

## Evaluation of capillary electrophoresis for determining the concentration of dissolved silica in geothermal brines

E. Santoyo<sup>a,\*</sup>, R. García<sup>b</sup>, A. Aparicio<sup>b</sup>, Surendra P. Verma<sup>a</sup>, M.P. Verma<sup>c</sup>

<sup>a</sup> *Centro de Investigación en Energía, Universidad Nacional Autónoma de México, Priv. Xochicalco s/no., 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*

<sup>c</sup> *Unidad de Geotermia, Instituto de Investigaciones Eléctricas, Apdo. Postal 1-475, Cuernavaca, Morelos 62001, México*

### Abstract

The determination of silica concentrations in geothermal brines is widely recognized as a difficult analytical task due to its complex chemical polymerization kinetics that occurs during sample collection and chemical analysis. Capillary electrophoresis (CE) has been evaluated as a new reliable analytical method to measure silica (as silicates) in geothermal brines. Synthetic and geothermal brine samples were used to evaluate CE methodology. A capillary electrophoresis instrument, Quanta 4000 (Waters–Millipore) coupled with a Waters 820 workstation was used to carry out the experimental work. The separation of silicates was completed in  $\sim 5.5$  min using a conventional fused-silica capillary ( $75 \mu\text{m}$  i.d.  $\times 375 \mu\text{m}$  o.d.  $\times 60$  cm total length). A hydrostatic injection (10 cm for 20 s at  $25^\circ\text{C}$ ) was employed for introducing the samples. The carrier electrolyte consisted of 10 mM sodium chromate, 3 mM tetradecyltrimethyl-ammonium hydroxide (TTAOH), 2 mM sodium carbonate, and 1 mM sodium hydroxide, adjusted to a pH  $11.0 \pm 0.1$ . Silicates were determined using an indirect UV detection at a wavelength of 254 nm with a mercury lamp and with a negative power supply ( $-15$  kV). A good reproducibility in the migration times (%R.S.D.  $\sim 1.6\%$ ) based on six non-consecutive injections of synthetic brine solutions was obtained. A linear response between silica concentration and corrected peak area was observed. Ordinary (OLR) and weighted (WLR) linear regression models were used for calculating silica concentrations in all samples using the corresponding fitted calibration curves. The analytical results of CE were finally compared with the most probable values of synthetic reference standards of silica using the Student's *t*-test. No significant differences were found between them at  $P = 0.01$ . Similarly, the atomic absorption spectrometry (AAS) results were also compared with the most probable concentrations of the same reference standards, finding significant differences at  $P = 0.01$ .

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Hydrothermal waters; Separation methods; Silica scaling; Geochemistry; Silicates; Linear regression

### 1. Introduction

Silica is one of the major components of the Earth's crust [1]. The processes of water–rock interaction that occur inside deep geothermal reservoirs produce hot saline fluids or brines [2]. These brines normally have temperatures between  $250$  and  $300^\circ\text{C}$ , and contain significant amounts of dissolved silica as orthosilicic acid ( $\text{H}_4\text{SiO}_4^\circ$ ) among other components [3]. The brines usually become supersaturated

with  $\text{H}_4\text{SiO}_4^\circ$  as a result of temperature changes that occur inside geothermal wells or reservoirs [3]. At hydrothermal conditions,  $\text{H}_4\text{SiO}_4^\circ$  polymerizes to form siloxane bonds and undergoes partial dehydration [ $\text{Si}_2\text{O}(\text{OH})_6$ ]. With the size increase of these polymers, colloidal silica particles ( $>5$  nm) are mainly formed by homogeneous nucleation, which can form large solid scales of amorphous silica ( $\text{SiO}_2$ ) after flocculation or coagulation processes [1,4]. These deposits represent a serious problem for the operation of geothermal power plants [2,3]. The knowledge of silica chemistry is essential for the geothermal industry not only for preventing silica scaling problems during production and reinjection of brines but also to compute deep reservoir temperatures [5]. This

\* Corresponding author. Tel.: +52 (55) 56229774; fax: +52 (55) 56229791.

E-mail address: [esg@cie.unam.mx](mailto:esg@cie.unam.mx) (E. Santoyo).

knowledge is generally obtained from chemical analyses of silica carried out in geothermal brines [6,7]. The availability of reliable analytical techniques and the strict quality control of these analyses are therefore crucial for a better understanding of the above geochemical processes [6]. From the analytical point of view, silica species may be grouped into two categories [8]. The first includes silica reactive species, such as orthosilicic acid ( $\text{H}_4\text{SiO}_4^\ominus$ ) or low polymerized silicates (e.g.,  $\text{H}_6\text{Si}_2\text{O}_7$ ). The second contains complex polymers (i.e., colloidal particles), which require some chemical pre-treatment for their conversion into chemical reactive species [9,10].

The colorimetry technique (CO) has been traditionally used for the analysis of reactive silica in a wide variety of matrices [1]. These procedures involve the formation of colored silicomolybdate complexes (yellow or blue), which are typically used to determine molybdate-reactive silica at low concentrations [10,11]. These methods are recognized as time-consuming techniques because they are very slow, tedious, and subject to many interferences. The determination of total and dissolved silica in aqueous samples has also been performed using atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), and electrothermal atomic absorption spectrometry (ETAAS) [1,6,8,12]. Other analytical techniques for measuring silica include ion chromatography (IC) [13–16], ICP-atomic emission spectrometry (ICP-AES) [6,17], and ICP-mass spectrometry (ICP-MS) [6,18]. IC methods based on UV–vis detection after a post-column reaction have been commonly used to analyze soluble silica in the form of molybdate-reactive orthosilicic acid [14]. Other IC procedures for analyzing silicates include conductivity measurements as fluorosilicates [13,15,16].

Ion exclusion chromatography (IEC) in combination with ICP-MS has been also proposed for a direct determination of dissolved silica [18]. In this method, ICP is considered as a suitable source for the measurement of total silica (reactive and polymeric), since it enables the colloidal particles to be destroyed in the plasma and quantified along with the reactive species [19]. Although numerous techniques have been successfully employed for the determination of silica in a wide variety of matrices, the analysis of geothermal brines still faces problems with the sampling and analytical procedures, which have limited its precision and accuracy [6,7]. Such problems are generally related to the silica polymerization and precipitation, as well as to the high concentrations present in these samples [1,2]. Verma et al. [6] carried out a comprehensive inter-laboratory study to evaluate most of the available techniques for determining silica in geothermal waters. In this study, it was recognized that the analysis of silica is a difficult task that involves large analytical errors in most of the methods used by international geochemistry laboratories. Taking into account such problems, new techniques for analyzing geothermal brines with a high concentration of silica are therefore

required and still represent an analytical challenge to be achieved.

Capillary electrophoresis (CE) has emerged as a viable method for the determination of inorganic anions in an extensive diversity of matrices [20]. Several reviews dealing with the application of CE for measuring anions have been reported in the literature (e.g. [21,22]). However, the use of CE for analyzing geological matrices (such as hydrothermal waters) has been seldom reported (e.g. [23]). Moreover, the analysis of silica or silicates by CE in this type of matrices has not been explored yet. On the basis of a comprehensive literature survey, the unique application for determining silica by CE was conducted by Barciela-Alonso and Prego, who proposed to use an indirect detection by UV–vis (at 254 nm) for the analysis of low concentrations of silicates in river waters [24]. These authors pointed out that the analysis of silicates in saline samples could present some problems due to matrix interferences caused by the high content of chlorides. However, such problems were not actually evaluated in their study and no electropherograms were presented supporting this statement.

In the present CE study, we have focused on the analysis of geothermal brines with a moderate salinity. Even though the chloride compositions in these matrices can range from 100 up to 3000  $\text{mg L}^{-1}$ , depending on the geological site where the wells are drilled, as well as the prevailing water–rock interaction processes [2].

In this work, the CE methodology proposed by Barciela-Alonso and Prego [24] has been the subject of additional research for measuring silica (as silicates) in geothermal brines. The suitability of this new application of the CE (in terms of the electrolyte composition, separation, detection, precision, and accuracy), the evaluation of interferences, and the optimization of the migration time were defined as objectives for determining the optimum analytical conditions. The analytical results of CE were finally compared with the most probable values of synthetic reference standards of silica using Student's *t*-test. Similarly, the atomic absorption spectrometry (AAS) results were also compared with the most probable concentrations of the same reference standards. Details of this comparative analysis are also outlined.

## 2. Experimental

### 2.1. Capillary electrophoresis instrumentation

A Quanta 4000 CE instrument (Waters, Millford, MA, USA) coupled with a negative power supply and an indirect UV detection system was used for the analyses. The separation voltage applied was  $-15 \text{ kV}$  (under such operating conditions a current of  $40 \pm 1 \mu\text{A}$  was typically measured). The UV detection system was set at a wavelength of 254 nm using a mercury lamp. Data acquisition and the instrument operation were controlled with a Waters 820 Workstation. CE analytical data were recorded at a transfer rate of 20 points per

Table 1

Comparison of results obtained for the determination of silica in synthetic reference standards and actual geothermal brines using CE and AAS techniques

Synthetic reference std.	Concentration <sup>a</sup> (mg L <sup>-1</sup> )	OLR silica concentration (mg L <sup>-1</sup> )		WLR silica concentration (mg L <sup>-1</sup> )	
		CE	AAS	CE	AAS
M-1	109 ± 14	110 ± 2	98 ± 3	113 ± 1	96 ± 1
M-2	222 ± 18	227 ± 5	190 ± 5	229 ± 3	180 ± 3
M-3	1164 ± 180	1106 ± 18	960 ± 20	1139 ± 12	914 ± 22
M-4	2060 ± 340	2400 ± 60	1920 ± 60	2438 ± 27	1827 ± 41
Sample					
M-5	–	825 ± 14	790 ± 23	843 ± 7	756 ± 16
M-6	–	826 ± 15	805 ± 26	844 ± 8	817 ± 19

<sup>a</sup> The most probable concentration values compiled from an inter-laboratory calibration study [6]. Standard deviation errors of concentration data were computed using error propagation equations [30].

second using the Millennium 2000 software. The separation of silicates was carried out using a conventional fused-silica capillary (75 µm i.d. × 375 µm o.d. × 60 cm total length) with the detection window placed 7.5 cm from the receiving electrolyte end to the detector cell. The capillary was maintained at a temperature of 25 °C. All samples were introduced into the capillary by a hydrostatic injection (elevating the sample 10 cm for 20 s). Before initiating the tests, the CE equipment was set in operation for 10 min with sodium hydroxide 0.1 N (0.4 g NaOH per 100 mL Milli-Q water) followed by 15 min with a flush with Milli-Q water (for thermal equilibration) and stabilizing by another flush period of 15 min with the working electrolyte. The capillary was rinsed for 3 min with Milli-Q water between measurements for preventing plugging problems.

## 2.2. Chemical reagents and procedures

Standard and electrolyte solutions were prepared with Milli-Q water (with a specific resistivity of 18 MΩ cm), which was produced by a deionized water purification unit (Millipore, Barcelona, Spain). All chemicals were of analytical-reagent grade. The working electrolyte consisted of a mixture of 10 mM sodium chromate, 3 mM tetradecyltrimethyl-ammonium hydroxide (TTAOH; Waters, Millford, MA, USA), 2 mM sodium carbonate, and 1 mM sodium hydroxide, adjusted to a pH 11.0 ± 0.1. Fresh working electrolyte was daily prepared, filtered through a 0.2 µm pore size membrane filter (Millipore, USA), and degassed with a vacuum system prior to use.

Silica stock solutions containing 1000 mg L<sup>-1</sup> (±1%) were prepared using a certified standard of sodium silicate (Fischer Scientific Company, USA). Standard working solutions for CE analyses (ranging from 5 to 80 mg L<sup>-1</sup>) were also prepared by successive dilution of the stock standard solution with Milli-Q water. All standards and electrolytes were prepared and stored in polypropylene containers (volumetric flasks and bottles) for avoiding contamination because it is well known that analytical errors in silica analyses can be attributed to storing water and standards in glass containers [25].

## 2.3. Sample collection and handling

Four synthetic reference standards (SRS; M-1, M-2, M-3, and M-4) were used as suitable samples for evaluating the accuracy of the CE method. The SRS solutions were prepared for an inter-laboratory calibration survey by dissolving silicate minerals in alkaline solutions [6]. The sole purpose of this study [6] was to evaluate the quality of silica analyses in geothermal matrices. The SRS contained silica concentrations typically present in actual geothermal brines but without the presence of other anions that could interfere with the silica analysis. The most probable concentration values of silica in these standards (inferred from the inter-laboratory calibrations) are summarized in Table 1. For avoiding silica precipitation, the SRS were substantially undersaturated at room temperature (pH >9), which means that their concentrations were stable for transportation and storage.

Two actual geothermal brine samples (M-5 and M-6) were simultaneously collected from the same well (H-1) drilled in the Los Humeros geothermal field, Mexico [26] to evaluate the effect of acidification on the sampling technique [2]. Thus, these samples were used for evaluating the silica analysis capability of CE as well as to assess the effects of the sampling techniques. The collection of geothermal brines for silica analysis generally requires a previous acidification of the samples for maintaining all the silica in solution (i.e., for avoiding silica precipitation when the sample cools down to room temperatures) [2]. The first geothermal sample (M-5) was directly collected (500 mL) from the well and filtered without any acidification. The second sample (M-6) was filtered and acidified using a few drops of diluted HCl (1:1) to pH <3 to help preserve silica in solution. These geothermal samples were stored in polypropylene bottles (vol. 125 mL; previously cleaned with diluted HNO<sub>3</sub> and five times washed with Milli-Q water to prevent any background contamination) following standard sampling procedures suggested for geothermal fluids [2,7]. In the laboratory, all samples were kept at ~5 °C and again filtered through a filter-membrane (0.2 µm) before injection into the CE instrument to prevent any fouling problem.

### 3. Results and discussion

#### 3.1. Electrolyte selection, separation and detection

The physicochemical properties that exhibit the silicates as anions, such as the apparent mobility, the dissociation constant ( $pK_a$  9.8 for a  $pH > 9$ , or full ionization at a  $pH > 10.5$ ), and the UV absorptivity have enabled that sodium chromate solutions be suggested as suitable electrolytes for measuring silicates as anions [24]. The UV absorbance of the electrolyte is supplied by the chromophoric ion of chromate, while the non-absorbing species are detected by light absorption changes due to a displacement of the absorbing co-ion. Electrolytes based on different compositions of sodium chromate (with an ionic strength that ranges from 5 to 10 mM) mixed with some cationic surfactants (or electroosmotic flow modifiers: OFM) have been suggested to improve the detection and analysis time of some inorganic anions [20]. Cetyltrimethyl-ammonium bromide (CTAB), tetradecyltrimethyl-ammonium bromide (TTAB), hexadecyltrimethyl-ammonium bromide (HTAB), and tetradecyltrimethyl-ammonium hydroxide (TTAOH) have been commonly recommended for applications that require the electroosmotic flow to be modified [24,27].

For the analysis of silicate species, TTAB has been successfully used for reversing the direction of the electroosmotic flow, as well as to increase the migration velocity [24]. A nearly constant behavior of TTAB concentration on the apparent mobility of silicates was observed for concentrations ranging from 0.2 to 0.6 mM [24]. In the present experimental work, two electrolytes based on different sodium chromate compositions were evaluated: (A) 5 mM sodium chromate and an electroosmotic flow modifier (0.2 mM TTAB) adjusted to a  $pH 11.0 \pm 0.1$ ; and (B) 10 mM sodium chromate, 3 mM TTAOH, 2 mM sodium carbonate, and 1 mM sodium hydroxide, also adjusted to a  $pH 11.0 \pm 0.1$ .

Before initiating the electrolyte evaluation and considering the chemistry of silica (through a  $pH$ -silica solubility diagram; modified after [28]), it was necessary to convert all dissolved silica ( $H_4SiO_4^\circ$ ) in the calibration standards and samples into chemical reactive species of  $H_3SiO_4^-$  (see Fig. 1). It was, therefore, important to increase the  $pH$  of all calibration silica standards and samples (synthetic and real geothermal brines) up to a stabilized value of  $11.0 \pm 0.1$  using an appropriate concentration of sodium hydroxide at  $25^\circ C$ . According to some works reported in the literature [1,28], the alkaline conversion reaction between  $H_4SiO_4^\circ$  and  $H_3SiO_4^-$  is quite fast, and equilibrium can be reached in a few minutes ( $\sim 5$  min). In this work, a much longer reaction time of 30 min was used to ensure a full ionization of the silicates as anions, as well as to verify a  $pH$  stabilization of the samples, although later experiments showed that a much shorter time of about 5 min would be sufficient for this purpose.

Silica standards with a neutral  $pH$  or slightly alkaline required a few drops of a 1 mM sodium hydroxide, while for acidified geothermal brines ( $pH < 3$ ), one or two drops

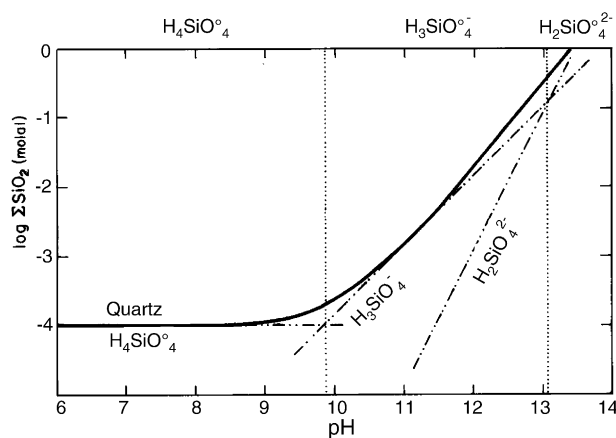
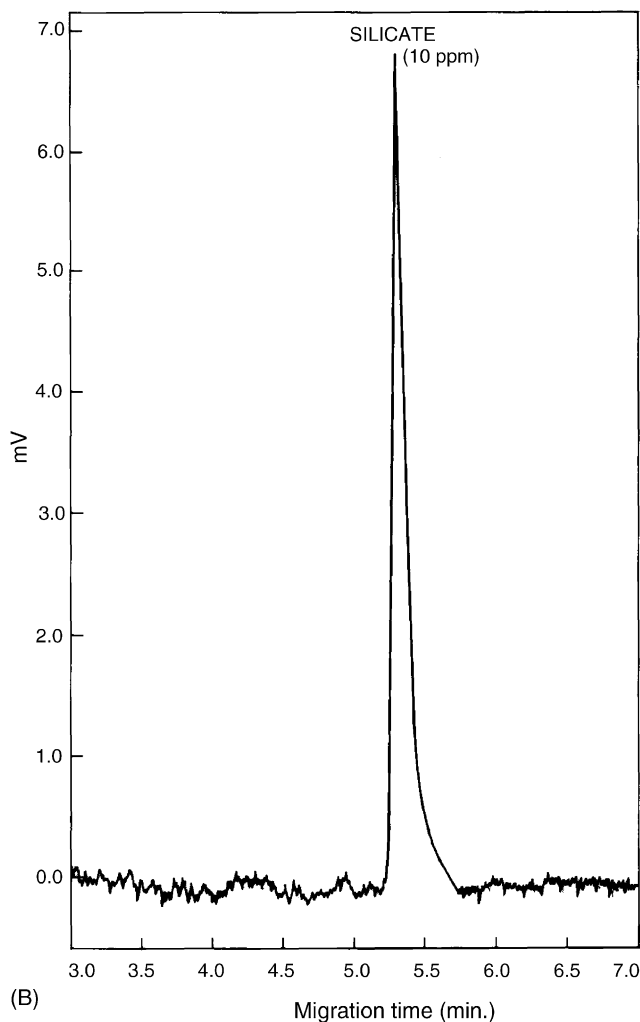
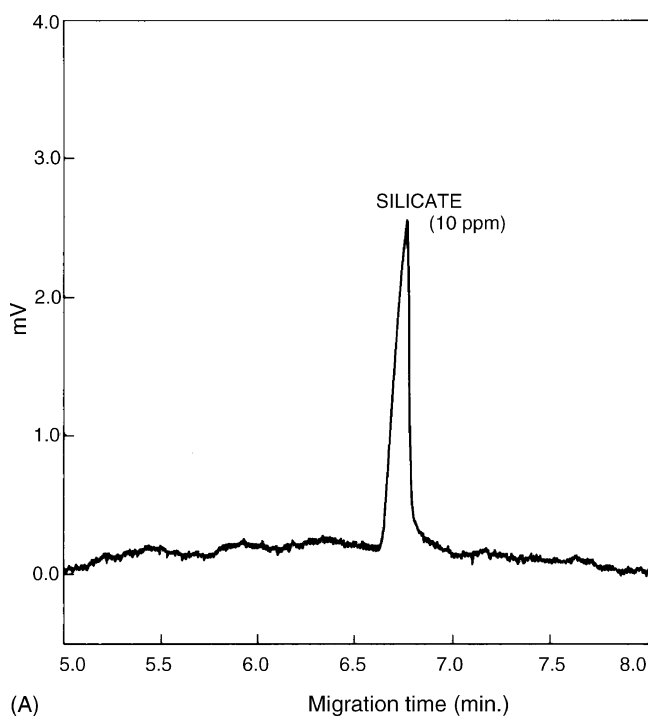


Fig. 1. Schematic diagram showing the effect of the silica solubility as function of  $pH$  (modified after [28]).

of a more concentrated solution of sodium hydroxide were needed.

Preliminary CE tests for selecting the most suitable electrolyte composition for detecting silicates were then carried out. Silica calibration standards containing 10 and  $80 \text{ mg L}^{-1}$  were employed for an appropriate evaluation of the analysis performance (sensitivity and migration times) using both the electrolytes A and B. Typical experimental electropherograms obtained with the  $10 \text{ mg L}^{-1}$  silica standard are shown in Fig. 2. As can be seen, the separation of the silicate anions was well resolved with both A and B electrolytes (Fig. 2A and B, respectively). Fairly symmetrical peak shapes were systematically observed, which demonstrate that the silicate and electrolyte mobilities were nearly the same (i.e., a mobility ratio,  $R = 1$ ). The migration times of silicate anion achieved with the use of the electrolyte B ( $\sim 5.5$  min) were less than those obtained for the electrolyte A ( $\sim 6.8$  min). All these migration times have been improved in comparison to the previous results ( $\sim 7.25$  min) found by Barciela-Alonso and Prego [24]. The results provided by the electrolyte B actually represent a reduction in the analysis time of about 32% without affecting the separation quality, which is confirmed by the symmetry of the analyte peaks. Such an optimization is also related to the apparent mobilities exhibited by the silicates in this experimental work (electrolytes A and B:  $0.39$  and  $0.47 \text{ cm}^2 \text{ kV}^{-1} \text{ s}^{-1}$ , respectively) which are greater than the value previously reported by Barciela-Alonso and Prego ( $\sim 0.36 \text{ cm}^2 \text{ kV}^{-1} \text{ s}^{-1}$ ) [24].

In relation to the detection, the electrolyte B provided a much better sensitivity for detecting silicates in comparison with the capability offered by the electrolyte A (see Fig. 2A and B). For the concentration levels of silica typically present in geothermal brines (from  $100 \text{ mg L}^{-1}$  up to  $2100 \text{ mg L}^{-1}$ ), the analysis capability provided by the electrolyte A could be sufficient. However, the sensitivity is improved by a factor of 2 or more with the use of the electrolyte B (Fig. 2B). The high concentration of chromate used in the electrolyte B together with the OFM composition produces an improvement in the



UV absorptivity, which enables the silicate species to be better detected. With this sensitivity improvement, the analysis of silica at trace levels of concentration could also be performed (e.g., for geothermal steam condensates, where the silica concentration ranges from a few  $\mu\text{g L}^{-1}$  to  $2\text{ mg L}^{-1}$  [3]).

These CE results enabled that the electrolyte B (with an ionic strength given by the mixture of 10 mM sodium chromate, 3 mM TTAOH, 2 mM sodium carbonate, and 1 mM sodium hydroxide,  $\text{pH } 11.0 \pm 0.1$ ) to be selected for carrying out a reliable CE evaluation for the determination of silicates in geothermal brines.

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

#### 3.2.1. Reproducibility

Precision tests based on six non-consecutive injections of samples containing different concentrations of silicates were performed. The synthetic reference standard (M-2) and the geothermal brine (M-5) were injected using appropriate dilution factors. The average results of the reproducibility (expressed as percentage of relative standard deviation, %R.S.D.) for the migration times, the peak areas and the peak heights were 1.6, 1.2, and 3.3%, respectively, which were quite satisfactory. Such reproducibility results were consistently observed for all standards and samples.

#### 3.2.2. Linearity

Seven concentration levels of silicate anion and three replicates of each standard were used for evaluating the linearity of the method. A linear response between the peak corrected area and the silicate concentration was obtained. The linearity was extended from a blank concentration up to a concentration level of  $80\text{ mg L}^{-1}$ . Linear calibration curves were fitted using both ordinary (OLR) and weighted (WLR) linear regression models for propagating the errors of both  $x$  (concentration) and  $y$  (response) variables [29–31]. For the OLR and WLR, the regression equations were given by the following coefficients (including their standard errors):  $y = -1042 (\pm 471) + 1280 (\pm 11)x$ ;  $y = -0.00226 (\pm 0.12143) + 1214 (\pm 5)x$ , respectively. Good squared linear correlation coefficients ( $r^2$ ) were obtained with both OLR and WLR regression

Fig. 2. (A) Electropherogram of a standard of silicates ( $10\text{ mg L}^{-1}$ ). The carrier electrolyte consisted of 5 mM sodium chromate and an electroosmotic flow modifier (0.2 mM TTAB) adjusted to a  $\text{pH } 11 \pm 0.1$ . Silica measurement was performed using an indirect UV detection at a wavelength of 254 nm with a mercury lamp and with a negative power supply ( $-20\text{ kV}$ ). Other operating conditions are summarized in Section 2. (B) Electropherogram of a standard of silicates ( $10\text{ mg L}^{-1}$ ). The carrier electrolyte consisted of 10 mM sodium chromate, 3 mM tetradecyltrimethyl-ammonium hydroxide (TTAOH), 2 mM sodium carbonate, and 1 mM sodium hydroxide, adjusted to a  $\text{pH } 11 \pm 0.1$ . Silica measurement was performed using an indirect UV detection at a wavelength of 254 nm with a mercury lamp and with a negative power supply ( $-15\text{ kV}$ ). Other operating conditions are summarized in Section 2.

models ( $r^2 > 0.9998$ ;  $n = 7$ ), implying statistically significant correlations at the 99% confidence level.

Even though both OLR and WLR models provided appropriate results for quantifying the silica content in all samples, the calibration curve fitted with the WLR model is suggested as the most suitable regression method for fitting the experimental data because it enables the heteroscedastic errors of  $y$  (instrument response) to be propagated in whole analysis [29]. Smaller propagated errors were also predicted when the WLR model was employed to compute the concentrations of the samples (Table 1).

### 3.2.3. Accuracy

Accuracy was evaluated by a statistical comparison between the most probable concentrations of the synthetic reference standards (reported from the inter-laboratory calibrations) and the concentrations calculated with the CE calibration curves using both OLR and WLR models (Table 1). For these purposes, Student's  $t$ -test using a comparison of two experimental means  $\bar{x}_1$  and  $\bar{x}_2$  was applied [i.e., taking the null hypothesis  $H_0: \mu_1 = \mu_2$  to test whether  $x_2$  (concentration of a synthetic reference standards obtained by CE) is statistically equal to  $x_1$  (most probable concentration of a synthetic reference standards) ( $H_0$  is valid) or they differ significantly from each other (alternative hypothesis  $H_1$  is valid)] [31]. No significant differences were found between them ( $H_0$  is valid) because the  $t$ -values computed from experimental data were less than the corresponding  $t$ -critical values at the 99% confidence level ( $P = 0.01$ ) for all cases (M-1 to M-4 in Table 1).

### 3.2.4. Limit of detection (LOD)

The LOD was determined using the "3 $s$  method" ( $s$  is "sample" standard deviation), which has been widely used [32]. This 3 $s$  method estimates, in a simple form, a LOD based on either a blank or a trace-level standard. The LOD computed was  $0.15 \text{ mg L}^{-1}$ , which was sufficiently low for a reliable determination of silicates in geothermal brines. A further optimization of this LOD was not necessary due to the high concentration of silica present in most of these samples.

## 3.3. Applications, comparison with other techniques and interferences

### 3.3.1. Quantitative analyses

The CE method developed in this work was applied to the quantitative analysis of two geothermal brine samples (M-5 and M-6). Appropriate dilution factors were employed for calculating the silicate concentration of the samples using both OLR and WLR calibration curves (with a concentration range from 0 to  $80 \text{ mg L}^{-1}$ ).

For avoiding a possible overloading effect of the ion zone and some co-migration problems, after each sample injection the capillary was rinsed for 3 min with Milli-Q water

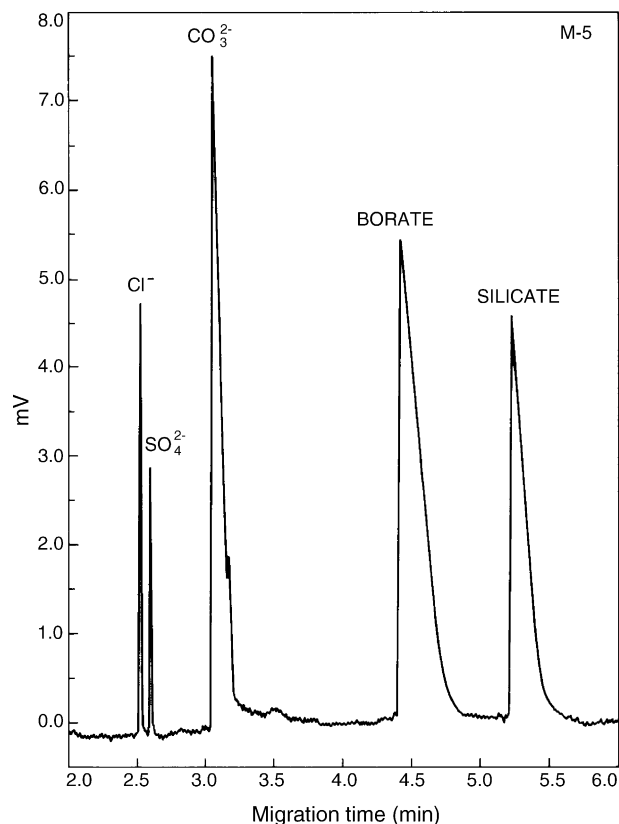


Fig. 3. Electropherogram of geothermal brine sample M-5. Operating capillary electrophoresis conditions are summarized in Fig. 2B. Chloride, sulfate, carbonate, and borate peaks were not quantified by CE.

and then for 2 min with the electrolyte solution. An electropherogram showing the efficient separation and detection of silicates for the geothermal sample M-5 is shown in Fig. 3. Chlorides, sulfates, carbonates and borates were also detected in these samples. However, these peaks were not quantified because it was not the objective of this experimental work. The quantitative results of silicate concentrations obtained by CE (including their errors) are also included in Table 1.

### 3.3.2. Comparison with the analytical results provided by AAS technique

The SRS and geothermal brine samples were also analyzed by AAS for comparison purposes. These results are summarized in Table 1. The analytical results of AAS obtained for the SRS were compared with the most probable values of synthetic reference standards of silica using the Student's  $t$ -test. Significant differences were found between them at  $P = 0.01$  (alternative hypothesis  $H_1$  is valid). Such systematic differences are consistent with the systematic underestimation provided by AAS technique because the AAS does not measure colloidal silica probably present in the samples.

### 3.3.3. Interferences

According to the typical anion concentrations reported for these geothermal samples (M-5 and M-6) [33], given by an average concentration of  $\text{Cl}^-$  ( $\sim 120 \text{ mg L}^{-1}$ ),  $\text{SO}_4^{2-}$  ( $\sim 114 \text{ mg L}^{-1}$ ),  $\text{CO}_3\text{H}^-$  ( $\sim 361 \text{ mg L}^{-1}$ ), and  $\text{B}^-$  ( $\sim 214 \text{ mg L}^{-1}$ ), the samples analyzed did not present any matrix interference problem because the migration times exhibited by chlorides and silicates were significantly different. This feature constitutes an advantage for the CE methodology because it has been possible to measure silica in brines containing up to  $150 \text{ mg L}^{-1}$  of chlorides without any interference problem. The analysis of more concentrated brines ( $\text{Cl}^- > 150 \text{ mg L}^{-1}$ ) by CE can be successfully performed by a rapid removal process of the interferences using commercial ion exchange cartridges (e.g., Ag packing), which have been employed in other separation techniques, such as ion chromatography [34].

Interferences due to a possible interaction between the solute and the capillary wall did not occur because this problem leads to band broadening, peak tailing, and irreproducibility of separations, which were not observed during the CE analyses. Furthermore, blank solutions were injected several times during the analysis for evaluating any possible background contamination produced. The electropherograms of these injections never showed any detector signal that could show silica traces due to a possible dissolution of the capillary fused silica. Finally, because the samples and the blank solutions were treated in the same way, any dissolution of the capillary should be present in both samples and blank solutions.

## 4. Conclusions

A new application of CE for determining silicates in geothermal brine samples has been successfully demonstrated. An electrolyte consisting of 10 mM sodium chromate, 3 mM tetradecyltrimethyl-ammonium hydroxide (TTAOH), 2 mM sodium carbonate, and 1 mM sodium hydroxide (with a  $\text{pH } 11 \pm 0.1$ ) was found suitable for detecting silica concentrations up to  $80 \text{ mg L}^{-1}$ . An optimized analysis time of less than 5.5 min was also achieved. The method provided satisfactory results for precision of migration times, resolution, and response linearity. Although the CE measurements were performed for the analysis of geothermal brines with a moderate composition of salts (chlorides), the use of this method in more concentrated samples must be conducted after a salt removal using appropriate ion exchange cartridges. The excellent sensitivity provided by this CE methodology should also be suitable for the analysis of silica at trace levels of concentration, e.g., for geothermal steam condensates.

On the basis of these results, CE technique might become an alternative quantitative technique to determine silica in geological samples and develop into a reliable analytical method to be used more frequently in other Earth science applications.

## Acknowledgements

Financial support from IN-104703 (DGAPA-UNAM, Mexico) and PB98-0668-002-01 (Ministerio de Educación y Ciencia, España) research projects are gratefully acknowledged. Partial financial support from Posgrado en Ingeniería (UNAM) is also recognized. We are also grateful to technicians of the Instituto de Ciencias Medio Ambientales and the Museo Nacional de Ciencias Naturales (CSIC) for all facilities provided to carry out this work. Mr. José Arroyo (Museo Nacional de Ciencias Naturales) helped us to draw the final versions of the figures. We are also grateful to two anonymous reviewers for helpful comments on an earlier version of this paper.

## References

- [1] R.K. Iler, *The Chemistry of Silica*, Wiley, New York, USA, 1979.
- [2] K. Nicholson, *Geothermal Fluids: Chemistry and Exploration Techniques*, Springer-Verlag, Berlin Heidelberg, Germany, 1993.
- [3] V.V. Potapov, G.A. Karpov, V.M. Podverbnyi, *Theor. Found. Chem. Eng.* 36 (2002) 589.
- [4] H.P. Rothbaum, B. Anderson, A. Rhode, *Geothermics* 8 (1979) 1.
- [5] S.P. Verma, E. Santoyo, *J. Volcanol. Geoth. Res.* 79 (1997) 9.
- [6] M.P. Verma, E. Tello, F. Sandoval, R. Tovar, J.L. Martínez, *Geothermics* 31 (2002) 677.
- [7] M.S. Lico, Y.K. Kharaka, W.W. Carothers, V.A. Wright, *United States Geological Survey, Water-Supply* (1988).
- [8] M. Burguera, J.L. Burguera, P. Carrero, C. Rondón, *Talanta* 58 (2002) 1157.
- [9] S. Mercado, E. Santoyo, H. Gamiño, H. López-Rubalcaba, *Geoth. Res. Council Trans.* 9 (1985) 263.
- [10] American Public Health Association (APHA), *Standard methods for the examination of water and wastewater*, American Public Health Association, Washington, DC, USA, 1992.
- [11] *Annual Book of ASTM Standards, Water and Environmental Technology, Standard Test Method for Silica in Water, Designation D 859-88*, vol. 11.01, ASTM, Philadelphia, USA, 1990.
- [12] M.C. Giacomelli, O. Largiuni, G. Piccardi, *Anal. Chim. Acta* 396 (1999) 285.
- [13] J.P. Wilshire, *LC* 1 (1983) 290.
- [14] Dionex, *Dionex Application Update* AU 113 (1989) 1.
- [15] H.-B. Li, F. Chen, *J. Chromatogr. A* 874 (2000) 143.
- [16] Q. Xu, C. Xu, W. Zhang, Y.P. Wang, L.T. Jin, H. Haraguchi, A. Itoh, K. Tanaka, *Chromatographia* 53 (2001) 81.
- [17] K. Fujiwara, E.P.H. Wagner, B.W. Smith, J.D. Winefordner, *Anal. Lett.* 29 (1996) 1985.
- [18] A. Hioki, J.W.H. Lam, J.W. McLaren, *Anal. Chim. Acta* 416 (2000) 21.
- [19] S. George, S.M. Steinberg, V. Hodge, *Chemosphere* 40 (2000) 57.
- [20] D.R. Baker, *Capillary Electrophoresis*, John Wiley & Sons, New York, USA, 1995.
- [21] P. Doble, P.R. Haddad, *J. Chromatogr. A* 834 (1999) 189.
- [22] A.H. Harakuwe, P.R. Haddad, *J. Chromatogr. A* 834 (1999) 213.
- [23] E. Santoyo, R. García, R. Abella, A. Aparicio, S.P. Verma, *J. Chromatogr. A* 920 (2001) 325.
- [24] M.C. Barciela-Alonso, R. Prego, *Anal. Chim. Acta* 416 (2000) 21.
- [25] J. Zhang, C.J. Fischer, P.B. Ortner, *Water Res.* 33 (1999) 2879.
- [26] S.P. Verma, *Chem. Geol.* 164 (2000) 35.

- [27] A. Weston, P.R. Brown, HPLC and CE: Principles and Practice, Academic Press, London, UK, 1997.
- [28] D. Langmuir, Aqueous Environmental Geochemistry, Prentice-Hall, New Jersey, USA, 1997.
- [29] S.P. Verma, E. Santoyo, *J. Chromatogr. A* 997 (2003) 171.
- [30] P.R. Bevington, Data Reduction and Error Analysis for Physical Sciences, McGraw-Hill, New York, 1969.
- [31] J.N. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, Prentice-Hall, Edinburgh, UK, 2000.
- [32] G.L. Long, J.D. Winefordner, *Anal. Chem.* 55 (1983)713.
- [33] R.M. Barragán, D. Nieva, E. Santoyo, E. González, M. Verma, J.M. López-Mendiola, *Geotermia Rev. Mex. Geoener.* 7 (1991) 23.
- [34] Dionex, OnGuard II Ag Cartridge Manual, Document No. 031688-05, 2003, p. 10.