'-bipyridinium hydroxide [10], Cu(II) or Ce(III) salts [8]. The use of cerium(III) was also reported for indirect fluorimetric detection of inorganic and some organic cations [11].

The methods for the calculation of stability constants has been recently reviewed [12]. Only relatively few papers are devoted to the CE determination of stability constants [13], although a series of papers on complex-forming equilibria in capillary isotachopheresis was published by Hirokawa et al. [14–17] some time ago. Effect of complex formation equilibria on the separation process in CE is still not completely understood.

To further elucidate the influence of metal–ligand equilibria on separations of cations, we studied the behaviour of metal sulfate complexes under CE conditions. Our decision to conduct a detailed study of sulfate–cation interactions was also based on our

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choice of copper sulfate as the UV background providing component in our CE electrolyte. On one hand, copper sulfate enables a sensitive indirect detection of ions being separated. On the other hand, sulfate undergoes strong complexing interactions with divalent metal cations and thus influences considerably their electrophoretic migration. A detailed study of that effect led to a development of new procedure for calculations of stability constants for sulfate complexes.

Our theoretical calculations and experimental results enabled us to optimize the composition of a previously described electrolyte [18] for determination of all alkali metals and alkaline earths in the presence of ammonium in various types of water samples. Relative retention times of several other cations have also been determined.

2. Experimental

2.1. Instrumentation

CE measurements were carried out using SpectraPHORESIS 2000 (Thermo Bioanalysis Corporation, CA, USA) with untreated fused-silica capillary, I.D. 75 μm (Avery Dennison, MA, USA), total capillary length 66 cm, length up to detector window was 58.5 cm, applied voltage was 20 kV, temperature was maintained at 30°C. Indirect detection at 215 nm was used throughout the work, if not stated otherwise. Prior to use the capillary was washed for 5 min with 1 mol/l NaOH at 60°C, then another 5 min with 0.1 mol/l NaOH at 60°C, followed by 10 min in water at 30°C. Finally, we washed the capillary for 10 min with the electrolyte at 30°C. Before each measurement, the capillary was washed with water and then with the working electrolyte. The samples were injected by hydrodynamic injection for 1 s, using a vacuum (1.5 p.s.i. relative to ambient pressure; 1 p.s.i.=6894.76 Pa).

2.2. Chemicals

Stock solutions of copper sulfate and copper perchlorate were 0.1 mol/l. Copper perchlorate was

prepared from copper chloride by adding slight excess of 70% perchloric acid and evaporating almost to dryness. Then, few drops of acid were again added, etc. This step was repeated several times. Final preparative step consisted of dissolution in water. Further, 0.1 mol/l stock solutions of NaClO_4 and Na_2SO_4 were prepared. Stock solutions of formic acid and 18-crown-6 were both 0.04 mol/l. Metal ions stock solutions (0.1 mol/l) were prepared from corresponding nitrates, sulfates or chlorides and were diluted with distilled water before use. Solutions were standardized using common alkalimetric or complexometric procedures [19]. 18-Crown-6 was from Aldrich (Milwaukee, USA), all other chemicals were of analytical-grade purity and were obtained from Lachema (Brno, Czech Republic). Double distilled water from quartz still was used for preparation of solutions used in this study. 18-Crown-6 is a skin irritant and all solutions containing this compound should be handled with care.

2.3. Calculations

Effective mobility was calculated according to the equation:

$$\mu_{\text{eff}} = \frac{l_{\text{tot}} l_{\text{det}}}{V} \left(\frac{1}{t_m} - \frac{1}{t_0} \right) \quad (1)$$

where l_{tot} is the total length of the capillary, l_{det} the length to the detector, V is voltage applied, t_m migration time of the cation and t_0 migration time corresponding to electroosmotic flow (EOF). The value of EOF was determined from the position of water peak (water dip) observed during indirect detection or using acetone as a neutral marker; both methods yield results in good agreement.

Electropherograms were recorded using PC 1000 Software, Version 2.6 (Thermo Separation Products, San Jose, USA) and the LABSTAT program (QM Service, Prague, Czech Republic) was used for statistical calculations.

For effective mobility μ_{eff} of a metal cation M in the presence of complexing ligand L the general relation applies (the charges are omitted for the sake of simplicity) [20]

$$\mu_{\text{eff}} = \frac{\sum_{i=0}^n \mu_{\text{ML}_i} \beta_i [\text{L}]^i}{\sum_{i=0}^n \beta_i [\text{L}]^i} = \frac{\mu_{\text{M}} \beta_0 + \mu_{\text{ML}} \beta_1 [\text{L}] + \mu_{\text{ML}_2} \beta_2 [\text{L}]^2 + \text{L} + \mu_{\text{ML}_n} \beta_n [\text{L}]^n}{\beta_0 + \beta_1 [\text{L}] + \beta_2 [\text{L}]^2 + \text{L} + \beta_n [\text{L}]^n} \quad (2)$$

where μ_{ML_i} are mobilities of individual species and β_i are overall stability constants (β_0 is assumed to be equal to 1).

For equilibria of divalent metal ions with sulfates and for low excess of the sulfate it is possible to neglect the formation of the higher (anionic) complexes and thus Eq. 1 can be simplified to:

$$\frac{1}{\mu_{\text{eff}}} = \frac{1}{\mu_{\text{M}}} (1 + \beta_1 [\text{L}]) \quad (3)$$

Eq. 3 indicates that reciprocal effective mobilities are linearly dependent on sulfate concentration in the background electrolyte (BGE). The value of μ_{M} is ionic mobility of the free cation M^{2+} . In all our calculations, we used either the simple graphical approach based on Eq. 3, or we evaluated the equilibria constants using the CELET program [21]. In the latter case, the calculations are based on the minimization of the sum of squares of residuals, i.e. the differences of experimental effective mobilities $\mu_{\text{eff, exp}}$ and mobilities calculated $\mu_{\text{eff, calcd}}$. Parameters, i.e. equilibria constants or specific mobilities of the individual ions, are then calculated from the position of the minimum of U given by the equation

$$U = \sum (\mu_{\text{eff, exp}} - \mu_{\text{eff, calcd}})^2 = \text{minimum} \quad (4)$$

3. Results and discussion

When using the BGE where copper sulfate is the main component, the migration behaviour of cations to be separated is influenced by the presence of sulfate anions [8], which is due to the formation of sulfate complexes [22]. In order to judge exactly this effect, the following study was done, using as a starting salt copper perchlorate and replacing continuously perchlorate with the sulfate anion. The reason why perchlorate was used is that it does not

form any, even weak, complexes with metal ions. A series of electrolyte solutions were made from the stock solutions so that copper concentration was maintained constant and concentration of sulfate varied. The value of pH was kept practically constant in the range 4.85–4.90. Measured dependences of the effective mobilities of the metal ions on total sulfate concentration are given in Fig. 1. However, simultaneously with the formation of sulfate complexes of the separated cations also sulfate complexes of Cu^{2+} are formed. This is demonstrated in the distribution diagram in Fig. 2. Thus a correction for sulfate consumed with Cu^{2+} ions should be done.

Complexation of the Cu^{2+} ions with sulfate anions was studied as follows: A series of BGEs was prepared by mixing the stock solutions of NaClO_4 and Na_2SO_4 so that the Na^+ concentration was kept constant (20 mmol/l), whereas sulfate concentrations varied in the range of 0–8 mmol/l. Migration times for Cu^{2+} ions were measured in those BGEs (using direct photometric detection at 215 nm) and the effective mobilities were calculated. The dependence of the reciprocal mobility on the sulfate concentration is linear in the examined range (Fig. 3) and this allows us to calculate the stability constant β_1 of the Cu^{2+} –sulfate complex with the aid of Eq. 3. An experimental arrangement was similar to that used in ion chromatographic measurements of stability con-

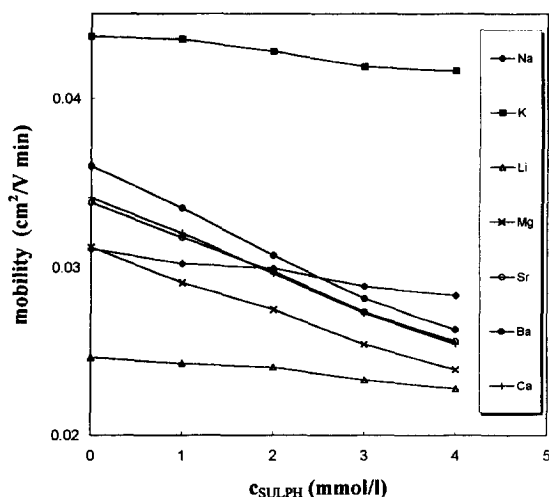


Fig. 1. Dependences of effective mobilities of several cations on total sulfate concentration.

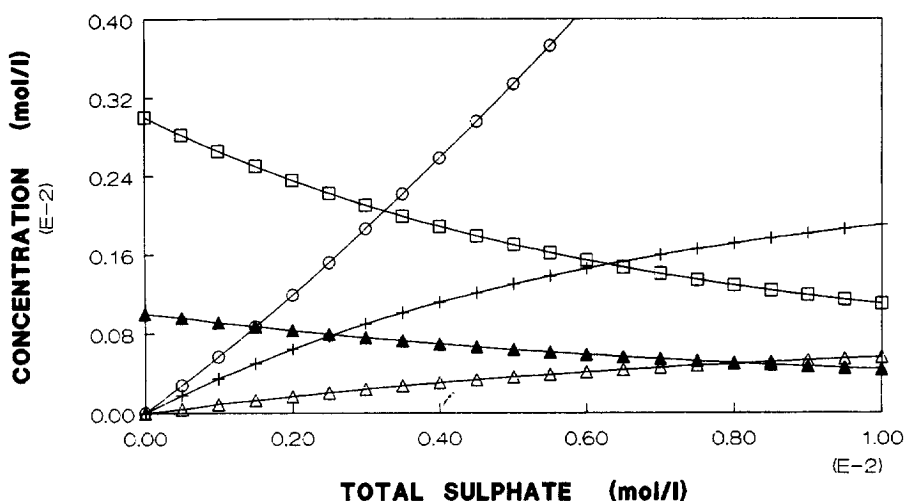


Fig. 2. Distribution of complex species as a function of total sulphate concentration. +, $[\text{CuSO}_4]$; Δ , $[\text{MgSO}_4]$; \circ , $[\text{SO}_4^{2-}]$; \square , $[\text{Cu}^{2+}]$; \blacktriangle , $[\text{Mg}^{2+}]$. $[[\text{Cu}(\text{ClO}_4)_2] + [\text{CuSO}_4]] = \text{const.} = 0.004 \text{ mol/l}$.

stants [23,24]. Thus obtained stability constant ($\log \beta_1 = 2.457$) was used for calculations of the concentration of “available” (free) sulfates in the BGEs containing copper sulfate (see above).

Dependences of the reciprocal effective mobilities on free sulfate concentration are given in Fig. 4. It can be seen that experimental plots satisfy well Eq. 3. Similarly as in Fig. 1 only some of the studied cations are given there. The other divalent cations

studied showed almost the same behaviour as Mg^{2+} cations. In all of the systems studied NH_4^+ exhibited the same retention characteristics as K^+ cation. From these plots the stability constants of sulfate complexes can be calculated using Eq. (3). Obtained values corrected to zero ionic strength using Davies relation [25] are given in Table 1. The data were also

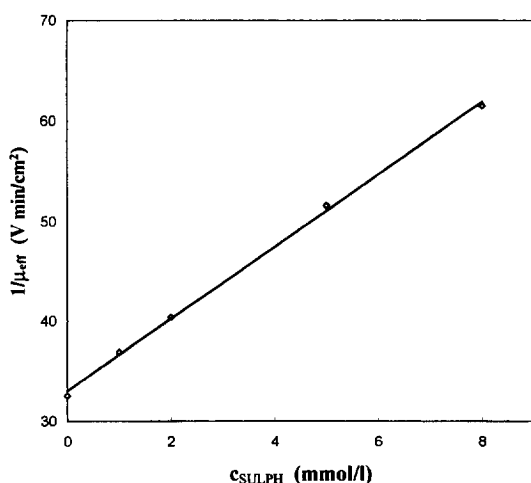


Fig. 3. Dependence of reciprocal effective mobility of Cu^{2+} ion on sulfate concentration.

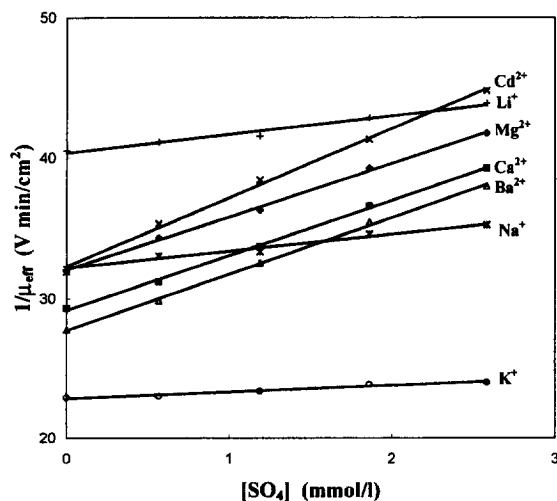


Fig. 4. Graphical estimation of stability constants for several metal-sulfate complexes. $1/\mu_{\text{eff}}$ as a function of the free sulphate concentration.

Table 1
Stability constants ($\log \beta_1$) of sulfate complexes, $I=0$

Cation	This work		Literature data [Ref.]	
	Graphical approach	CELET program		
Li ⁺		0.274±0.009	0.64 [22]	
Na ⁺		0.773±0.020	0.70 [22]	
K ⁺		0.632±0.011	0.85 [22]	
Mg ²⁺	2.49±0.04	2.110±0.008	2.23 [22]	
Ca ²⁺	2.551±.013	Cu ²⁺	2.146±0.033	
			2.151±0.007	2.31 [22], 2.0 [34]
Sr ²⁺	2.524±0.041	Cu ²⁺	2.313±0.022	
			2.095±0.010	2.55 [22]
Ba ²⁺	2.586±0.039	Cu ²⁺	2.133±0.042	
			2.511±0.014	2.7 [22], 2.3 [34]
Mn ²⁺	2.578±0.030		2.359±0.042	
			2.185±0.004	2.26 [22], 2.17±0.03 [24]
Zn ²⁺	2.590±0.092	Cu ²⁺	2.305±0.015	
			2.177±0.015	2.38 [22], 2.29±0.04 [24]
Co ²⁺	2.586±0.088	Cu ²⁺	2.211±0.053	
			2.209±0.014	2.36 [22], 2.19±0.04 [24]
Ni ²⁺	2.591±0.036	Cu ²⁺	2.354±0.044	
			2.181±0.005	2.32 [22], 2.16±0.03 [24]
Cd ²⁺	2.601±0.058	Cu ²⁺	2.188±0.019	
			2.205±0.012	2.46 [22], 2.29±0.06 [24]
			2.184±0.043	
	Average	Cu ²⁺	2.244±0.035	2.36 [22]

evaluated using CELET program [21] and the results are in Table 1, as well. Estimation a priori of the stability constant of the Cu²⁺–sulfate complex is not necessary when using the CELET program for the evaluation of stability constants; it can be calculated together with the stability constants of the separated cations.

It might be seen that CE method for the determination of stability constants yields quite good results, in satisfactory agreement with the results obtained by the other methods. Similar graphical treatment as in this work has already been used for the determination of stability constants of divalent metal ions with 2-hydroxyisobutyric acid (HIBA) [13]. Our measurements were done at varied ionic strength ($I=0.012$ – 0.016). However, the relative error so produced was estimated to be lower than about 2%. Furthermore, it was necessary to make correction for complexation of copper(II) with sulfate anions and this is done easily when using CELET program. Graphical methods yields systematically higher values than CELET program. The explanation is

that in graphical approach complexation of copper(II) was neglected. Stability constants obtained with CELET program should be considered more correct.

From theoretical relations and experimental plots it is evident that changing the sulfate concentration in BGE it is possible to influence migration behaviour of divalent cations but it is not possible to reach expressive improvement of their separation because of too small differences in the values of stability constants of sulfate complexes. On the other hand it is possible to influence successfully mutual separation of mono- and divalent cations because the complexation of alkali metals is much lower.

From published values of stability constants [26] and from electrophoretic measurements [13,27] it follows that the mobility of alkali metal ions and cations of alkaline earths can be influenced efficiently by addition of 18-crown-6. This effect was studied in detail in [27]. It is evident from published values that separation of K⁺ and NH₄⁺ ions can be improved (often utilized in CE [27]), but also sepa-

ration of Sr^{2+} and Ca^{2+} , which are co-migrating in the above mentioned sulfate electrolytes (see Fig. 1). Better separation of di- (poly-) valent metal ions can be achieved employing complexing activity of weak organic ligands such as lactic, acetic, glycolic, malonic and tartaric acids, HIBA, etc. [13,28–31].

Wojtusik and Harrold [18] achieved a very good separation of alkali and alkaline earth metal ions using BGE containing copper sulfate, 18-crown-6 and formic acid. We have therefore used in further work electrolyte containing: 4 mmol/l CuSO_4 , 4 mmol/l 18-crown-6 and 4 mmol/l formic acid, having pH 3.1. It can be seen from Fig. 5 that this electrolyte enables quite good separation of all alkali and alkaline earth cations, including ammonium.

Migration characteristics of some other metal cations were measured and calculated. Results are listed in Table 2. Several divalent cations show

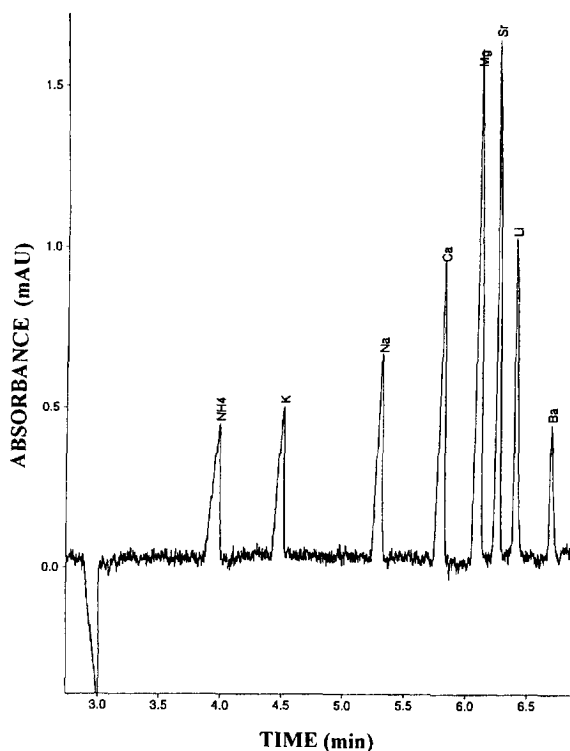


Fig. 5. Example of electropherogram for a mixture containing NH_4^+ (20 mg/l), K^+ (19.5 mg/l), Na^+ (11.5 mg/l), Ca^{2+} (20 mg/l), Mg^{2+} (12.2 mg/l), Sr^{2+} (43.8 mg/l), Li^+ (3.5 mg/l), and Ba^{2+} (68.7 mg/l). BGE: 4 mmol/l CuSO_4 , 4 mmol/l 18-crown-6, 4 mmol/l formic acid, pH 3.1. Indirect UV detection at 215 nm. Applied voltage 20 kV, hydrostatic injection for 1 s.

Table 2

Relative migration times of cations ($\text{Na}^+ = 1$)

Cation	Relative migration time	Cation	Relative migration time
Cs^+	0.73	Ni^{2+}	1.19
Rb^+	0.75	Li^+	1.20
NH_4^+	0.76	Ba^{2+}	1.24
K^+	0.85	Be^{2+}	1.27
Na^+	1.00	Pb^{2+}	1.34
Ca^{2+}	1.09	Al^{3+}	1.45
Mg^{2+}	1.15	Y^{3+}	1.59
Co^{2+}	1.17	La^{3+}	1.64
Sr^{2+}	1.18	In^{3+}	1.77
Zn^{2+}	1.18	Fe^{2+}	1.92
Mn^{2+}	1.18		

BGE: 4 mmol/l CuSO_4 , 4 mmol/l 18-crown-6, 4 mmol/l formic acid, pH 3.1.

migration times similar to Sr^{2+} , i.e. Co^{2+} , Zn^{2+} , Mn^{2+} and Ni^{2+} . These cations can interfere the determination of strontium. To reach better separation it would be necessary to apply some of the other complexing agents. However, in samples of natural waters these elements are usually present at low concentrations and their interferences thus need not be considered.

Detection limits were evaluated and compared (in Table 3) with those values reached during separation of alkali metal ions and alkaline earth with IC method [5,6], where Cu^{2+} salt was also the main component of mobile phase. With respect to the fact that both in CE and IC the same detection principle is used one should expect comparable detection limits. However, detection limit depends also on the

Table 3

Comparison of detection limits (mg/l) achieved with CE in this work and IC

Cation	CE, this work	IC [Ref.]
NH_4^+	1.48	
K^+	3.34	219 [6]
Na^+	1.58	24.8 [6]
Li^+	0.59	4.3 [6]
Mg^{2+}	0.96	18.3 [6], 1.08 [5]
Ca^{2+}	2.01	2.19 [5]
Sr^{2+}	4.47	5.84 [5]
Ba^{2+}	12.92	13.73 [5]

Detection limits correspond to the analyte concentration that produce signal of three times the baseline noise ($S/N=3$). BGE as in Table 2.

Table 4
Comparison of theoretical and measured responses in indirect photometric detection

Cation	Measured response (area %)	Calculated response (area %)
Mg ²⁺	7.3	6.7
Ca ²⁺	23.7	26.7
Sr ²⁺	15.0	13.3
Ba ²⁺	54.4	53.0

BGE as in Table 2.

shape of the peaks. This is governed in IC mainly by the retention time of the peak, while in CE it is given by the difference of effective mobilities between ion detected and the cation of BGE. First of all, however, sharpness of the peak is due to the separation efficiency of the method and this is much higher for CE. For example, just for comparison, for lithium peak the number of theoretical plates during CE separation was about 230 000, while at IC separation using convention cation-exchange column and 0.1 mol/l CuCl₂ as the eluent [6] the number of theoretical plates for a nice lithium peak was about 5700 only.

This difference in separation efficiency was pronounced for monovalent Na⁺, Li⁺ and K⁺ cations, especially. Good detection characteristics for lithium are also due to its low atomic mass. Indirect photometric detection is a general procedure in the sense that detector response related to the equivalent of separated ion is constant. This can be demonstrated by the example of a model mixture separation of the alkaline earth cations (Table 4).

A general disadvantage of indirect detection is its

limited dynamic range, which depends on the concentration of UV absorbing cation in the background electrolyte. According to our results the dependence of the detector response on the analyte concentration is linear up to 5 mmol/l level for divalent and at least up to 8 mmol/l for monovalent cations. These values are also dependent on the shape (width) of the peak and on the speed of ion transport to the sample zone (for detailed discussion see [8,32,33]).

The studied CE electrolyte was then used for the determination of alkali and alkaline earth metal ions in waters. The results are given in Table 5. The determination does not require any preliminary treatment of the samples except diluting. Different dilution was applied for the determination of sodium and for the other metal ions, respectively. Blank experiments were done but as water used for the dilution was twice distilled and there were no traces of metal ions determined, it was not necessary to make any subtraction of the blanks. Only samples with higher content of dissolved carbon dioxide were degassed in ultrasound bath. An example of the Vincentka mineral table water analysis is demonstrated in Fig. 6. This example shows also a good separation efficiency of CE method, which enable determination of low lithium content under the high excess of sodium.

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Table 5
Determination of alkali and alkaline earth metals in table and tap waters (mg/l)

Sample	K	Na	Li	Ca	Mg
Gloria	<DL	16±4	<DL	60±9	12±3
Mattoni	22±1	106±6	<DL	101±12	24±4
	ND ^a	119±11 ^a	<DL ^a	ND ^a	29±9 ^a
Podebradka	59±12	465±54	<DL	226±12	57±4
	ND ^a	667±19 ^a	<DL ^a	ND ^a	64±12 ^a
Vincentka	135±23	3002±167	9.1±1.2	93±12	9.4±2.1
	ND ^a	3360±170 ^a	11±2 ^a	ND ^a	14±4 ^a
Ida	14±5	134±5	<DL	156±12	30±4
Tap water	<DL	<DL	<DL	153±12	2.7±0.4

DL = detection limit, ND = not determined.

^a Results obtained by IC method [6]. BGE as in Table 2.

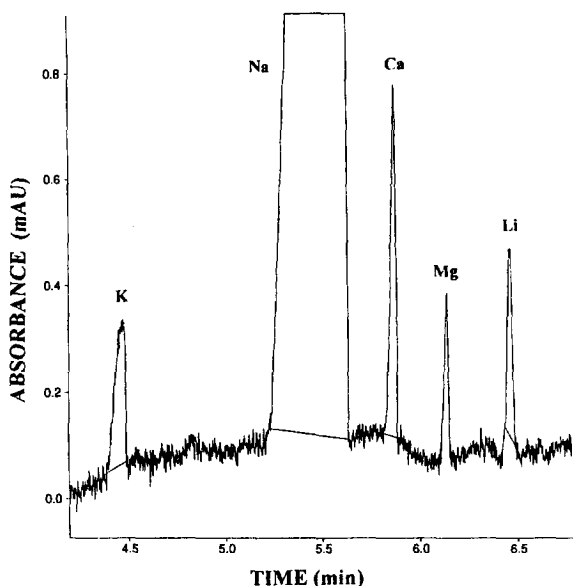


Fig. 6. Determination of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and Li^+ in mineral water Vincentka. Conditions as in Fig. 5, direct injection of the sample.

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