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# Capillary electrophoresis for measuring major and trace anions in thermal water and condensed-steam samples from hydrothermal springs and fumaroles

E. Santoyo<sup>a,\*</sup>, R. García<sup>b</sup>, R. Abella<sup>b</sup>, A. Aparicio<sup>b</sup>, S.P. Verma<sup>a</sup>

<sup>a</sup>Centro de Investigación en Energía, Universidad Nacional Autónoma de México, Privada Xochicalco s/n, Col. Centro, Apartado Postal 34, Temixco, Mor. 62580, Mexico

<sup>b</sup>Depto. Volcanología, Museo Nacional de Ciencias Naturales (CSIC), José Gutiérrez Abascal, 2, 28006 Madrid, Spain

## Abstract

A new application of capillary electrophoresis for measuring major and trace anions in thermal water and condensed-steam samples is presented. Ten fluid samples were collected from hydrothermal springs and fumaroles located in a volcanic zone of Deception Island, Antarctica. Anion separation was achieved in less than 6 min using indirect UV detection at 254 nm with a negative power supply (−15 kV). The electrolyte consisted of 4.7 mM sodium chromate, 4.0 mM electroosmotic flow modifier (OFM) hydroxide, 10 mM 2-(*N*-cyclohexylamino)ethanesulfonic acid and 0.1 mM calcium gluconate (pH 9.1). Major anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4\text{H}^{2-}$ , and  $\text{CO}_3\text{H}^-$ ) were measured using hydrostatic injection (10 cm for 30 s) at 25°C. Trace amounts of anions ( $\text{F}^-$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$ ) were better determined by electromigration injection (4 kV, 10 s) at 15°C. Good reproducibility of the migration times (<0.72% RSD), a satisfactory linear response and accuracy as well as acceptable detection limits were successfully obtained. © 2001 Published by Elsevier Science B.V.

**Keywords:** Water analysis; Geochemistry; Inorganic anions

## 1. Introduction

The determination of major and minor inorganic ions in geofluids (water or steam) is a fundamental analytical task required to address many diverse questions in Earth science studies [1,2]. Accurate and reliable analytical data of the chemical species present in such samples are essential to understand the physical and chemical processes in geothermal and volcanic systems [2–4]. Reliable geochemical data for studying the temporal evolution of some anion ratios, such as Br/Cl,  $\text{SO}_4/\text{Cl}$  or  $(\text{CO}_3 +$

$\text{HCO}_3)/\text{SO}_4$  are also required for building up helpful geochemical frameworks to monitor hazardous natural events such as volcano eruptions, seismic activities or earthquakes [5,6]. The development of highly sensitive and reliable analytical methods for determining inorganic anions in wide concentration levels is therefore required for any of these geochemical applications.

With the appearance of multi-element ion analysis and time-saving techniques, e.g., ion chromatography (IC), high-performance liquid chromatography (HPLC) or capillary electrophoresis (CE), the separation techniques started to replace the wet-chemical methods as routine analytical methods for major and trace inorganic ions, especially anions in a wide variety of samples (e.g., Refs. [7–9]). In spite of the

\*Corresponding author. Tel.: +52-5-6229-774; fax: +52-5-6229-742.

E-mail address: esg@mazatl.cie.unam.mx (E. Santoyo).

rapid growth of these separation techniques, their application for measuring anionic composition of geofluids has been greatly limited due to the rather complex chemical nature of these samples [1–4,10–11]. IC with electrical conductivity detection is probably the most popular method used for analyzing inorganic anions, in comparison with HPLC and CE [8,12]. A comprehensive book by Haddad and Jackson [8] reported around 50 experimental methodologies based on the development and application of IC for measuring inorganic anions in a wide variety of geological samples: natural waters, rocks, mud cores and volcanic ashes. Unfortunately, only a few IC experiments were oriented to analyze geothermal or volcanic fluids (e.g., Refs. [2,10,11]). Lash and Hill [10] evaluated the IC technique using a coupled electrical conductivity detection system for partially quantifying some anions ( $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $SO_4^{2-}$ ) in around 20 min. This methodology was the subject of additional research by Santoyo et al. [11] who reduced the analysis time to less than 8 min, using a chemical suppressed electrical conductivity detection system for the determination of five anions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ ) in geothermal brines.

Quantitative procedures based on the application of CE for detecting anions have been less developed in comparison with IC [9,12–15]. The first applications dealing with the use of CE for the determination of anions started in the 1980s. Such studies were reviewed comprehensively by Boček and Foret [16] who reported the capabilities of capillary isotachopheresis (ITP) and capillary zone electrophoresis (CZE) for anion separation. In the 1990s, the use of CE for analyzing anions significantly increased (e.g., Refs. [17,18]). At the present time, several reviews dealing with the use of CE to determine anions in miscellaneous applications have been reported (e.g., Refs. [12,19–21]). Doble and Haddad [19] discussed the advantages of the indirect photometric detection for analyzing anions considering factors that influence its sensitivity detection, such as, the background electrolyte (BGE) compositions, the buffering procedures of BGEs, the use of multiple co-ion electrolytes, and others.

In spite of the accelerated growth of CE in analyzing inorganic anions in a wide variety of samples, CE methodologies for quantifying the com-

position of geothermal and volcanic fluids are rarely found. The complex chemical nature of these fluids requires specific CE methodologies to be developed. Therefore, additional laboratory work must be carried out to develop CE methodologies and to promote new applications of CE in the Earth sciences. The aim of this paper is to present a new CE application for measuring major and trace inorganic anions in water and condensed-steam volcanic samples. In order to increase the detection sensitivity, capillary temperature and different injection modes (hydrostatic and electromigration) were investigated for measuring some anions at trace levels of concentration.

## 2. Experimental

### 2.1. Capillary electrophoresis instrumentation

A Quanta 4000 capillary electrophoresis instrument (Waters, Milford, MA, USA) coupled with a negative power supply and an indirect UV detection system was used for all separations. The separation voltage applied was  $-15$  kV. The UV detection system was set at a wavelength of 254 nm using a mercury lamp. Data acquisition and instrument control were carried out using Waters 820 Workstation. CE data were recorded at 20 points per second (using Millennium 2000 software). The separations were carried out using a conventional fused-silica capillary (60 cm  $\times$  75  $\mu$ m I.D.). Most of the CE analyses were carried out at 25°C. However, for increasing the detection sensitivity of some trace anions, a change in the capillary temperature to 15°C was performed. Samples were introduced either by hydrostatic or electromigration injection mode. Hydrostatic injection (10 cm for 30 s) at 25°C was used for introducing samples with a high anion concentration. Electromigration injection at 15°C was used for analyzing trace anions. Before initiating the tests, the instrument was set in operation for 10 min with 0.1 M sodium hydroxide (0.4 g NaOH per 100 ml Milli-Q water) followed by 10 min with a flush with Milli-Q water and stabilizing by another flush period of 10 min with the working electrolyte solution. Before each analysis, the capillary column was

equilibrated with the running electrolyte for 10 min and rinsed for 2 min with Milli-Q water.

## 2.2. Chemical reagents and procedures

Standard solutions were prepared using Milli-Q water (18 m $\Omega$  cm) produced from a purification system (Millipore, Barcelona, Spain). All chemicals were of analytical-reagent grade. The working electrolyte consisted of a mixture of 4.7 mM sodium chromate, 4.0 mM OFM hydroxide, 10 mM 2 (*N*-cyclohexylamino)ethanesulfonic acid (CHES) and 0.1 mM calcium gluconate, pH 9.1 (Waters). Anion stock solutions containing 1000 mg l<sup>-1</sup> were prepared from sodium or potassium salts using standard procedures recommended by the ASTM [22]. Standard working solutions were prepared weekly by diluting the stock solutions with Milli-Q water. Fresh working electrolyte was daily prepared, filtered through a 0.45- $\mu$ m pore size membrane filter (Millipore) and degassed with a vacuum system prior to use.

## 2.3. Sample collection and handling

Ten fluid samples were collected from thermal springs and fumaroles located in a volcanic zone of Deception Island, Antarctica [23]. Six samples were condensed-steam type and the remaining corresponded to thermal waters. All samples were pre-filtered and stored in polypropylene containers (volume 125 ml; previously cleaned with diluted HNO<sub>3</sub> and washed five times with Milli-Q water to prevent any background contamination) following standard sampling procedures suggested for sampling geothermal fluids and recommended for both anion and cation determinations [24]. All samples stored at ~5°C were filtered once more through a filter-membrane (0.2  $\mu$ m) before injection into the CE system to avoid any fouling problem.

## 3. Results and discussion

### 3.1. Electrolyte selection

According to the ionic mobilities, p*K* values and the UV absorptivity, many electrolyte solutions con-

taining sodium chromate as a carrier electrolyte for indirect absorbance detection have been identified as the most suitable electrolytes for determining inorganic anions (e.g., Refs. [13,20,21]). Three electrolytes based on sodium chromate are essentially recommended: (A) 4.6 mM sodium chromate and 0.46 mM CIA-Pak OFM Anion BT, pH 8.1; (B) 4.0 mM sodium chromate, 0.3 mM CIA-Pak OFM Anion BT and 0.16 mM sodium tungstate, pH 8.0 and (C) 4.7 mM sodium chromate, 4.0 mM OFM hydroxide, 10 mM CHES and 0.1 mM calcium gluconate, pH 9.1. A preliminary CE test for choosing the most appropriate electrolyte to be used in this experimental work was performed. Electrolytes A and B provided a very similar separation pattern with an average time of analysis of ~3.5 min (Fig. 1a). When electrolyte C was used the analysis time was increased up to ~6 min. A change in the electrophoretic mobilities of Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>2</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> was also observed (Fig. 1b). Such differences enabled Cl<sup>-</sup> and NO<sub>2</sub><sup>-</sup> ions to migrate before Br<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, respectively. These new mobilities offer an advantage for analyzing geofluids because it is very likely that some of these samples have a high concentration of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. Thus, the migration sequence obtained with electrolyte C would be more suitable for avoiding co-migration problems of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> with their respective neighbor ions. According to these results and considering the satisfactory detection sensitivity, electrolyte C was selected for use in all the experimental work.

### 3.2. Separation of anions

Separation of an eight-anion standard (A-1) by CE consisting of inorganic anions (Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub>H<sup>2-</sup>, and CO<sub>3</sub>H<sup>-</sup>) with a similar concentration level of 5 mg l<sup>-1</sup> (except the carbonate ion: 10 mg l<sup>-1</sup>) was carried out (Fig. 1b). The separation of the anions was well resolved within ~6 min. Symmetrical peak shapes of most anions were obtained, except for the carbonate asymmetrical peak which shows a slight tail. Such a problem is probably attributed to the electrostacking condition which could be present in hydrostatic injections, because the ionic strength of the samples is probably lower than the carrier electrolyte.

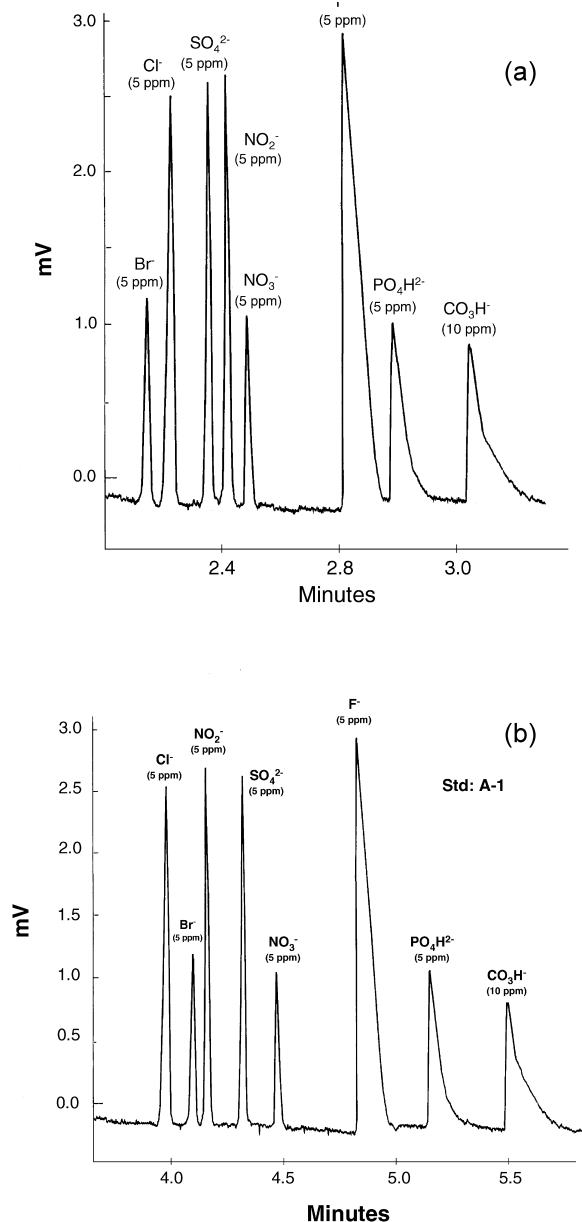


Fig. 1. (a) Electropherogram of a separation pattern of eight inorganic anions. Indirect UV detection at 254 nm (Hg lamp). BGE, 4.6 mM sodium chromate and 0.46 mM CIA-Pak OFM Anion BT, pH 8.1. Capillary temperature, 25°C; separation voltage, -20 kV; and a hydrostatic injection (10 cm height for 30 s) of a standard anion solution A-1. (b) Separation of inorganic anions by CE with indirect UV detection at 254 nm (Hg lamp). The electrolyte was 4.7 mM sodium chromate, 4.0 mM OFM hydroxide, 10 mM CHES and 0.1 mM calcium gluconate (pH 9.1). Capillary temperature, 25°C; separation voltage, -15 kV; hydrostatic injection of a standard solution A-1. Other operating conditions are summarized in Section 2.1.

Romano and Krol [13] pointed out that the presence of an asymmetrical peak is strongly attributed to the excessive amount of carbonate contained either in standards or samples.

### 3.3. Reproducibility of the CE method, linearity, accuracy and limits of detection

Reproducibility tests based on eight injections of an eight-anion standard (A-12) consisting of Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub>H<sup>2-</sup> and CO<sub>3</sub>H<sup>-</sup> were performed. Reproducibility data of NO<sub>2</sub><sup>-</sup> were not estimated since it is not expected to be present in geological samples. Reproducibilities of migration times, peak areas and peak heights were estimated using standard A-12 with a hydrostatic injection at 25°C (Table 1). The relative standard deviations (RSDs) of migration times, peak areas and peak heights were less than 0.72, 3.7 and 2.8%, respectively. Six concentration levels of each anion and five replicates of each concentration level were used for evaluating the linearity response (Table 2).

The accuracy of analyses was determined from the y-intercept of a linearity plot (containing an external standard with known concentration) according to a well-established statistical method suggested by Kuhn and Hoffstetter-Kuhn [25]. In all anion plots, the origin of the axis was found within a 95% confidence interval which indicated that the accuracy of the method was rather satisfactory.

The limit of detection (LOD) of each anion, defined as the detectable concentration of an anion giving a peak three-times as high as the background noise (*N*) was also calculated (Cl<sup>-</sup>: 0.125 mg l<sup>-1</sup>;

Table 1

Reproducibility tests based on eight injections of a standard mixture of anions (A-12)

Inorganic anion	RSD (%)		
	Migration time	Peak area	Peak height
Cl <sup>-</sup>	0.521	1.501	0.892
Br <sup>-</sup>	0.689	3.010	1.257
SO <sub>4</sub> <sup>2-</sup>	0.589	1.743	0.920
NO <sub>3</sub> <sup>-</sup>	0.623	3.020	2.270
F <sup>-</sup>	0.653	1.504	2.750
PO <sub>4</sub> H <sup>2-</sup>	0.718	3.698	1.853
CO <sub>3</sub> H <sup>-</sup>	0.701	1.160	1.900

Table 2

Results of the linearity evaluation using anion standards with six concentration levels and five replicates

Anion	Migration time (RSD, %)	Concentration range (mg l <sup>-1</sup> )	Linearity	r <sup>2</sup>
Cl <sup>-</sup>	0.521	5–80	y=627.4x+279.1	0.999
Br <sup>-</sup>	0.689	0.1–0.5	y=9223.4x–14.4	0.935
SO <sub>4</sub> <sup>2-</sup>	0.589	2–80	y=537.8x+312.4	0.998
NO <sub>3</sub> <sup>-</sup>	0.623	1–40	y=451.2x+238.3	0.996
F <sup>-</sup>	0.653	2–80	y=2085.2x+176.0	0.999
PO <sub>4</sub> H <sup>2-</sup>	0.718	1–12	y=824.9x–95.7	0.996
CO <sub>3</sub> H <sup>-</sup>	0.701	10–80	y=420.6x+907.8	0.999

Br<sup>-</sup>: 0.15 mg l<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup>: 0.125 mg l<sup>-1</sup>; NO<sub>3</sub><sup>-</sup>: 0.125 mg l<sup>-1</sup>; F<sup>-</sup>: 0.060 mg l<sup>-1</sup>; PO<sub>4</sub>H<sup>2-</sup>: 0.15 mg l<sup>-1</sup>; and CO<sub>3</sub>H<sup>-</sup>: 0.325 mg l<sup>-1</sup>). Such LODs were determined by successive dilution of a standard solution. Although, the LODs achieved with the present CE methodology were slightly high, they were rather suitable for most of the analyzed samples. Further optimization of LODs was only required for some samples with very low concentrations of Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, for which electromigration injection mode was used to increase the sensitivity of the technique.

### 3.4. Quantitative analysis of thermal water and condensed-steam samples

Four thermal water samples (B-2, B-3, B-4, and B-5) and six condensed-steam samples (B-11, B-13, B-14, B-15, B-16, and B-17) were analyzed. In order to avoid a possible overloading effect of the ion zone as well as some co-migration problems, after each sample injection the capillary was rinsed for 2 min with Milli-Q water and then for 2 min with electrolyte solution. Figs. 2 and 3 present two electropherograms showing the anion separation obtained in the CE analysis of the samples B-3 and B-15, respectively.

An efficient separation of the anion peaks was clearly achieved. Anion composition of these samples was chemically characterized by moderate concentrations of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub>H<sup>-</sup>. Very low concentrations of Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and F<sup>-</sup> were also detected in some samples. NO<sub>2</sub><sup>-</sup> and PO<sub>4</sub>H<sup>2-</sup> anions were not found in any sample. The concentration of the major anions was calculated as the mean value from three injections, the precision errors were less

than 1.8, 3.1 and 1.3% for Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub>H<sup>-</sup>, respectively.

A quantitative analysis was carried out by use of appropriate calibration curves for each anion detected. The analyzed samples showed a wide concentration range of Cl<sup>-</sup> (7.0–148 mg l<sup>-1</sup>), SO<sub>4</sub><sup>2-</sup> (1.97–42.6 mg l<sup>-1</sup>), F<sup>-</sup> (0.060–0.0171 mg l<sup>-1</sup>) and CO<sub>3</sub>H<sup>-</sup> (12.6–93.1 mg l<sup>-1</sup>) in Table 3.

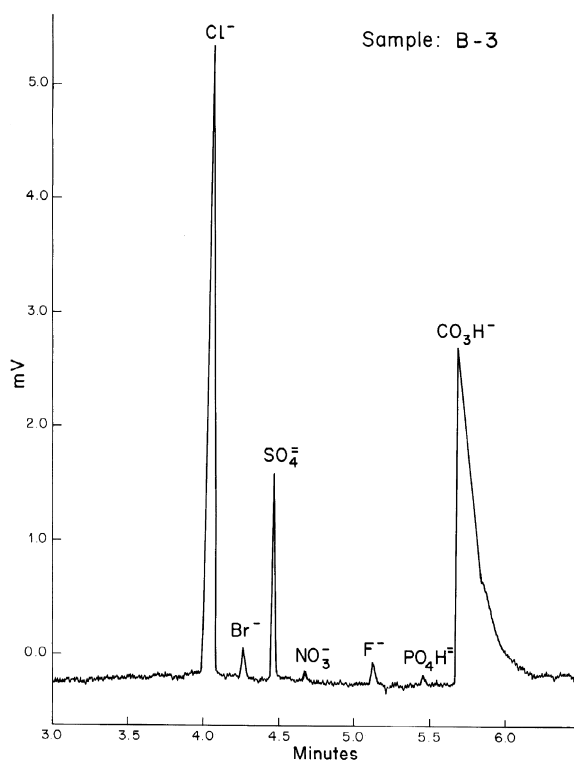


Fig. 2. Electropherogram of the thermal water sample: B-3. CE operating conditions are summarized in Fig. 1b.

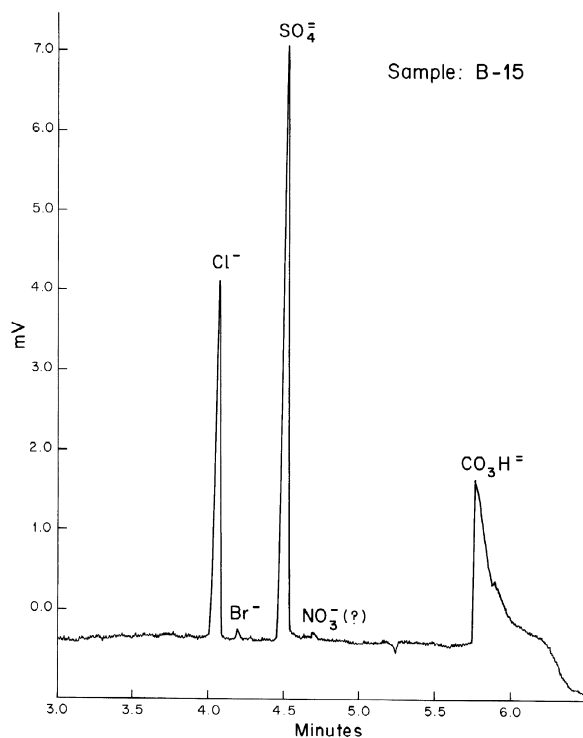


Fig. 3. Electropherogram of the condensed-steam sample: B-15. CE operating conditions are summarized in Fig. 1b.

### 3.5. Influence of injection mode on the bromide and nitrate analysis

Small peaks of Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and F<sup>-</sup> were poorly detected in samples B-3 and B-15 (Figs. 2 and 3) when they were introduced by hydrostatic injection at 25°C. These CE signals could easily be reported below their LODs. However, in order to provide a

better quantification of these trace anions, an improvement in the technique was implemented. Electromigration injection (often also called electrokinetic injection) was investigated for solving these detection problems. Although, electromigration mode is a controversial sampling technique, it is highly recommended for increasing the detection sensitivity even at the loss of the precision and accuracy of CE [21].

In order to avoid some co-migration problems, effects of capillary temperature were also explored. Capillary temperature has been identified as a highly effective parameter for enhancing the separation efficiency of ions during CE analyses [4,26]. On the basis of this capability, the trace analyses were performed using a capillary temperature of 15°C. Fig. 4a and b present two simplified electropherograms showing the effects of the hydrostatic and electromigration injection modes on both the anion separation and detection of sample B-15 at 15°C. An amplification of the voltage scale from 0.0 to 1.4 mV was used for a better analysis of the results.

The effect of capillary temperature on the separation of Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> using the hydrostatic injection mode is also shown in Fig. 4a. The separation of these four anions was achieved in less than 4.8 min, a slightly longer time than the separation time recorded at 25°C (4.6 min: Fig. 3). Concerning the detection sensitivity, Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> peaks again exhibited almost the same voltage response (less than 0.15 mV) like the CE results obtained at 25°C (Fig. 3).

A notable increase in the detection sensitivity was obtained when the electromigration mode (4 kV, 10

Table 3

Capillary electrophoresis results obtained during the analysis of inorganic anions in thermal water and condensed-steam samples collected in the volcanic zone of Deception Island, Antarctica

Anion	Anion concentration ( $\pm\sigma_c$ ) (mg l <sup>-1</sup> )									
	B-2	B-3	B-4	B-5	B-11	B-13	B-14	B-15	B-16	B-17
Cl <sup>-</sup>	31.3 ( $\pm 0.5$ )	16.8 ( $\pm 0.3$ )	50.9 ( $\pm 0.7$ )	73.0 ( $\pm 1.1$ )	148.0 ( $\pm 2.2$ )	14.3 ( $\pm 0.2$ )	25.9 ( $\pm 0.4$ )	10.3 ( $\pm 0.2$ )	7.0 ( $\pm 0.1$ )	21.1 ( $\pm 0.3$ )
SO <sub>4</sub> <sup>2-</sup>	8.9 ( $\pm 0.2$ )	3.24 ( $\pm 0.06$ )	13.6 ( $\pm 0.2$ )	42.6 ( $\pm 0.7$ )	21.0 ( $\pm 0.4$ )	2.89 ( $\pm 0.05$ )	3.56 ( $\pm 0.06$ )	12.8 ( $\pm 0.4$ )	1.97 ( $\pm 0.03$ )	4.6 ( $\pm 0.1$ )
Br <sup>-</sup> <sup>a</sup>	n.d.	0.125 ( $\pm 0.004$ )	n.d.	n.d.	n.d.	n.d.	n.d.	0.105 ( $\pm 0.003$ )	n.d.	n.d.
NO <sub>3</sub> <sup>-</sup> <sup>a</sup>	0.98 ( $\pm 0.03$ )	0.105 ( $\pm 0.003$ )	n.d.	n.d.	n.d.	n.d.	n.d.	0.101 ( $\pm 0.003$ )	n.d.	n.d.
F <sup>-</sup>	0.171 ( $\pm 0.003$ )	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.060 ( $\pm 0.001$ )	0.11 ( $\pm 0.002$ )
CO <sub>3</sub> H <sup>-</sup>	93.1 ( $\pm 1.1$ )	37.7 ( $\pm 0.4$ )	n.d.	83.7 ( $\pm 1.0$ )	12.6 ( $\pm 0.1$ )	48.3 ( $\pm 0.6$ )	60.4 ( $\pm 0.7$ )	25.1 ( $\pm 0.2$ )	61.8 ( $\pm 0.7$ )	20.1 ( $\pm 0.2$ )

<sup>a</sup>CE analyses carried out with an electromigration injection mode; <LOD=below the limit of detection; n.d.=not detected;  $\sigma_c$ =concentration error.

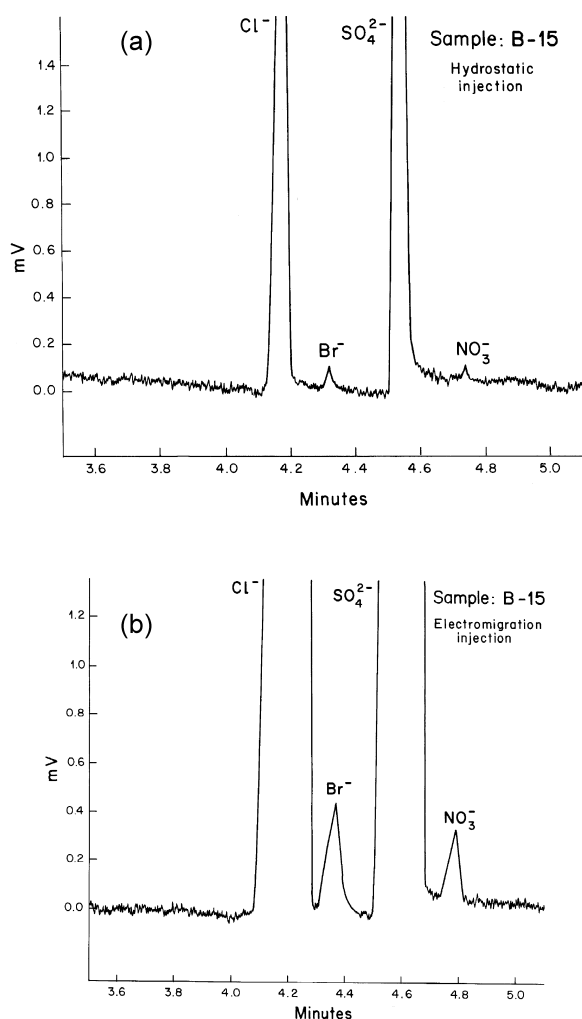


Fig. 4. (a) Part of an electrochromatogram of the condensed-steam sample (B-15) obtained at a capillary temperature of 15°C and using a hydrostatic injection (10 cm for 30 s). Other operating conditions are summarized in Fig. 1b. (b) Part of an electrochromatogram of the condensed-steam sample (B-15) obtained at a capillary temperature of 15°C and using an electromigration injection (4 kV, 10 s). BGE composition and other operating conditions are summarized in Fig. 1b. Note  $\text{Br}^-$  and  $\text{NO}_3^-$  peaks are better detected.

s) was used for injecting the sample (see Fig. 4b). Using this injection mode,  $\text{Br}^-$  and  $\text{NO}_3^-$  peaks exhibited a better sensitivity (less than 0.4 mV) for their quantification using an appropriate calibration curve (0.1 to 0.3 mg l<sup>-1</sup>;  $r=0.89$ ,  $n=6$ ). The effect of capillary temperature on the separation time for the four anions was the same (<4.8 min). Such

results clearly show that the electromigration injection coupled with a capillary temperature of 15°C is most suited for a better determination of inorganic anions at trace levels of concentration. Under such CE conditions, low concentration ranges of  $\text{Br}^-$  (0.105–0.125 mg l<sup>-1</sup>) and  $\text{NO}_3^-$  (0.105–0.125 mg l<sup>-1</sup>) were successfully measured in some samples (See Table 3).

#### 4. Conclusions

A new application of CE for determining inorganic anions in geological samples has been demonstrated. An electrolyte consisted of 4.7 mM sodium chromate, 4.0 mM OFM hydroxide, 10 mM CHES and 0.1 mM calcium gluconate (pH 9.1) was found suitable for detecting anions. Major anions in thermal waters and condensed-steam samples, using hydrostatic injection at 25°C, were successfully measured. An optimized separation of all anions in less than 6 min was achieved. Electromigration injection (4 kV, 10 s) at 15°C was an appropriate method for increasing the sensitivity and to measure anions at trace concentration levels. Clearly, the CE technique is becoming a valuable quantitative technique to determine major and trace anions in a wide range of geological samples. Shortly, it will become a reliable analytical method to be used frequently in any Earth science application.

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