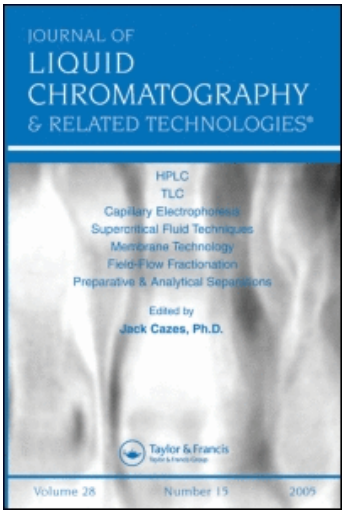

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Kobayashi, J. , Shirao, M. and Nakazawa, H.(1998) 'Simultaneous Determination of Anions and Cations in Mineral Water by Capillary Electrophoresis with a Chelating Agent', Journal of Liquid Chromatography & Related Technologies, 21: 10, 1445 — 1456
To link to this Article: DOI: 10.1080/10826079808000526
URL: http://dx.doi.org/10.1080/10826079808000526

J. LIQ. CHROM. & REL. TECHNOL., 21(10), 1445–1456 (1998)

SIMULTANEOUS DETERMINATION OF ANIONS AND CATIONS IN MINERAL WATER BY CAPILLARY ELECTROPHORESIS WITH A CHELATING AGENT

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ABSTRACT

Anions and cations in mineral water were simultaneously measured by capillary electrophoresis with a chelating agent. Ions studied were chloride, sulfate, sulfite, nitrate, nitrite, fluoride, formate, and acetate for anions, and magnesium, calcium, copper, lead and zinc for cations. They were separated in a fused-silica capillary (50 cm X 50 μm i.d.) filled with 300 mM borate buffer (pH 9.0) containing a cationic surfactant and a chelating agent as the electro-osmotic flow modifier and chelator, respectively. The method was successfully applied to the determination of ions in mineral water.

INTRODUCTION

Ion analysis is performed mainly with an ion chromatograph (IC). Perhaps the main reason has been its ability to provide rapid and simple solutions to a large number of analytical problems, particularly the determination of inorganic anions and short-chained carboxylic acids.[1]

On the other hand, capillary electrophoresis (CE) is one of the electrophoretic methods and is better than conventional gel electrophoresis in quantitation and rapidity, and equivalent to IC in analysis of ionic substances, in particular. CE has some advantages over IC. For example, a faster flow-rate of the mobile phase can be used to minimize separation time (in IC, limited by the strength of the column packings) and the apparatus can be cleaned more easily after the proposed substances are detected (in IC, necessity to wait until most substances in a sample are eluted from the analytical column). CE has been noted as a rapid and reproducible microscale technique for analysis of various ionic substances, especially such low molecular weight ones as amino acids,[2] peptides,[3] organic acids,[4] drugs,[5] etc. However, this new technique is not fully exploited for analysis of minerals because the detection is generally by ultraviolet (UV) spectral absorbance and minerals have poor UV absorbance.[6]

In this study, we developed analytical conditions for the simultaneous determination of anions and cations in mineral water by CE. It is now widely recognized for IC that a complete analysis of anions and cations in water can be achieved only with relatively complex techniques such as coupled separation modes[7] or mobile phase gradient IC.[8] These techniques are time-consuming and need tedious operation. For proposed ions, we selected chloride, sulfate, sulfite, nitrate, nitrite, fluoride, formate, and acetate for anions, and magnesium, calcium, copper, lead, and zinc for cations, which are controlled in tap water or are thought to relate to acid rain and snow. In addition, the method was used to measure ions in mineral water.

EXPERIMENTAL

Reagents

All special-grade salts (calcium chloride, magnesium sulfate, potassium nitrate, ammonium acetate, sodium formate, sodium sulfite, sodium nitrite, sodium fluoride, cupric sulfate, lead nitrate, and zinc nitrate) were purchased from Kanto Kagaku. An ethylenediaminetetraacetic acid disodium salt (EDTA) and n-tetradecyltrimethylammonium bromide (TTAB) were obtained

from Dojin Laboratories and Tokyo Kasei Kogyo, respectively. Sodium tetraborate (borax, Wako Pure Chemical Industries) was used for the preparation of migration buffers.

Stock solutions (100 mM) were prepared by dissolving each salt in water. Standard solutions were prepared by diluting stock solutions appropriately with water or 5 mM EDTA solution. Migration buffer was composed of 300 mM borate (pH 9.0), 0.5 mM TTAB, and 0.5 mM EDTA.

The pHs of the carrier solutions were adjusted by adding dilute boric acid or sodium hydroxide solution to the borax solution.

All solutions were prepared with distilled and deionized water.

Instrumental

Capillary electrophoresis was carried out with a Quanta 4000 system with a Model 820 data station (Waters) and a 20-position carousel was used in all experiments. It proved necessary to collect data at 20 points per second because of the very narrow peak widths and running time resulting in CE. The separations were carried out by using a conventional uncoated fused-silica capillary tube (50 cm X 50 μm i.d.) obtained from Waters. On-column flow cells were created by removing a small portion of the capillary's polyimide coating by burning. While the Quanta 4000 is capable of both hydrostatic and electromigration injections, hydrostatic injection was used to introduce the samples in this work. Water samples were elevated to a height of 10 cm for 10 seconds. The injection volume was calculated as approximately 12 nL. Detection was carried out at 185 nm by the direct method. The applied voltage was 10 kV using a negative power supply. Capillary, reservoirs and sample vials were kept in a temperature-controlled room at 25 ± 2°C. The capillary tubing was filled with a carrier solution for 5 min under vacuum after being washed with water and 1 M NaOH for 2 min each under vacuum for each measurement. Specific operating conditions are provided in the figure legends.

Mineral Water Samples

Thirteen kinds of mineral water were purchased from the market or donated by the importer. The countries of origin were Japan (one kind, No. 1), America (two, No. 2-3), Canada (two, No. 4-5), Australia (three, No. 6-8), France (one, No. 9), Norway (one, No. 10), Finland (one, No. 11), Korea (one, No. 12) and Italy (one, No. 13, carbonated).

Strategy of This Study

To detect anions and cations simultaneously, we decided to form anionic chelates with cations in the presence of a chelating agent and allow them to migrate in the same direction as the other anions in a capillary tube. For its potential to chelate with many metal ions, EDTA was selected as the chelating agent.

As most EDTA metal chelates show absorption maxima at wavelengths around 190 nm,[9] 185 nm was decided as the detection wavelength.

EDTA forms most metal chelates at alkaline pH and can attain high sensitivity at 185 nm. And for the migration buffer agent, we selected borate, which is an inorganic salt and has an alkaline pKa.

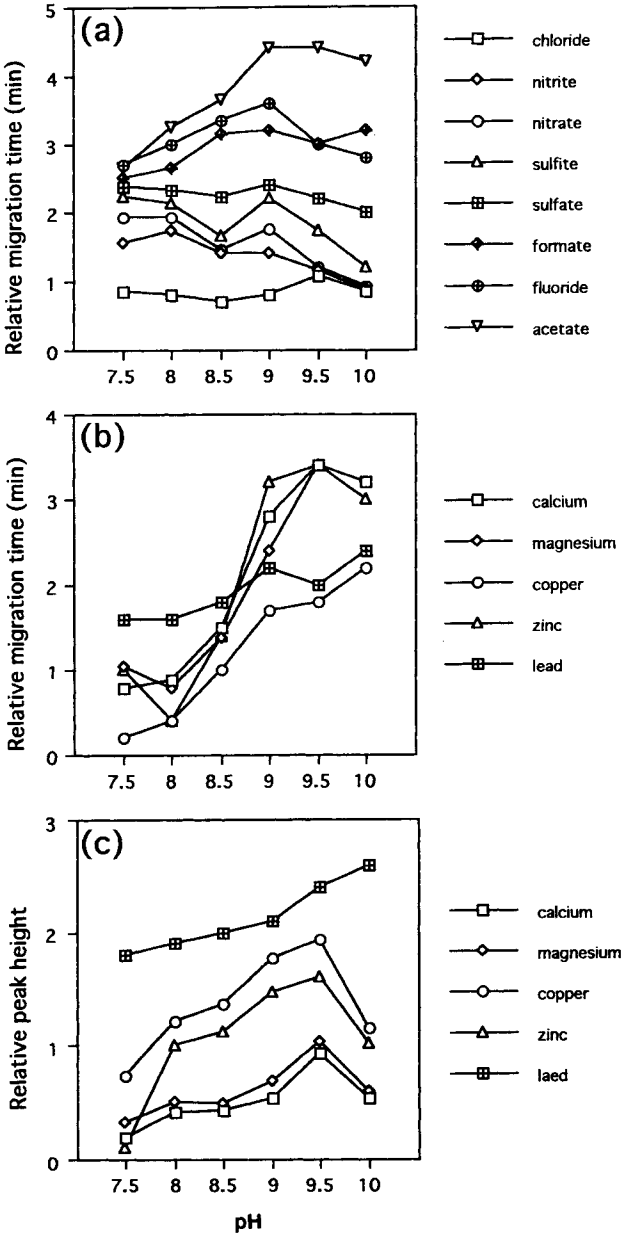
In CE, the direction and magnitude of the bulk fluid flow, or electro-osmotic flow (EOF), is dictated by the charge on the inner wall of the capillary. In conventional CE using a fused-silica capillary, the direction of the EOF is toward the negative electrode at most pH values, hence detection is carried out at this end.

Under the influence of an applied potential, inorganic anions migrate rapidly toward the positive (non-detection) electrode and are typically not quantitated as they have excessive migration times or are not eluted at all.

Only anions with a mobility less than that of the EOF can be determined by this approach. However, the addition of a cationic surfactant such as TTAB to the electrolyte has been demonstrated to significantly reduce migration time for small anionic species by reversing the EOF. Therefore we selected TTAB for a detergent, and determined its concentration of TTAB.

It is well known that the sensitivity and resolution of each ion can be affected by varying the properties of the capillary tube (structure of inner wall, length, inner diameter, and so on). In this study, the optimum conditions were investigated by using a tube (50 cm X 50 μm i.d.).

Figure 1. (right) Effect of pH on Migration/Chelation of Anions and Cations (a) Separation of anions; (b) Separation of cations; (c) Chelation of cations. Buffer: 100 mM borate/NaOH + 1 mM TTAB + 1 mM EDTA. All tested samples consisted of 10 mM salt and 10 mM EDTA each. Operating conditions were the same in test.



RESULTS AND DISCUSSION

Optimized Conditions for Water Analysis

Buffer

Figure 1 shows the effect of the pH of the borate buffer at 100 mM on the migration time of anions, cations, and metal chelation. Satisfactory results were obtained with borate buffer at pH 9.0 in respect of peak resolution, stability of the baseline, and operation time. Similar resolution was obtained with buffers of pH 7.0, but the shapes of the peaks were far inferior to those at pH 7.0. Moreover when we studied the concentration, the optimum was achieved at 300 mM.

Detergent

Detergents in a migration buffer affect EOF, background absorbance, migration rate, and peak separation. Optimum separation was obtained at 0.5 and 5.0 mM TTAB. But above 2.0 mM TTAB, the baseline noise was greater, and sensitivity was worse. At 0 mM TTAB, a few peaks as chloride were detected in the broadening shape. We decided on 0.5 mM TTAB in the migration buffer.

EDTA

EDTA can form stable chelates with many multivalent metal ions. Some of the chelates, however, will dissociate into metal ions and EDTA at low EDTA concentration.[10] So, first we investigated EDTA concentration in the buffer. When 100 mM EDTA was added to the sample, the concentration in the buffer allowed almost no chelation. But separation was effected, and 0.5 mM EDTA was optimum.

EDTA in sample solutions affects not only chelation, but also the unreacted EDTA peak in the electropherogram. Although EDTA concentration in a migration buffer causes almost no chelation, we thought EDTA in the buffer would act as a depressant to decompose the chelates in a capillary tube, similar to the addition of reacting reagents to the mobile phase on HPLC.[11] Optimum EDTA concentration in sample solutions depends on the amounts of the proposed cations, which vary with the sample. In this study, 100 mM EDTA was used under a basic condition, and EDTA concentration was controlled according to the size of the EDTA peak in the electropherogram.

Table 1

Reproducibility of Migration Time and Peak Height/Area*

Ions	Migration Time (CV, %)	Peak Height (CV, %)	Peak Area (CV, %)
Anions			
Chloride	0.74	1.12	1.76
Sulphate	0.25	8.47	8.62
Sulphite	0.49	3.98	5.76
Acetate	0.36	2.13	5.12
Formate	0.31	1.18	4.36
Fluoride	0.56	6.62	4.52
Nitrate	0.33	0.98	0.71
Nitrite	0.29	1.25	1.78
Cations			
Calcium	0.73	1.36	2.84
Magnesium	0.28	1.00	2.26
Copper	0.17	2.02	3.25
Zinc	0.26	1.88	2.27
Lead	0.30	0.08	0.19

* All experiments were performed at each 1 mM sample solution. CV: coefficient of variation.

Running Voltage

By applying a higher voltage, the separation of the metals was improved, and the retention time was shortened. But the time constant to record electropherograms was regulated by the capacity of the data station. And a strong electric current should be avoided in order to suppress Joule heat generation. As a result, 10 kV was used, which current was about 50 μA, and the running time was 15 min. At 20 kV, half the running time was obtained, but detection and determination were not appropriate.

Temperature

It is known that the temperature in the capillary greatly affects electrophoresis. As the instrument used in this study had no temperature

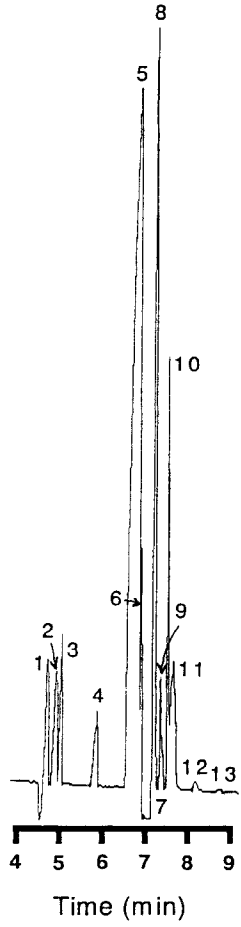


Figure 2. Standard Electropherogram of Anion and Cation Mixture. Symbols: 1, chloride; 2, nitrate; 3, sulfate; 4, formate; 5, EDTA; 6, Cu-EDTA; 7, fluoride; 8, Pb-EDTA; 9, Mg-EDTA; 10, Ca-EDTA; 11, Zn-EDTA; 12, acetate; 13, unknown. Working conditions were the same in test.

control system except the forced cooling of the capillary by a fan, the influence of the temperature of the laboratory on the reproducibility of the analysis was investigated. From the results with a standard solution in a laboratory without air conditioning, the migration time was greatly affected. In contrast, results obtained in an air-conditioned room (25 ± 2°C) showed good reproducibility. Thus, all subsequent experiments were carried out in an air-conditioned room.

Table 2

Detection Limits and Determination Ranges of Several Ions*

Ions	Range (PA)	(r, PH)	Limit (μM, PH)	Range (PA)	(r, PA)	Limit (μM, PA)
Chloride	10μM ~ 0.1 mM	0.998	2.5 μM	100 μM ~ 10mM	0.995	15 μM
Nitrate	10 μM ~ 0.1 mM	0.998	1.8 μM	50 μM ~ 10 mM	0.999	7.1 μM
Calcium	10 μM ~ 80 μM	0.997	0.5 μM	100 μM ~ 10 mM	0.997	2.0 μM
Magnesium	10 μM ~ 0.2 mM	0.997	0.6 μM	20 μM ~ 10 mM	0.999	2.1 μM
Copper	10 μM ~ 1.0 mM	0.996	1.4 μM	100 μM ~ 10 mM	0.997	5.2 μM
Zinc	10 μM ~ 1.0 μM	0.997	1.8 μM	80 μM ~ 10 mM	0.998	5.2 μM

* Experiments were performed between 10 μM and 10 mM. Detection limits (lower) were calculated from each calibration curve by 3 S.D. method. r, correlation coefficients; PH, peak height; PA, peak area.

Reproducibility

In a quantitative analysis using CE, the reproducibility of EOF and sample size are very important to obtain a reproducible peak height and peak area. Table 1 shows the reproducibility of migration times, peak heights, and peak areas of all ions. Electrophoretic mobilities of chelates were very reproducible, though migration time and the time necessary for the water zone of a sample to reach the detector showed a little daily variation. The reproducibilities of peak height and peak area are enough for quantitative determination.

Calibration

As shown in Fig. 2, the peaks with the migration times of 7.4 min for Mg and 7.7 min for Ca were detected on the electropherogram of a tapwater sample, and identified as EDTA-Mg and EDTA-Ca by the facts that mixed analyses with the standard sample solutions afforded increases in the peak areas and that they were not detected without adding EDTA to the electrolyte and samples to be injected. The linearity of the method was evaluated between 10 μM and 10 mM with respect to both peak-area and peak-height responses of several ions.

As the dynamic ranges for peak area were wider than those for peak height, calculations were carried out by using the peak area. The limits of detection of ions were 0.5-2.5 μM by the peak height method (Table 2).

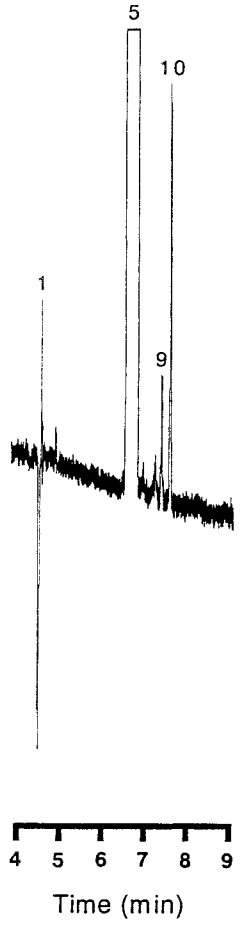


Figure 3. Detection of Anions and Cations in Tapwater. Experimental conditions were as follows: A migration buffer was composed from 0.5 mM TTAB and 300 mM borate/NaOH buffer (pH 9.0). A tapwater sample was prepared by adding 10 mM EDTA and stand for above 30 mins. Instrumental conditions were the same in text. Symbols were the same in Fig.2.

Determination of Ions in Aqueous Samples

Fig. 3 shows a electropherogram of ions in a tapwater sample using the developed method. Not only anions but also cations in aqueous samples have been able to be detected.

Table 3

Determination of Ions in Mineral Waters

No.	Countries	Chloride	Nitrate	Sulphate	Calcium	Magnesium
1	Japan	5.6	N.D.	N.D.	0.8	10.2
2	USA	N.D.	2.8	N.D.	14.9	5.5
3	USA	8.7	3.5	N.D.	1.2	12.1
4	Canada	3.0	N.D.	N.D.	1.9	6.4
5	Canada	15.8	N.D.	N.D.	N.D.	12.8
6	Australia	6.8	N.D.	N.D.	9.2	25.6
7	Australia	22.2	7.2	N.D.	6.8	6.2
8	Australia	13.8	8.1	N.D.	N.D.	2.1
9	France	24.2	6.3	N.D.	1.8	5.1
10	Norway	3.2	2.4	N.D.	7.8	46.8
11	Finland	10.1	2.8	2.6	14.6	90.6
12	Korea	1.4	N.D.	N.D.	11.1	47.2
13	Italy	49.6	N.D.	N.D.	21.2	102.8

* Unit: ppm. N.D.: not determined.

As shown in Table 3, the proposed ions in the 19 mineral water samples were determined by the peak area method. Calcium and magnesium were detected in almost all mineral waters, but other ions were not. In this study, we found that the ionic composition of mineral waters were different according to the sampling site.

CONCLUSIONS

In this study, the authors aimed at developing simultaneous determination of anions and cations, which were detected as their anionic chelates with EDTA. We have found the fundamental conditions for the determination of ions in waters by capillary electrophoresis.

By using detection at 185 nm and an applied voltage of 10 kV, favorable separation was achieved in a fused-silica capillary of 50 cm X 50 μm filled with 300 mM borate buffer (pH 9.0), 0.5 mM TTAB and 0.5 mM EDTA.

The results obtained in this study suggest that CE is a promising method for simultaneous determination of anions and cations in aqueous samples. By coupling the electrophoresis with colored metal complex formation, the separation and the sensitivity of detection of metals have been enhanced.

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Received July 15, 1997
Accepted August 9, 1997
Manuscript 4549