Short communication

Determination of trace level anions in snow samples by capillary electrophoresis with sample stacking

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Abstract

Trace level Cl^-, SO_4^{2-} and NO_3^- in snow samples were determined by capillary electrophoresis with the sample stacking enrichment technique to improve the detection sensitivity. The conditions of separation of standard ions (Br^-, Cl^-, SO_4^{2-}, NO_2^- and NO_3^-) were optimized. During stacking run, large enrichment factor and good reproducibility of migration times could be achieved with electromigration injection. However, the reproducibility of peak areas was poor, and at the same time, quantitation became difficult because the enrichment factor was influenced by the ionic strength of standard ion mixtures and the real samples. Using Br^- as an internal standard, standard addition method was used for the quantitative determination of anions in snow sample by electromigration injection. The results were consistent with those of ion chromatography. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Capillary electrophoresis (CE) has been successfully applied to the analysis of a variety of anionic solutes in several complex samples [1–7]. It offers significant improvement over ion chromatography (IC) in efficiency, low run cost and analysis time [1,2]. However, the major disadvantages of CE are its low concentration sensitivity and poor reproducibility in quantitation of trace ions. In glaciology, the determination of Cl^-, SO_4^{2-} and NO_3^- in snow sample is very important. The concentration of these anions in snow sample is useful for deducing the change in climate and pollution in the environment. The level of anions in snow sample is about sub-ppm, therefore, it is difficult to determine the trace

level anions accurately by CE with commonly used injection mode. The sample stacking injection technique was used for improving the detection sensitivity, and large enrichment factors could be achieved [8–13].

Sample stacking is a method of sample concentration [14,15]. The sample is dissolved in solution that has a lower conductivity than the run buffer, and the solute ions rapidly migrate through the dilute sample plug until they reach the concentration boundary between the sample plug and the run buffer. The solute encounters a lower field, slows down and forms a narrow zone. The detection sensitivity was improved. This technique was suitable for the determination of trace level anions. However, one problem in the determination of trace ions by CE was that the enrichment factor was influenced by the ionic strength of standard ion mixtures and the real samples. Jackson and Haddad

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[3] gave accurate quantitation for the analysis of anions in waters by adding a constant amount of a non-interfering anion to normalize the ionic strength of both standard solutions and samples. This approach was less attractive for samples of higher ionic strength due to reducing the enrichment factors. This could be overcome by adding an internal standard to the standard solutions or the real samples [13,16].

To our knowledge, only a few papers for determination of anions in snow sample by CE were published. The aim of this paper is to establish a new method for quantitative determination of trace level anions in snow samples. In order to enhance the detection sensitivity, the sample stacking enrichment technique was used. Using Br^- as an internal standard, the peak areas of Cl^-, SO_4^{2-}, NO_3^- relative to Br^- as response factor, quantitative determination of anions in snow samples was carried out with standard addition method.

2. Experimental

2.1. Instrumentation

All the CE experiments were carried out on a Bio-Focus 3000 CE system (Bio-Rad Labs., Hercules, CA, USA). A negative power supply was used for all separation, and the separation voltage applied was -10.0 kV. The separation capillary was untreated fused-silica capillary of 35 cm (30 cm effective length)×50 μm I.D.×350 μm O.D. The column temperature was thermostatted at 20°C.

The IC measurements were carried out on a Dionex Model 2010i IC system.

2.2. Reagents and materials

All chemicals were of analytical-reagent grade. The deionized water (Milli-Q) was used to prepare all solutions (Millipore, Bedford, MA, USA). 2-Aminopyridine was purchased from Beijing Chemical Plant (Beijing, China). Cetyltrimethylammonium bromide (CTAB) was provided by Xi'an Chemical Plant (Xi'an, China). CrO_4^{2-} used for CE was prepared by dilution of CrO_3 in deionized water. The stock solutions of Br^-, Cl^-, SO_4^{2-}, NO_2^-, NO_3^-, 0.1 mol/l each, were prepared by dissolving the respec-

tive sodium salts in deionized water. The buffer pH was adjusted with 0.1 mol/l NaOH.

2.3. Snow sample collection and handling

Snow samples were collected from No. 1 of Tianshan Mountains (elevation from 3800 m a.s.l. to 4500 m a.s.l.) in May 1996. Each sample was stored in two new polyethylene bottles, one of which was filtered using a prerinsed, 47-mm Gelman A/E glass fiber filter with ca. 1 μm pore size. Prior to bottling, bottles were filled with sample water, agitated and then decanted at least three times in order to avoid any contamination. Discharge was measured at the Dry Cirque by Lanzhou Institute of Glaciology and Geocryology, using a standard concrete gauging station, continuous stage-height recorder, and a current meter.

2.4. Procedure for electrophoresis

At the beginning of each day, the capillary was rinsed with 0.1 mol/l NaOH solution for 10 min, and then with deionized water and running buffer for 4 min, respectively. During the interval of two runs, the capillary was rinsed with running buffer for 2 min. Indirect UV detection was accomplished at 254 nm. Sample was injected for 10 s at -5.0 kV or pressure injected for 8 p.s.i. s (1 p.s.i.=6894.76 Pa). The injection volume of pressure injection is 15.6 nl. The injection quantity of electromigration injection was dependent on their mobilities and concentrations.

3. Results and discussion

3.1. Optimization for separation of anions

The influence of the buffer pH on separation of Br^-, Cl^-, SO_4^{2-}, NO_2^-, NO_3^- was studied. The background electrolyte system, i.e., $6\cdot10^{-3}$ mol/l 2-aminopyridine–$3\cdot10^{-3}$ mol/l chromate–$5\cdot10^{-5}$ mol/l CTAB was chosen for this purpose. The buffer pH varied from 7.5 to 9.5. The observed electrophoretic mobilities of anions increased, but the resolution decreased with increasing buffer pH, and

even SO_4^{2-} and NO_2^- overlapped at pH>8.5. The electrolyte system had been optimized at pH 8.2.

The influence of the concentration of CTAB on separation was studied. The concentration of CTAB varied from 0 to $3 \cdot 10^{-4}$ mol/l. The observed electrophoretic mobilities of anions increased, but the resolution of anions decreased with increasing concentration of CTAB. The baseline separation of Br^-, Cl^-, SO_4^{2-}, NO_2^- and NO_3^- was achieved in the concentration range from $5 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ mol/l. In this paper, $5 \cdot 10^{-5}$ mol/l CTAB was selected.

When $6 \cdot 10^{-3}$ mol/l 2-aminopyridine as a buffer was added to the system, the baseline resolution of anions and good baseline in snow sample were all achieved. The electropherogram for separation of standard ions is shown in Fig. 1.

3.2. Reproducibility of the method and detection limits

Reproducibilities of migration times and peak areas were tested with electromigration injection (5.0 kV, 10 s) using a standard solution containing Br^-, Cl^-, SO_4^{2-}, NO_3^- (2×10^{-5} mol/l). The relative

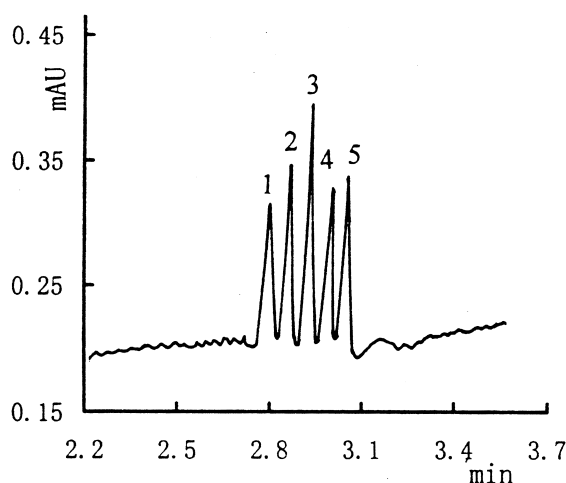Fig. 1. The electropherogram for the separation of Br^-, Cl^-, SO_4^{2-}, NO_2^- and NO_3^-. Conditions: capillary, 35 cm (30 cm effective length)×50 μm I.D.×350 μm O.D.; background electrolyte, $6 \cdot 10^{-3}$ mol/l 2-aminopyridine, $3 \cdot 10^{-3}$ mol/l chromate, $5 \cdot 10^{-5}$ mol/l CTAB (pH 8.2); applied voltage, −10.0 kV; pressure injection (8 p.s.i. s). The concentration of Br^-, Cl^-, SO_4^{2-}, NO_2^- and NO_3^- in standard solution is $2 \cdot 10^{-5}$ mol/l. Peaks: 1=Br^-, 2=Cl^-, 3=SO_4^{2-}, 4=NO_2^-, 5=NO_3^-.

standard deviations (R.S.D.s) of peak areas and migration times ($n=9$) were no more than 13.8% and 0.6%, respectively. Using Br^- as an internal standard, the R.S.D.s of peak areas and migration times of Cl^-, SO_4^{2-}, NO_3^- to Br^- ($n=9$) were <3% and <0.2%, respectively. Better reproducibility can be obtained with an internal standard than without an internal standard. The results are shown in Table 1. The detection limits, defined as a detectable concentration of an anion giving a peak twice as high as the background noise (N), were $1 \cdot 10^{-7}$ mol/l for Cl^-, SO_4^{2-} and NO_3^-.

3.3. Quantitation

Since the level of anions in snow sample was about sub-ppm, it was difficult to determine them by commonly used injection mode. Sample stacking injection was used for improving the sensitivity. Snow sample was diluted in deionized water not in background electrolyte. However, the major disadvantage of this technique for analysis of trace ions was difficult to make quantitative determination because the difference in ionic strength of the standard ion mixtures and samples led to different enrichment factor in the enrichment step. This shortcoming was overcome by adding a constant amount of non-interfering anion to normalize the ionic strength of standard ion mixtures and real sample [3], but this approach was not suitable for the determination of sample with higher ionic strength and scarce sample.

In this experiment, standard addition method was

Table 1
Reproducibilities of migration times and peak areas of Cl^-, SO_4^{2-} and NO_3^-

	R.S.D. (%)		
	Cl^-	SO_4^{2-}	NO_3^-
Migration time	0.6	0.6	0.6
Migration time relative to Br^-	0.1	0.1	0.2
Peak area	13.5	13.8	12.4
Peak area relative to Br^-	2.1	2.9	3.0

Conditions: capillary, 35 cm (30 cm effective length)×50 μm I.D.×350 μm O.D.; background electrolyte, $6 \cdot 10^{-3}$ mol/l 2-aminopyridine, $3 \cdot 10^{-3}$ mol/l chromate, $5 \cdot 10^{-5}$ mol/l CTAB (pH 8.2); applied voltage, −10.0 kV; electromigration injection (−5.0 kV, 10 s).

Table 2
Results for determination of Cl^-, SO_4^{2-} and NO_3^- in a snow sample from Tianshan Mountain

Method	Sample	Determination (ppm)		
		Cl^-	SO_4^{2-}	NO_3^-
CE	GEL1	0.621	0.720	0.261
	GEM1	0.672	0.603	0.237
IC	GEL1	0.577	0.631	0.323
	GEM1	0.625	0.524	0.270

Conditions as in Table 1.

applied to analysis of two snow samples (GEL1, GEM1). In six 5.0-ml volumetric flasks, 2.0 ml snow sample and 1.0 ml Br^- ($2 \cdot 10^{-4}$ mol/l) were added, respectively, and then 0, 0.25, 0.50, 0.75, 1.00, 1.25 ml $2 \cdot 10^{-4}$ mol/l standard solution of Cl^-, SO_4^{2-} and NO_3^- were added in turn, and finally diluted to scale with deionized water. Using the peak areas of Cl^-, SO_4^{2-} and NO_3^- relative to Br^- as response factor, standard addition method was used for quantitation of Cl^-, SO_4^{2-} and NO_3^- in snow samples. The anions PO_4^{3-}, CO_3^{2-} and small amount of NO_2^- did not interfere the determination of Cl^-, SO_4^{2-} and NO_3^-
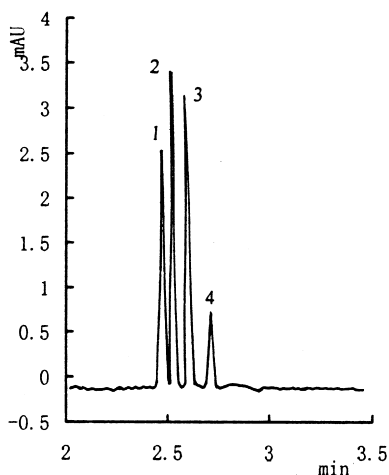

Fig. 2. The typical electropherogram for the separation of anions in a snow sample. Conditions: electromigration injection (5.0 kV, 10 s), other conditions as in Fig. 1. The concentration of Br^- in snow sample is $4 \cdot 10^{-5}$ mol/l. snow sample, GEL1. Peaks: 1=Br^- (internal standard), 2=Cl^-, 3=SO_4^{2-}, 4=NO_3^-.

in snow samples. The results obtained by CE were consistent with those of IC (see Table 2). The typical electropherogram for separation of anions in snow sample is shown in Fig. 2.

4. Conclusions

Separation of anions and determination of trace level Cl^-, SO_4^{2-} and NO_3^- in snow sample by CE in the presence of 2-aminopyridine–chromate–CTAB system with the sample stacking enrichment technique were investigated. High sensitivity and good reproducibility of migration times could be obtained by electromigration injection. The difficulty in quantitation could be solved by using Br^- as an internal standard, and using the peak area relative to Br^- as response factor. Trace level Cl^-, SO_4^{2-} and NO_3^- in snow sample could be determined quantitatively with standard addition method. The results were consistent with those of IC.

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