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Improved selectivity of anions with methanol as additive Determination of Cl^-, NO_3^- and SO_4^{2-} in river water by capillary electrophoresis

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Abstract

A method for separation and determination of Cl^-, NO_3^- and SO_4^{2-} in river water by capillary electrophoresis with indirect UV detection was described. A background electrolyte consisting of sodium borate, chromate and cetyltrimethylammonium bromide (CTAB) was employed for the separation. Methanol as additive was added to the system for improving separation selectivity of NO_3^- and SO_4^{2-} through adjusting the elution order of anions. High concentrations of SO_4^{2-} did not interfere with the determination of NO_3^- because SO_4^{2-} was eluted later than NO_3^-. The effects of the concentration of sodium borate and CTAB on separation were also examined. The detection limits of Cl^-, NO_3^- and SO_4^{2-} were $1 \cdot 10^{-7}$ mol/l. The concentration of Cl^-, NO_3^- and SO_4^{2-} in river water was determined quantitatively using NO_2^- as an internal standard. Standard addition recoveries of the Cl^-, NO_3^- and SO_4^{2-} in the river water sample were between 89~105%. The results were consistent with those obtained by ion chromatography. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Environmental analysis; Inorganic anions; Chloride; Nitrate; Sulfates

1. Introduction

Recently, the separation of ionic species by capillary electrophoresis (CE) has been gaining more attention. It offers significant improvement over ion chromatography (IC) in efficiency, low run cost and analysis time [1,2]. This technique has been successfully applied to the analysis of a variety of anionic solutes in several complex samples [3–14]. In most of these papers, the separation was accomplished by using chromate or pyromotallitic acid as a UV-absorbing agent by indirect UV detection.

The simultaneous determination of Cl^-, SO_4^{2-} and NO_3^- in river water is very important for studying pollution in river waters. Though many applications for the determination of anions were accomplished by the commonly used method, when we used the methods for analyzing the anions of Wulumuqi river water (Xinjiang province, China), poor baseline was obtained and trace level NO_3^- could not be determined accurately. This is due to a complex matrix and the presence of the large amount of SO_4^{2-} in the river water. The SO_4^{2-} was eluted faster than NO_3^- and influenced the determination of NO_3^-.

In CE, organic solvents are usually used for improving resolution of metal ions from another higher concentration of metal ion [14–16], but they

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were seldom employed for improving the selectivity of inorganic anions [17,18]. Buchberger and Haddad [17] used 30% methanol as additive to alter migration order of anions in the chromate–cetyltrimethylammonium bromide (CTAB) electrolyte, however, NO_2^- and NO_3^- could not be baseline separated.

Another problem is detection. To improve the detection sensitivity, the sample stacking enrichment technique was used for analyzing the trace level anions in the river water, but the difference in ionic strength of the samples led to different enrichment factor [3,7,8,14,15]. This led to difficulty in quantitation. Jackson and Haddad [5] gave an accurate quantitation for the analysis of anions by adding a constant amount of a non-interfering anion to normalize the ionic strength of both standard solutions and samples. If the ionic strength is not normalized, the shortcoming could also be overcome by using an internal standard to standard solutions or samples [19–21].

The aim of the work is to develop a feasible method for determination of anions in the river water containing high concentrations of SO_4^{2-}. In order to obtain good baseline and determine the trace level anions, sodium borate as a buffer was added to the electrolyte, and small amount of methanol (10%) was employed to alter the migration order of NO_3^- and SO_4^{2-}. High concentrations of SO_4^{2-} did not disturb the determination of NO_3^-. The determination of Cl^-, NO_3^- and SO_4^{2-} was accomplished with internal standard curve. The results were consistent with those obtained by IC.

2. Experimental

2.1. Instrumentation

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 separations, and the separation voltage applied was −10.0 kV. The separation capillary was an untreated fused-silica capillary of 35 cm (30 cm effective length)×50 μm I.D.×350 μm O.D. The column temperature was maintained at 20°C. Indirect UV detection was accomplished at 254 nm. Sample was

pressure injected for 8 p.s.i. s (1 p.s.i.=6894.76 Pa) or electromigration injected for 10 s at −5.0 kV.

The values measured by IC 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). Sodium borate and sodium chromate were purchased from Beijing Chemical Plant (Beijing, China). CTAB was provided by Xi'an Chemical Plant (Xi'an, China). The stock solutions of Cl^-, SO_4^{2-}, NO_2^- and NO_3^-, 0.1 mol/l each, were prepared by dissolving the respective sodium salts in deionized water. The electrolyte pH was adjusted with 0.1 mol/l NaOH.

2.3. Sample collection

River water sample was collected in August 1997. 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.

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.

3. Results and discussion

3.1. Effect of background electrolyte on separation of Cl^-, SO_4^{2-}, NO_2^-, NO_3^-

In our initial experiment, poor baseline was obtained when we analyzed the anions in the river water in commonly used chromate–CTAB system. This may be because the buffer capacity of the chromate–CTAB system is poor. Therefore, sodium

borate was used as a buffer. Effect of the concentration of sodium borate on separation was examined by use of $5 \cdot 10^{-3}$ mol/l CrO_4^{2-} as a UV-absorbing agent and $5 \cdot 10^{-4}$ mol/l CTAB as electro-osmotic flow (EOF) modifier (pH 9.5). The concentration of sodium borate varied from 1 to $10 \cdot 10^{-3}$ mol/l. The apparent electrophoretic mobilities of the anions decreased, especially that of SO_4^{2-} decreased significantly with increasing the concentration of sodium borate, as seen in Fig. 1. This is because the EOF decreased with increasing concentration of sodium borate and μ_{ep} of SO_4^{2-} was influenced by ionic strength more significantly than those of Cl^-, NO_2^-, NO_3^-. At the same time, the resolution of SO_4^{2-} and NO_3^- also decreased with increasing concentration of sodium borate. The SO_4^{2-} and NO_3^- were partly separated when the concentration of sodium borate was at $5 \cdot 10^{-3}$ mol/l, and the two anions were completely overlapped when the concentration of sodium borate was at $>7 \cdot 10^{-3}$ mol/l. The baseline separation and good baseline were all achieved when the concentration of sodium borate was at $3 \cdot 10^{-3}$ mol/l.

Effect of the concentration of CTAB on separation was also investigated. In order to decrease analysis time, alkyl ammonium was usually used for suppression or reversal of EOF, anions were detected under
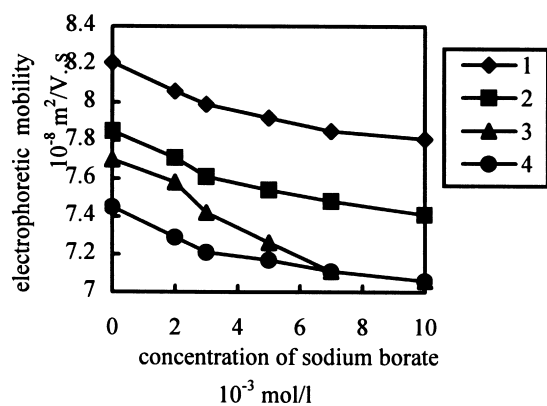

Fig. 1. Effect of the concentration of sodium borate on apparent electrophoretic mobility. Conditions: capillary, 35 cm (30 cm effective length)×50 μm I.D.×350 μm O.D.; background electrolyte, $5 \cdot 10^{-3}$ mol/l CrO_4^{2-} and $5 \cdot 10^{-4}$ mol/l CTAB at pH 9.50; applied voltage, −10.0 kV; peaks: 1=Cl^-, 2=NO_2^-, 3=SO_4^{2-}, 4=NO_3^-.

a negative voltage [22]. In this experiment, CTAB was chosen as EOF modifier, the concentration of CTAB varied from 0.1 to $1 \cdot 10^{-3}$ mol/l. The apparent electrophoretic mobilities and resolution of anions increased, but column efficiency decreased with increasing the concentration of CTAB. The SO_4^{2-} and NO_3^- peaks were completely overlapped when the concentration of CTAB was at $1 \cdot 10^{-4}$ mol/l. The baseline separation of the two anions was achieved when the concentration of CTAB was at $5 \cdot 10^{-4}$ mol/l.

The buffer containing $5 \cdot 10^{-3}$ mol/l CrO_4^{2-}, $3 \cdot 10^{-3}$ mol/l sodium borate and $5 \cdot 10^{-4}$ mol/l CTAB (pH 9.5) was chosen for separation of Cl^-, SO_4^{2-}, NO_2^- and NO_3^- standard solution. NO_3^- could not be determined accurately in the river water because the SO_4^{2-} and NO_3^- peaks overlapped when large amounts of SO_4^{2-} existed in the river water. The electropherograms were shown in Fig. 2.

3.2. Effect of organic solvent on separation

Usually, methanol and CH_3CN were used to improve the resolution of metal ions from another high concentration of metal ion [14–16], but the solvents were seldom used to improve the resolution of anions [17]. Buchberger and Haddad used 30% methanol as additive to alter the migration order of the anions in chromate–CTAB system, but NO_2^- and NO_3^- could not be baseline separated. In this experiment, we expected that NO_3^- and SO_4^{2-} were determined accurately by altering the migration order of anions. Methanol as additive was added to the sodium borate–chromate–CTAB system. The effect of methanol on separation was studied systematically. The concentration of methanol varied from 0 to 15%. The apparent electrophoretic mobilities of anions decreased, and especially that of SO_4^{2-} decreased significantly with increasing concentration of methanol in the electrolyte. The SO_4^{2-} and NO_3^- peaks completely overlapped in 5% methanol. NO_3^- migrated faster than SO_4^{2-} and peak crossover occurred when the amount of methanol in the buffer was increased to 10%. It was methanol that improved the selectivity and adjusted the elution order of inorganic anions. This is because μ_{ep} and μ_{eo} decreased with increasing concentration of methanol,
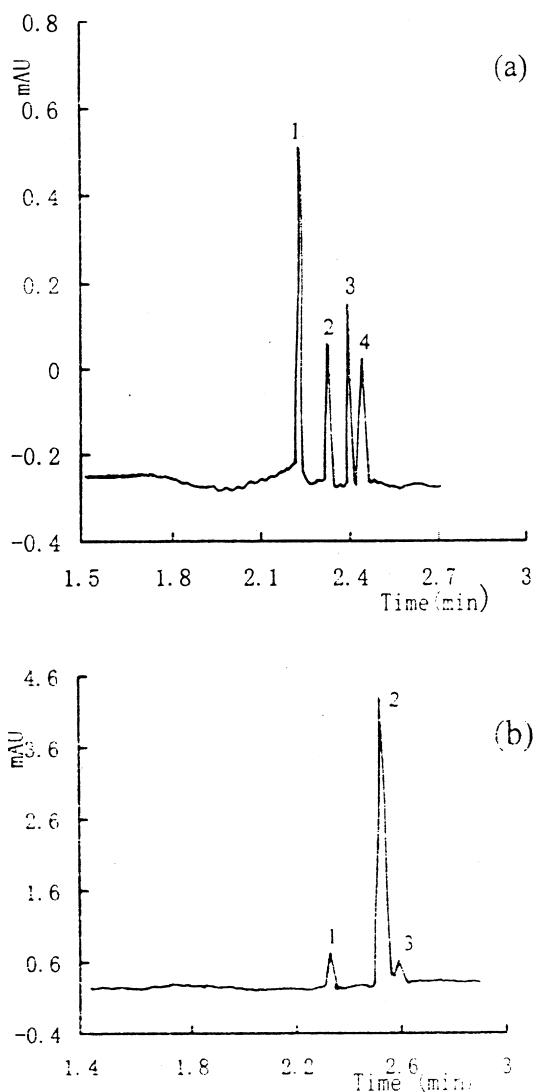
Fig. 3. Effect of the concentration of methanol on apparent electrophoretic mobility. Conditions as in Fig. 2. Peaks: $1=Cl^-$, $2=NO_2^-$, $3=SO_4^{2-}$, $4=NO_3^-$.

electrophoretic mobilities of anions decreased. Effect of the concentration of methanol on apparent electrophoretic mobility of anions and resolution of SO_4^{2-} and NO_3^- were shown in Figs. 3 and 4.

The larger amount of methanol affected the separation efficiency and caused peak tailing owing to broadening of the peak shape. When the anions were eluted in the buffer containing 15% methanol, peak tailing of SO_4^{2-} appeared. Therefore, 10% methanol in the buffer was used for the separation of anions; high concentration of SO_4^{2-} did not disturb the determination of NO_3^-. The electropherogram for separation of standard solutions is shown in Fig. 5.

Fig. 2. Electropherogram for separation of anions. Conditions: $3\cdot10^{-3}$ mol/l sodium borate, other conditions as in Fig. 1. Pressure injection (8 p.s.i. s). (a) Separation of the four Cl^-, NO_2^-, SO_4^{2-} and NO_3^- standard solution. The concentration of NO_2^-, SO_4^{2-} and NO_3^- is $2\cdot10^{-5}$ mol/l, and the concentration of Cl^- is $4\cdot10^{-5}$ mol/l Peaks: $1=Cl^-$, $2=NO_2^-$, $3=SO_4^{2-}$, $4=NO_3^-$. (b) Separation of the Cl^-, SO_4^{2-} and NO_3^- of the river water in the presence of higher concentrations of SO_4^{2-}. The water sample was not diluted. Peaks: $1=Cl^-$, $2=SO_4^{2-}$, $3=NO_3^-$.

Fig. 4. Effect of the concentration of methanol on resolution of SO_4^{2-} and NO_3^-. Conditions as in Fig. 3.

which leads to decrease in apparent electrophoretic mobilities [23,24]. The higher the charge of the anions was, the more significantly the apparent
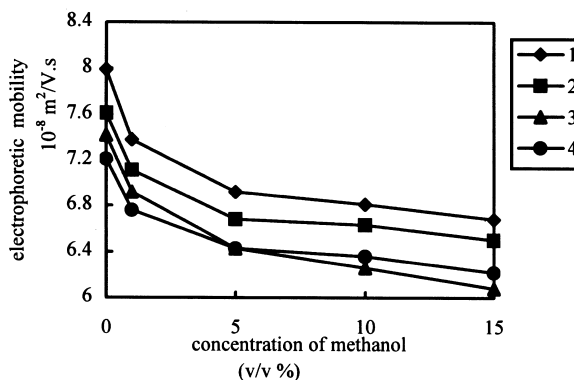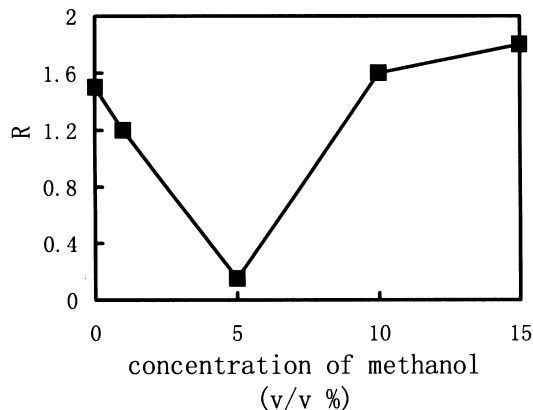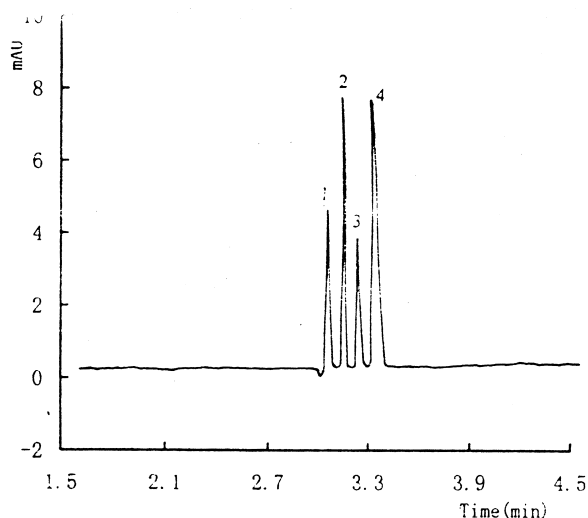
Fig. 5. Electropherogram for separation of four anions. Conditions: methanol (10%, v/v), other conditions as in Fig. 2. Electromigration injection (5.0 kV, 10 s). The concentration of Cl^-, NO_3^- and SO_4^{2-} is $2 \cdot 10^{-5}$ mol/l and the concentration of NO_2^- is $4 \cdot 10^{-5}$ mol/l. Peaks: 1=Cl^-, 2=NO_2^-, 3=NO_3^-, 4= SO_4^{2-}.

3.3. Reproducibility of the method and detection limits

Reproducibilities of migration times and peak areas were tested using a standard solution containing Cl^-, NO_3^-, SO_4^{2-} ($2 \cdot 10^{-5}$ mol/l) and NO_2^- ($4 \cdot 10^{-5}$ mol/l). The relative standard deviations of peak areas and migration times ($n=9$) were <7.5% and <0.4%, respectively. In addition, using NO_2^- as an internal standard, the relative standard deviations of peak areas and migration times of Cl^-, NO_3^- and SO_4^{2-} to NO_2^- ($n=9$) were <2.5% and <0.2%, respectively. 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^-, NO_3^- and SO_4^{2-}. The results are shown in Table 1.

3.4. Quantitation

In order to improve detection sensitivity, the sample stacking injection technique was used for the determination by electromigration injection. Using this technique, sample was diluted in deionized

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

	R.S.D. (%)		
	Cl^-	NO_3^-	SO_4^{2-}
Migration time	0.3	0.3	0.4
Relative migration time to NO_2^-	0.1	0.1	0.2
Peak area	5.4	7.5	7.5
Relative peak area to NO_2^-	2.5	0.8	0.7

Conditions: capillary, 35 cm (30 cm effective length)×50 μm I.D.×350 μm O.D.; background electrolyte, $3 \cdot 10^{-3}$ mol/l sodium borate, $5 \cdot 10^{-3}$ mol/l CrO_4^{2-} and $5 \cdot 10^{-4}$ mol/l CTAB at pH 9.50; applied voltage, -10.0 kV. Electromigration injection (5.0 kV, 10 s).

water, but the difference in ionic strength of sample and ionic conductivity of each ion led to different enrichment factor. This led to poor correlation coefficients of each regression equation between peak area and anion concentration. This shortcoming could be overcome by adding NO_2^- as an internal standard to the each standard solution. Using the peak areas of Cl^-, NO_3^- and SO_4^{2-} relative to NO_2^- as response, the response showed good linearities with the concentration of each ion, and the correlation coefficients were more than 0.997. The results are shown in Table 2.

In a 5.0-ml volumetric flask, 2.0 ml river water sample and 1.0 ml NO_2^- ($2 \cdot 10^{-4}$ mol/l) was added, and then diluted to mark with deionized water. The sample was employed for electrophoresis. The Cl^-, NO_3^- and SO_4^{2-} in the river water were identified by the migration time of each ion relative to NO_2^-. The concentration of Cl^-, NO_3^- and SO_4^{2-} in the sample was obtained with the linear equation. The electropherogram for separation of anions in river water

Table 2
The linear equation, linear range and correlation coefficient (r) of Cl^-, NO_3^- and SO_4^{2-}

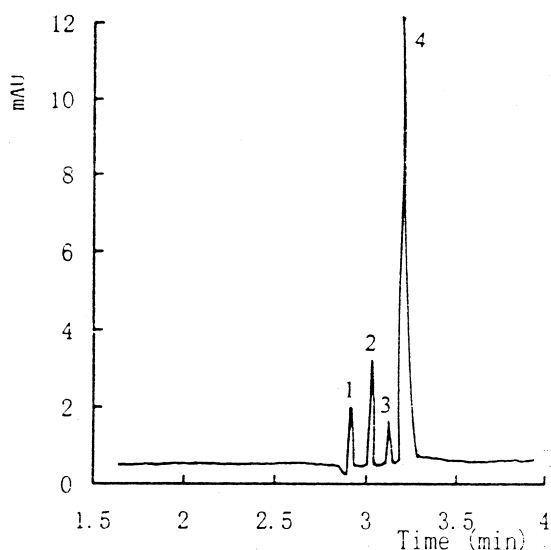| Anion	Linear equation	Linear range ($\cdot 10^{-4}$ mol/l)	r
Cl^-	$y=0.3353x-0.1225$	0.06~4	0.998
NO_3^-	$y=0.5971x-0.1399$	0.04~4	0.999
SO_4^{2-}	$y=0.2755x-0.1307$	0.01~4	0.997

Conditions as in Table 1.

Fig. 6. Electropherogram for separation of anions in river water. Conditions as in Fig. 4. Dilute factor 2.5. The concentration of NO_2^- is $4·10^{-5}$ mol/l. Peaks: 1=Cl^-, 2=NO_2^- (internal standard), 3=NO_3^-, 4=SO_4^{2-}.

is shown in Fig. 6. Small amounts of the SiO_3^{2-} anion did not disturb the determination of the three anions since it migrated more slowly than Cl^-, NO_3^- and SO_4^{2-}. The results were compared with those obtained by IC (see Table 3).

3.5. Recovery

To verify the accuracy of this method, three different amounts of standard solutions ($1·10^{-4}$ mol/l Cl^-, NO_3^- and SO_4^{2-}) were added to the real samples, respectively. $4·10^{-5}$ mol/l NO_2^- as an internal standard was added to samples. The samples were diluted to identical volume. The three samples were determined by the method, respectively. The results of standard addition recoveries of chloride, nitrate and sulfate are listed in Table 4. The recoveries were 96.4~101% for Cl^-, 88.7~93.7% for NO_3^- and 94.2~105.2% for SO_4^{2-}.

4. Conclusions

Separation and determination of Cl^-, SO_4^{2-}, NO_2^- and NO_3^- in river water by CE was investigated. Good baseline was obtained when sodium borate as a buffer was employed. The migration order of anions was altered in the electrolyte containing 10% methanol. The SO_4^{2-} ion was eluted later than NO_3^-, and it did not disturb the determination of Cl^-, NO_3^- in the presence of high concentrations of SO_4^{2-}. The de-

Table 3
Results for determination of Cl^-, NO_3^- and SO_4^{2-} in river water from the Wulumuqi river

Method	Sample	Determination ($·10^{-5}$ mol/l)		
		Cl^-	NO_3^-	SO_4^{2-}
CE	GHS.FW	3.21	2.63	21.70
IC	GHS.FW	3.09	2.93	23.68

Conditions as in Table 1.

Table 4
Recoveries (R) of Cl^-, NO_3^- and SO_4^{2-} in river water sample from the Wulumuqi river

Sample	Dilution	Ion	Concentration ($·10^{-5}$ mol/l)			Recovery (%)
			Sample	Added	Determined	
GHS.FW	1:2.5	Cl^-	1.284	1	2.266	98.2
		NO_3^-	1.052	1	1.939	88.7
		SO_4^{2-}	8.68	1	9.732	105.2
	1:2.5	Cl^-	1.284	2	3.301	100.9
		NO_3^-	1.052	2	2.874	91.1
		SO_4^{2-}	8.68	2	10.608	96.4
	1:2.5	Cl^-	1.284	4	5.14	96.4
		NO_3^-	1.052	4	4.80	93.7
		SO_4^{2-}	8.68	4	12.467	94.2

Conditions as in Table 1.

termination was accomplished with an internal standard curve. The results were consistent with those obtained by IC.

Acknowledgements

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