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Short communication

Determination of the petroleum tracers nitrate and thiocyanate in subterranean waters by capillary ion electrophoresis

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Abstract

The petroleum tracers nitrate and thiocyanate in subterranean waters were determined by capillary ion electrophoresis using direct UV detection. The high concentrations of salts in subterranean waters made the determination difficult. Taking sodium chloride to represent salts in subterranean waters, the effect of high concentrations of salts in samples on the determination was examined. Because of electrostacking and its inverse process, different concentrations of salts in samples could cause different peak heights and peak widths of constant concentration of an anion, but the peak area remained constant. The experimental results showed that the determination of the tracers was feasible using peak areas. By using 100 mM sodium chloride with 2.0 mM cetyltrimethylammonium chloride as carrier electrolyte solution, determination of nitrate and thiocyanate was accomplished at concentrations of sodium chloride in the sample from 0 to 200 mM. Standard addition recoveries of the tracers in four subterranean water samples were between 91 and 113%.

1. Introduction

Capillary ion electrophoresis (CIE), introduced at the beginning of this decade [1–4] is a capillary electrophoretic technique optimized for the rapid determination of low-molecular-mass inorganic and organic ions. Although CIE is a recent separation and analysis technique, it has gained many applications after several years of development. It has been used to determine anions in environmental waters [5], high-purity

water in the power industry [6], urine [7], milk [8], food samples [9], in the pulp and paper industry [10], alumina production [11], prenatal vitamin formulations [12], bulk drugs and intermediates [13] and explosives residues [14], etc. A number of difficult and challenging problems in ion chromatography (IC) can be solved by using CIE.

Jones and Jandik [15] determined anions with disparate concentrations, e.g., impurities in 99.9% pure solid terephthalic acid. Whereas in IC consideration must be given to the total ion-exchange capacity of the column, moderate ion-exchange capacity columns reduce the risk of sample overloading at the cost of short analysis times. The re-equilibration time alone can ex-

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ceed 1 h after a column is overloaded. In the determination of the petroleum tracers nitrate and thiocyanate, a similar situation will be encountered.

Nitrate and thiocyanate are used as petroleum tracers in the Tuha oil field to investigate the stratigraphic structure, the distribution of oil deposits and the effectiveness of water blocking. Since subterranean water contains very high concentrations of chloride, sulfate and carbonate salts, etc., e.g., the concentration of chloride can reach tens of grams per litre, the determination of tracers by IC is difficult. In a previous study [16] we investigated a CIE method using direct UV detection for their separation, and the effect of high concentrations of salts in samples on the separation was examined. The experimental results showed that because of electrostacking, the high concentrations of salts in subterranean water caused quantification problems. The CIE separation studied was unsatisfactory, so the determination of the tracers was not carried out.

In this work, 100 mM sodium chloride solution containing 2.0 mM cetyltrimethylammonium chloride (CTAC) was used as a carrier electrolyte solution, and the CIE determination of the petroleum tracers nitrate and thiocyanate was accomplished at concentrations of sodium chloride in the sample from 0 to 200 mM.

2. Experimental

2.1. Apparatus

The CE system employed was a Quanta 4000 (Waters Chromatography Division of Millipore, Milford, MA, USA) with a negative power supply. Direct UV detection was accomplished with a zinc lamp and a 214-nm optical filter. Data acquisition was carried out with a Waters Millennium 2010 Chromatography Manager with a bus satellite interface and a LAC/E module connecting the data station with the CE system. Data collection was initiated by a signal cable connection between the Quanta 4000 and the bus satellite interface.

2.2. Carrier electrolyte solution

CTAC was used as an electroosmotic flow modifier and a carrier electrolyte solution of 100 mM sodium chloride containing 2.0 mM CTAC was prepared as described previously [16].

2.3. Standard solutions

Analytical-reagent grade sodium or potassium salts were used to prepare 1000 ppm anion stock standard solutions containing a single anion. All mixed anion solutions consisted of ten anions: fluoride, chloride, bromide, iodide, nitrite, nitrate, sulfate, phosphate, carbonate and thiocyanate; of these, only five, bromide, iodide, nitrite, nitrate and thiocyanate, have UV absorbance at 214 nm and gave response signals in our experiments. Five mixed anion solutions containing 1, 4, 10, 20 and 40 ppm of each anion were prepared to obtain calibration graphs. Another five mixed anion solutions containing 10 ppm of each of the above-mentioned ten anions with an additional 20 ppm of thiocyanate, 10 ppm of nitrate, 10 ppm of nitrite, 20 ppm of bromide or 20 ppm of iodide separately were prepared for the purpose of peak identification on the electropherograms. Mixed anion solutions were prepared not only with deionized water, but also with 12.5, 50 or 100 mM sodium chloride solutions. Polyethylene containers were utilized for the mixed anion solutions.

2.4. Electrophoresis

A Waters Accu-Sep polyimide-coated fused-silica capillary was used throughout. The capillary dimensions were 75 μm I.D., 60 cm total length and 52 cm from the point of injection to the detector cell. The capillary was flushed with 1 M potassium hydroxide for 1 h and then equilibrated with carrier electrolyte solution before use. All injections were performed in the hydrostatic mode at a height of 10 cm for 30 s. The applied voltage for each run was 10 kV. A 2-min capillary purge with carrier electrolyte solution by a vacuum applied to the receiving

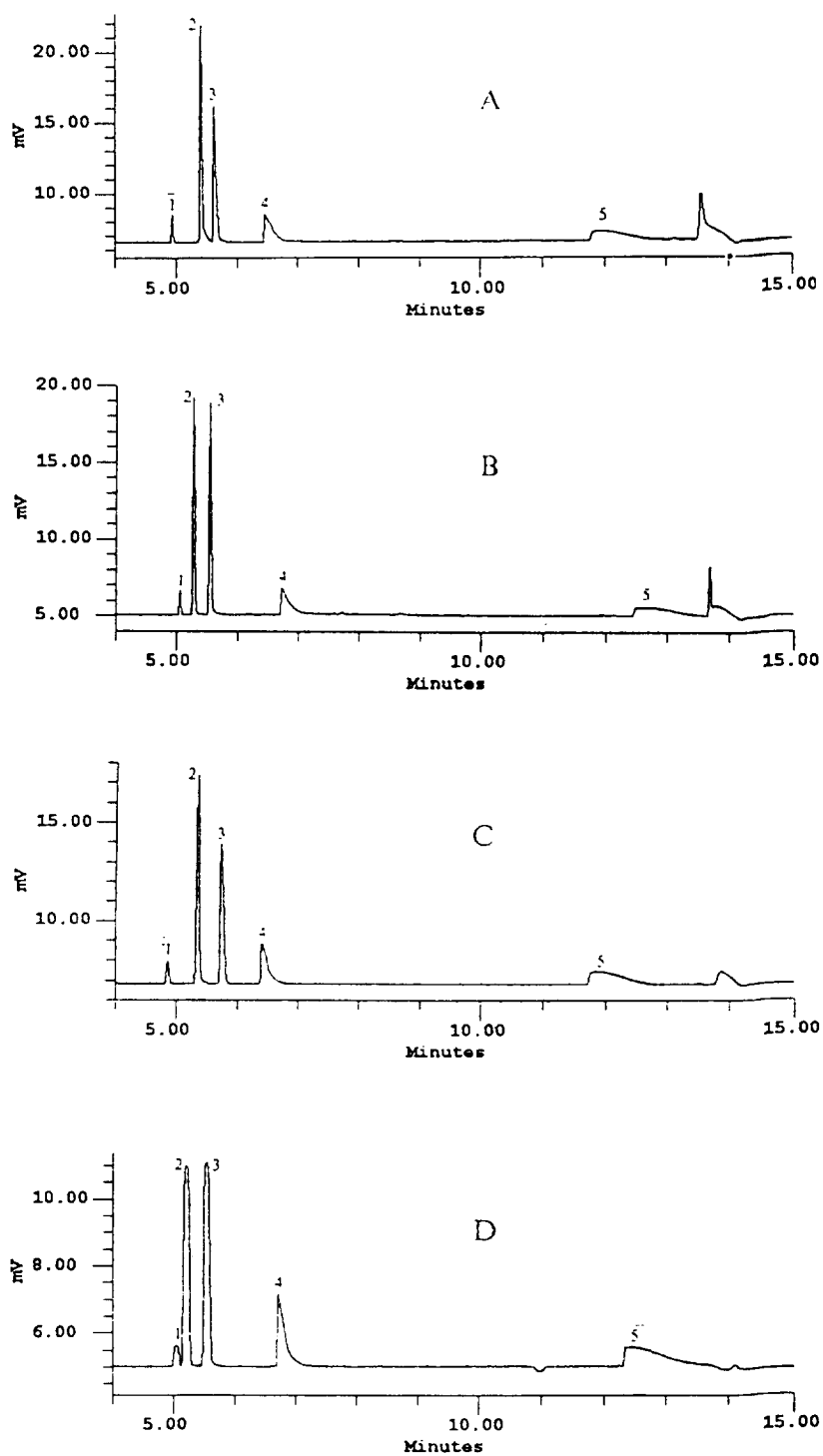


Fig. 1. Effect of the concentration of sodium chloride in the sample on the CIE separation of anions. Current: $85 \mu\text{A}$. Concentration of sodium chloride in sample: (A) 0; (B) 12.5; (C) 50; (D) 100 mM. Peaks: 1 = bromide; 2 = nitrite; 3 = nitrate; 4 = iodide; 5 = thiocyanate. The concentration of each anion in sample was 20 ppm.

electrolyte vial was performed prior to each injection.

3. Results and discussion

Taking sodium chloride to represent salts in subterranean water, the effect of high concentrations of salts in the samples on the CIE separation of anions was examined and the results are illustrated in Fig. 1.

It can be seen from Fig. 1 that high concentrations of chloride in the samples did not cause any baseline disturbances, such as negative peaks covering the bromide peak as occurred in our previous study [16]. The different anionic form of the electroosmotic flow modifier, previously bromide and now chloride, was the reason. Bromide made the carrier electrolyte solutions generate UV absorption at 214 nm, and the presence of chloride in the samples displaced bromide and caused a decrease in absorbance. Chloride is a UV-transparent anionic form, so negative peaks disappeared. Similar phenomena were also observed by Jones and Jandik [15] and Jackson and Haddad [17].

In Fig. 1, there are five peaks belonging to bromide, nitrite, nitrate, iodide and thiocyanate. Because iodide and thiocyanate are hydrophobic anions, their peaks were asymmetric and showed strong tailing due to hydrophobic interactions between them and CTAC. In comparison with iodide and thiocyanate, bromide, nitrite and nitrate gave more symmetrical peaks. It can be seen from Fig. 1 that an increase in the concentration of sodium chloride in the sample caused changes in peak height and width of the

symmetrical peaks of bromide, nitrite and nitrate, but caused less change in the asymmetric peaks of iodide and thiocyanate. When the concentration of sodium chloride in the sample was 12.5 mM, the highest and narrowest peaks of nitrite and nitrate were observed. On increasing the concentration of sodium chloride in the sample from 12.5 to 50 and 100 mM, the peaks widened.

The detection limit was defined as a detectable concentration of an anion giving a peak twice as high as the background noise (N). For a defined change in anion concentration, its corresponding change in peak height was calculated from the slope (SL) of the calibration graph of the anion of peak height versus anion concentration from 1 to 40 ppm. All correlation coefficients of the calibration graphs were calculated and were higher than 0.99. Detection limits calculated as $2N/SL$ (experimental data for $N = 55 \mu\text{V}$) are given in Table 1 for different concentrations of sodium chloride in the samples. It can be seen that when the concentration of sodium chloride in the sample was 12.5 mM, nitrite and nitrate had the lowest detection limits. The detection limits of nitrite and nitrate increased with increasing concentration of sodium chloride in the sample from 12.5 to 100 mM. However, the detection limit of bromide increased steadily with increasing concentration of sodium chloride in sample, whereas the detection limits of iodide and thiocyanate was relatively unchanged.

The separation efficiency was represented by the theoretical plate number, N , which was calculated from $N = 5.54 (t_R/w)^2$, where t_R is the migration time and w is the peak width at half-height. Theoretical plate numbers for bromide,

Table 1
Effect of concentration of sodium chloride in sample on detection limit

Concentration of NaCl in sample (mM)	Detection limit (ppb)				
	Bromide	Nitrite	Nitrate	Iodide	Thiocyanate
0	996	162	278	1468	5036
12.5	1396	154	182	1853	6820
50	1762	204	332	1617	4785
100	3088	368	350	1709	6286

Table 2
Effect of concentration of sodium chloride in sample on separation efficiency of bromide, nitrite and nitrate

Concentration of NaCl in sample (mM)	Theoretical plate number		
	Bromide	Nitrite	Nitrate
0	147 300	120 100	82 900
12.5	167 000 ^a	142 800	127 200
50	63 000 ^b	57 700	46 100
100	21 300 ^b	15 700	17 900

^a Average of only four values because of detection sensitivity limitation.

^b Average of only three values because of detection sensitivity limitation.

nitrite and nitrate at different concentrations of sodium chloride in the sample were calculated and are given in Table 2. Each theoretical plate number in Table 2 is the average of five results which were obtained by the separation of five mixed anion solutions containing 1, 4, 20 and 40 ppm of each anion. It can be seen from Table 2 that when the concentration of sodium chloride in the sample was 12.5 mM, bromide, nitrite and nitrate had the highest theoretical plate numbers, and then increasing the sodium chloride concentration in sample from 12.5 to 50 and 100 mM resulted in a decrease in the theoretical plate numbers. The theoretical plate numbers of iodide and thiocyanate are not shown in Table 2 because they varied with the concentration of iodide and thiocyanate in sample, as illustrated in Table 3. Because the peaks of iodide and thiocyanate were not significantly affected by high concentrations of sodium chloride in the

Table 3
Effect of concentration of iodide and thiocyanate in sample on their separation efficiency (theoretical plate number)

Anion	Concentration (ppm)				
	1	4	10	20	40
Iodide	— ^a	35 500	21 300	11 000	6 200
Thiocyanate	— ^a	7 900	4 100	2 100	1 200

^a Not measured because of detection sensitivity limitation.

samples, each value in Table 3 is the average of four values obtained by the separation of four mixed anion solutions with 0, 12.5, 50 and 100 mM of sodium chloride in the sample. It can be seen from Table 3 that increasing concentrations of iodide and thiocyanate in the sample resulted in a decreased separation efficiency, which could be attributed to the tailing peaks.

The reason for the above effects of high concentrations of sodium chloride in samples on the CIE separation of anions can be explained as follows. In capillary electrophoresis, when the ionic strength of the sample is lower than that of the carrier electrolyte solution, electrostacking occurs and the sample ion will be stacked in a narrow zone [17–23]. However, when the ionic strength of the carrier electrolyte solution is lower than that in the sample, a peak broadening mechanism will result from anti-stacking and the sample ion will be diffused in a broad zone. When stacking or anti-stacking occurs, there is also an accompanying phenomenon, laminar flow, which originates from the different local electroosmotic flow caused by the non-uniform distribution of the electric field strength and will broaden a separated sample zone [19]. When the concentration of sodium chloride in the sample is higher than that in the carrier electrolyte solution, it can be concluded that the length of the separated zone will always increase with increasing concentration of sodium chloride in the sample because of the effects of anti-stacking and laminar flow broadening. However, when the concentration of sodium chloride in the sample is lower than that in the carrier electrolyte solution, it can be concluded that stacking and laminar flow broadening will function against each other so that the optimum concentration of sodium chloride in the sample for a minimum length of a separated zone is somewhere between zero and the concentration of sodium chloride in carrier electrolyte solution. In this experiment, the concentration of sodium chloride in the carrier electrolyte solution was 100 mM, and the optimum concentration of sodium chloride in the sample was 12.5 mM.

In the determination of anions in subterranean water, 100 mM sodium chloride solution con-

Table 4

Statistics of migration time of each anion at different concentrations of sodium chloride (0, 12.5, 50 and 100 mM) and different concentrations of each anion (1, 4, 10, 20 and 40 ppm) in sample

Anion	Br ⁻	NO ₂ ⁻	NO ₃ ⁻	I ⁻	SCN ⁻
Average (min)	5.0 ^a	5.3	5.6	6.6 ^b	12.2 ^b
Lowest (min)	4.8	5.2	5.5	6.3	11.4
Highest (min)	5.1	5.5	5.8	6.9	12.9
R.S.D. (%)	1.9 ^a	1.6	2.1	3.0 ^b	3.5 ^b

^a Calculated from only fourteen values because of detection sensitivity limitation.

^b Calculated from only sixteen values because of detection sensitivity limitation.

taining 2.0 mM CTAC was chosen as the carrier electrolyte solution because it gave lower detection limits in comparison with a lower concentration of sodium chloride, and it was also suitable for samples with higher concentrations of salts. With a concentration of sodium chloride in the sample of 0, 12.5, 50 or 100 mM, separations of five mixed anion standard solutions that contained 1, 4, 10, 20 and 40 ppm of each anion were accomplished, and the statistics of the migration times of each anion at different concentrations of sodium chloride and each anion in the sample are presented in Table 4. It can be seen from Table 4 that considering the differences between the migration times of each anion and the reproducibility of the migration

Table 6

Regression equations between peak area (A , μVs) and anion concentration (C , ppm)

Anion	Regression equation	Correlation coefficient
Bromide	$A = 178C + 15$	0.9998
Nitrite	$A = 1682C + 858$	0.9998
Nitrate	$A = 1589C + 808$	0.9997
Iodide	$A = 967C - 205$	0.9816
Thiocyanate	$A = 1324C + 965$	0.9999

time of each anion, it was feasible to identify a peak from the migration time when a real sample with unknown concentrations of salts and anions was separated. This is very useful for routine analysis.

As different concentrations of salts in samples could cause different peak heights at a constant concentration of an anion, the simplest approach to achieve accurate quantification by peak height was to use the standard additions calibration technique [16]. However, it was discovered that the peak area for a constant concentration of an anion remained constant regardless of the concentration of salts in the sample, which is demonstrated in Table 5. Although the R.S.D.s of the peak areas in Table 5 was not very low, the data were still acceptable for quantification purposes. Using the average peak area calculated from four values at different concentrations of sodium chloride in the sample (0, 12.5, 50 and 100 mM), regression equations between peak

Table 5

Reproducibility of peak area at different concentrations of sodium chloride in sample (0, 12.5, 50 and 100 mM)

Concentration of anion in sample (mM)	R.S.D. (%)				
	Bromide	Nitrite	Nitrate	Iodide	Thiocyanate
1	— ^a	18.0	20.3	— ^a	— ^a
4	19.9 ^b	11.8	7.2	14.9 ^c	10.3
10	18.8 ^b	5.1	10.8	15.8	11.3
20	9.7	8.2	15.8	7.2	15.4
40	13.5	9.3	11.3	6.6	8.4

^a Not measured because of detection sensitivity limitation.

^b Three values were measured because of detection sensitivity limitation.

^c Two values were measured because of detection sensitivity limitation.

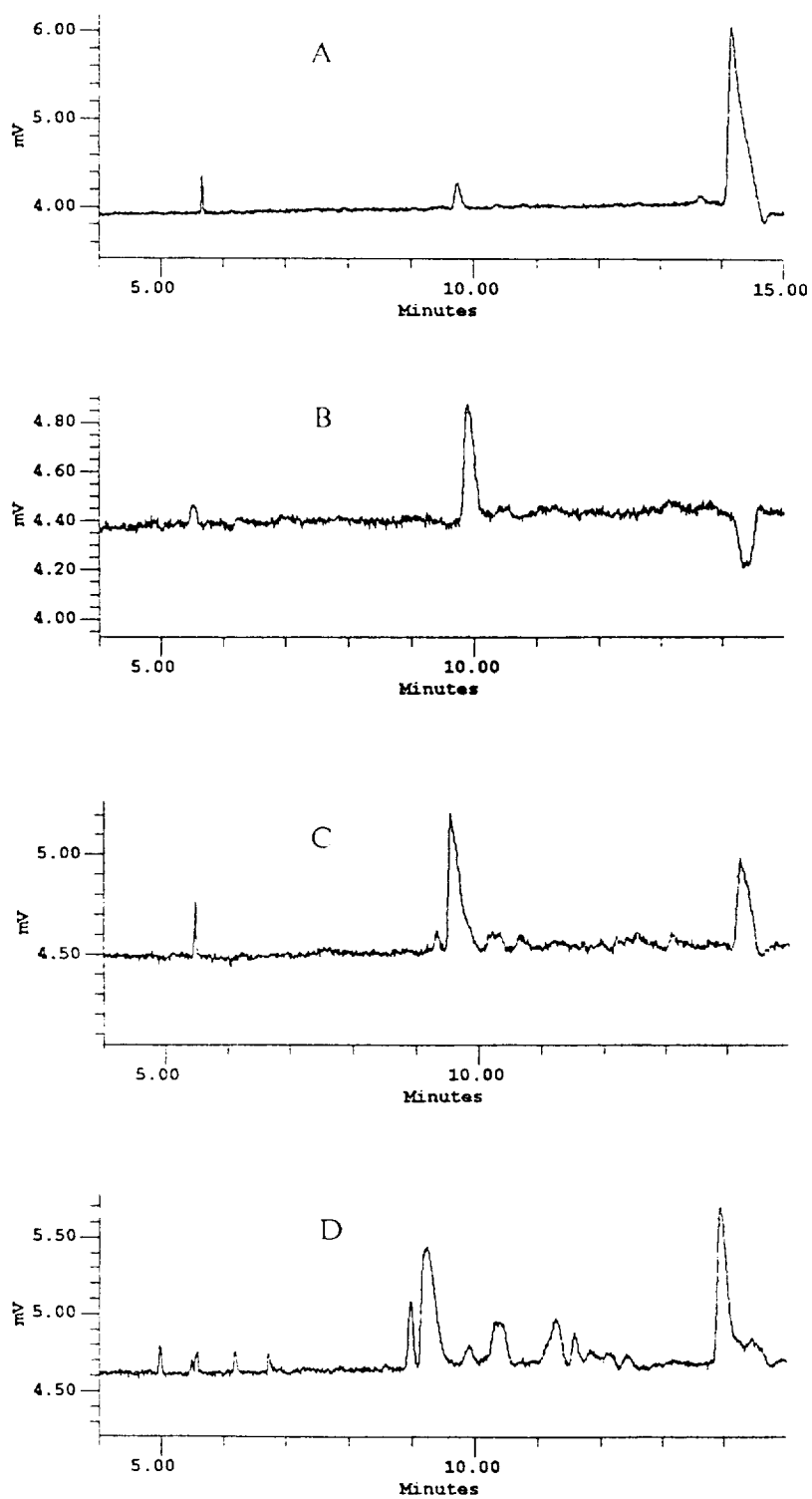


Fig. 2. CIE separations of four subterranean water samples. (A) L8-19; (B) WX3-82; (C) HT1; (D) S13-12.

Table 7
Compositions of four subterranean water samples

Ion	Concentration ^a (mM)			
	L8-19	WX3-82	HT1	S13-12
Na ⁺ K ⁺	11.2	557.3	269.3	57.7
Ca ²⁺	0.7	37.9	2.6	2.1
Mg ²⁺	0.4	2.7	2.1	0.3
Cl ⁻	3.4	619.1	228.7	37.9
SO ₄ ²⁻	3.1	1.6	5.9	0.8
HCO ₃ ⁻	3.7	16.1	36.8	22.8
CO ₃ ²⁻	0.1	0.0	0.7	0.8

^a Determined by titrimetric method.

area and anion concentration were obtained and are given in Table 6. It can be seen from Table 6 that the correlation coefficients of each regression equation were very good. It should be notified that when the concentration of sodium chloride in the sample was 200 mM, a successful separation of anions by using 100 mM sodium chloride solution containing 2.0 mM CTAC as carrier electrolyte solution was also achieved, and the peak area at a constant concentration of an anion remained the same as that when the concentration of sodium chloride in the sample was 0, 12.5, 50 and 100 mM. However, when the concentration of sodium chloride in the sample was 400 mM, the separation deteriorated because too broad peaks of bromide, nitrite and

nitrate caused the resolution to decrease significantly.

A standard additions recovery test was applied to four subterranean water samples, L8-19, WX3-82, HT1 and S13-12. The compositions of the four samples are given in Table 7. CIE separations of these samples are illustrated in Fig. 2, where it can be seen that S13-12 had a more complex composition, leading to many small peaks on its electropherogram. The last peak in the four electropherograms near 15 min was probably caused by water and other neutral compounds. The four subterranean water samples contained nitrate, iodide and thiocyanate, which were determined from the migration times shown in Table 4, and their concentrations were described as the blank concentrations of the three samples and calculated with the equation $C = A/SL$, where C is the concentration, A the area of the peak and SL the slope of the regression equation given in Table 6. Because the linearity range of the regression equation was from 1 to 40 ppm, concentrations lower than 1 ppm were calculated by the above method. After 10 ppm of nitrate, thiocyanate and/or iodide had been added to the four samples, after CIE separation the recoveries of the three anions in the four samples were calculated and are given in Table 8. It can be seen that the recoveries were between 90.8 and 113.4%.

Table 8
Recoveries of nitrate, thiocyanate and/or iodide in four subterranean water samples

Sample	Dilution	Ion	Concentration (ppm)		Recovery (%)
			Blank	Determined	
L8-19	1:2	Nitrate	0.5	11.8	113
		Thiocyanate	0.0	9.1	91
WX3-82	1:5	Nitrate	0.4	10.5	101
		Thiocyanate	0.0	9.4	94
HT1	1:10	Nitrate	0.0	11.1	111
		Thiocyanate	0.0	10.1	101
		Iodide	0.0	10.0	100
S13-12	1:2	Nitrate	0.0	10.6	106
		Thiocyanate	0.6	10.0	93
		Iodide	0.5	10.1	96

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