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Suppressed ion chromatography for monitoring chemical impurities in steam for geothermal power plants

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Abstract

A suppressed ion chromatography (IC) technique has been evaluated as a chemical monitoring tool for detecting major anions (F^- , Cl^- , NO_3^- and SO_4^{2-}) of condensed steam in geothermal power plants. It is shown that the suppressed IC technique provides a suitable means for preventing possible damage to generating equipment in the geothermal industry. An electrical conductivity detector (0.1 μS sensitivity) with an anion-exchange column (IonPac AS4A-SC), a micro-membrane suppressor (AMMS II), and an isocratic high-pressure pump system were successfully used for detecting low concentrations of inorganic anions. Method detection limits for the anions of interest were <0.184 mg/L. Details of the IC methodology as well as some experimental results obtained during its application for the chemical monitoring of geothermal steam pipes are also described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Process control; Geothermal fluids; Inorganic ions

1. Introduction

The exploitation of geothermal resources for generating electricity has shown considerable progress in Mexico [1]. Two-phase (water–steam) reservoirs are being commercially exploited in some Mexican geothermal fields [2]. A working generating fluid with a high steam quality must be efficiently separated from the geothermal fluid (water–steam mixture) produced in such natural systems [3,4]. The presence of liquid in the steam could cause serious problems of scaling and corrosion in the generation equipment (e.g. turbine blades) due to the high

salinity present in the liquid phase [4]. An efficient separation of steam from the mixture is normally controlled, in situ, by a correct throttling of the liquid and steam levels inside the separators. In spite of this operation, an in-situ chemical analysis of the steam composition in order to monitor its inorganic ionic impurities is required. This chemical control would provide a signal if inappropriate operation of the separators occurs, thus avoiding serious damage to the generation equipment. Such chemical monitoring should, therefore, constitute an integral part of the operation of power generators in the geothermal industry.

To address this special need, in-situ analysis of the inorganic anion composition in geothermal steam samples has been suggested as a monitoring analytical tool. From the geochemical point of view, the

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composition of major anions can be reliably used as a chemical indicator, since it is representative of the ionic impurities present in the steam [5]. Since the anion concentrations expected in geothermal steam would generally be very low, highly sensitive analytical techniques with low detection limits are required.

In the last few years, numerous analytical techniques applied in the geosciences have shown remarkable progress [6,7]. Increased sensitivities and higher precision and accuracy continue to result in lower detection limits. In this context, high-performance ion chromatography (IC) has been well established as a low-cost analytical technique for determining a wide range of inorganic ions with high sensitivity [8–10]. Without doubt, the chemical analysis of inorganic anions in a single run constitutes one of the best applications of IC [11–14].

Non-suppressed and suppressed conductivity detections are the preferential modes for measuring inorganic anions. The first detection mode is typically used with a single chromatographic column with an eluent that is not chemically modified prior to entering the detector [9,15–17]. The second detection mode is characterized by using suppression devices that enable the chemical structure of the anions to be converted from a salt to their conjugated acid just prior to the conductivity detector [17–19]. Such a chemical suppression lowers the background conductance of the eluent and improves the overall conductance of the analyte, leading to lower detection limits.

Advances in the analysis of anions by IC have shown that optimized suppressed IC systems can provide detection limits that are up to 10 times lower than non-suppressed systems [20,21]. This clearly explains why suppressed anion-exchange chromatography is routinely used as the preferred detection mode for the determination of anions. Sodium hydroxide or carbonate–hydrogencarbonate buffers are usually the working eluents used in optimized suppressed IC [10,11]. Such buffers have the chemical property that they can be converted into species of low conductance, such as water or H_2CO_3 , after exchanging their cations for hydrogen ions by the use of suitable suppression devices, such as packed-bed chemical suppressors, hollow fiber suppressors, micro-membrane suppressors, self-regenerating auto-

suppressors or self-regenerating ultra suppressors. High signal-to-noise ratios are generally achieved with chemical suppression, extending the linear dynamic concentration range of the analyses from mg/L down to $\mu\text{g/L}$ levels. Such concentration ranges are generally sufficient for any complex IC application where a trace analysis of anions is required.

Even though the suppressed IC technique for separating inorganic anions has been extensively developed, quantifying anions in different types of chemical matrices, at low concentrations, continues to be an important analytical contribution for the development of ion chromatography. With this consideration and taking advantage of the detection capabilities shown by suppressed anion-exchange chromatography, a simple in-situ IC procedure for determining anions in geothermal steam matrices was developed. The determination of the major inorganic anions (i.e. F^- , Cl^- , NO_3^- and SO_4^{2-}) in condensed steam samples was defined as the main analytical task for this new IC application. Such an IC technique was applied as a reliable analytical tool for monitoring the chemical impurities in geothermal steam. Our goal is to describe the suppressed IC system used and to report the experimental results obtained during the chemical monitoring of steam pipelines of a Mexican geothermal power plant.

2. Experimental

2.1. Instrumentation

The configuration of the ion chromatograph used consisted of a high-pressure isocratic pump (LC-250, Perkin-Elmer, USA), an electrical conductivity detector with a range of sensitivity from $0.1 \mu\text{S}$ to 10 mS (Conductomonitor III, LDC Analytical, USA), and a manual injection valve with a sample loop of $50 \mu\text{L}$ (Rheodyne, USA). The ion chromatograph instrument was interfaced to an integrator-computer system (Nelson Analytical/Perkin-Elmer) for collecting chromatographic data. A Dionex AMMS-II anion micro-membrane suppressor was used in the IC analyses for improving both the detection limits and the signal-to-noise ratio. The suppression device uses a cation micro-membrane which is regenerated with

a continuous flow of 0.025 M H₂SO₄. The analytical separator columns used were Dionex IonPac AS4A-SC: 250×4 mm I.D. The separator column was protected with a guard column (Dionex IonPac AG4A-SC: 50×4 mm I.D.) to prevent fouling problems.

All experimental work was performed under isocratic eluent flow-rate conditions and at laboratory temperature. The operating conditions and eluents used by the suppressed IC system during the experimental runs are reported in Table 1. Before initiating the analyses, the suppressed IC system (flow paths, pump, and columns) was washed by flushing the system with deionized water (at a flow-rate of 1 mL/min) for ca. 1 h, followed by rinsing with the working eluent for ca. 25 min. The instrument was then set in operation for 30 min with an optimum flow-rate of working eluent solution (Table 1).

2.2. Chemical reagents, standard solutions, and eluents

All chemical reagents were of analytical-reagent grade and dissolved in deionized water (18 mΩ cm resistivity) for the preparation of standard solutions. Stock standard solutions of anions containing 1000 mg/L were prepared by dissolving appropriate amounts of primary anion salts according to the

standard methods recommended by the American Society for Testing and Materials, ASTM [22]. Stock standard solutions were stored at 5 °C. Standard working solutions at lower analyte concentrations (<10 mg/L) were prepared daily by diluting the stock solutions with deionized water. The working eluent consisted of a mixture of 1.8 mM sodium carbonate and 1.7 mM sodium hydrogencarbonate (pH 9.39). Fresh working eluent was prepared daily, filtered through a 0.2 μm pore size membrane filter (Millipore, USA), and degassed prior to use.

2.3. Samples

Six geothermal steam samples were collected in situ from different steam pipelines before the steam enters the generation turbines (U-5B, U-7B, A-9, A-22, A-41, and A-56). All the steam samples were condensed using a portable sampling device consisting of a double coil of stainless steel immersed in a cooling bath of water with ice. Two condensed steam samples were additionally collected at the turbine exit (U-5A and U-7A). All samples were handled carefully to avoid contamination and rapidly analyzed in the field geochemical laboratory at the geothermal power plant installations. Samples were pre-filtered through a 0.45-μm filter membrane (Millipore) to remove suspended matter and transferred into 125-mL polypropylene bottles previously

Table 1

Operating parameters used for anion separation by suppressed ion chromatography with an anion-exchange column (IonPac AS4A-SC) under isocratic flow-rate conditions

Chromatographic parameters	Description
<i>Analytical separation system</i>	
Guard column	IonPac AG4A-SC (50×4 mm I.D.)
Analytical column	IonPac AS4A-SC (250×4 mm I.D.)
Composition of the IC eluent	1.8 mM sodium carbonate– 1.7 mM sodium hydrogencarbonate (pH 9.39)
<i>Isocratic flow-rate conditions</i>	
Injection volume	50 μL
Optimum IC flow-rate	1.5 mL/min
<i>Detection system</i>	
Detector	Suppressed conductivity
Sensitivity	0.1 μS
Suppressor device	Dionex AMMS-II
Regenerant	0.025 M H ₂ SO ₄
Regenerant flow-rate	1.1 mL/min

washed according to the sampling techniques suggested for collecting geothermal fluids [5,23]. At the field geochemical laboratory, all samples were again filtered through a filter membrane (0.2 μm) before injection into the suppressed IC system in order to prevent fouling problems.

3. Results and discussion

3.1. Separation of anions

The use of the IonPac AS4A-SC column with an eluent mixture of 1.8 mM sodium carbonate and 1.7 mM sodium hydrogencarbonate has been typically adopted as a standardized IC method for separating anions [22,24]. The IC procedure specifies the use of suppressed conductivity detection with a suppression device operated under continuous chemical regeneration. According to the technical specifications, the substrate of the AS4A-SC column is ethylvinylbenzene (EVB) crosslinked with 55% divinylbenzene (DVB), a particle diameter of 13 μm , a latex diameter of 160 nm and a latex cross-linking of 0.5%, which together provide good ion-exchange selectivity [19]. All the anions are usually well resolved within 8 min. However, the time can be reduced by modifying the molar composition of the mobile phase, the eluent flow-rate, and the stationary phase composition or column temperature [19]. Shorter retention times can also be obtained due to a loss of column efficiency. In this work, the optimum eluent flow-rate was determined under isocratic flow-rate conditions using the well-known Van Deemter theory [10]. Experimental height equivalent to a theoretical plate (HETP) and flow-rate curves indicated that a flow-rate of 1.5 mL/min was the optimum value to be used in suppressed IC analyses. The use of the IonPac AS4A-SC column enabled an efficient separation of inorganic anions in less than 5 min (Fig. 1: standard 0.39 mg/L).

Such a short analysis time is rather anomalous. It could possibly be attributed either to a loss in column efficiency due to a prolonged use of the column or to small changes in the molar composition of the eluent used. The possible presence of metals or organic compounds due to fouling of the column

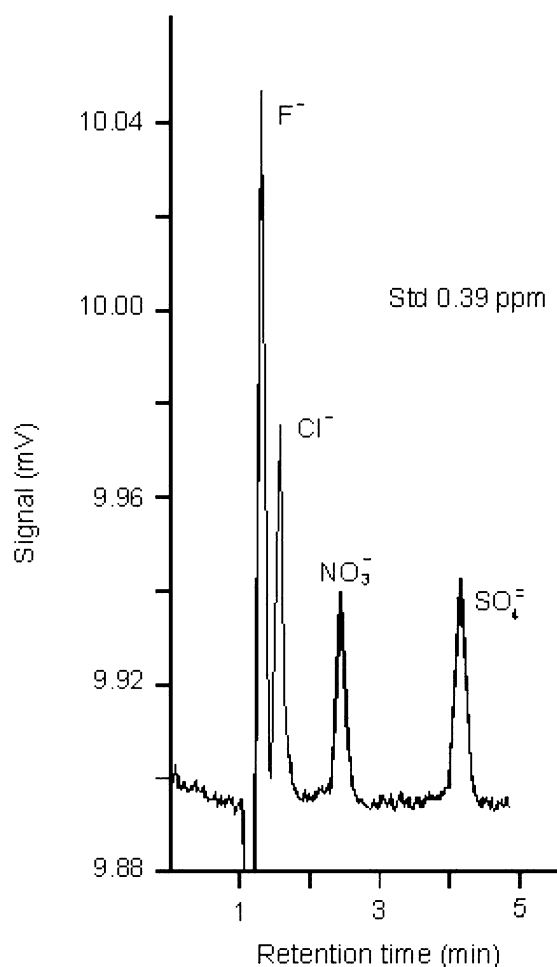


Fig. 1. Separation of inorganic anions of a standard mixture (0.39 mg/L). Conditions: suppressed conductivity detection at 0.1 μS (signal sensitivity); column, IonPac AS4A-SC; suppressor, AMMS II; eluent, 1.8 mM sodium carbonate–1.7 mM sodium hydrogencarbonate, pH 9.39, at a flow-rate of 1.5 mL/min; other chromatographic operating conditions are described in Table 1.

could also result in this behavior. Despite the short analysis time exhibited in these runs, all four anion peaks were well resolved at low concentrations (Fig. 2: standard 0.19 mg/L). A noisy baseline was observed in most of the IC chromatograms. Instability of the power supply at the field laboratory was identified as the main source of noise, since all IC runs were performed at the maximum sensitivity of the conductivity detector (0.1 μS).

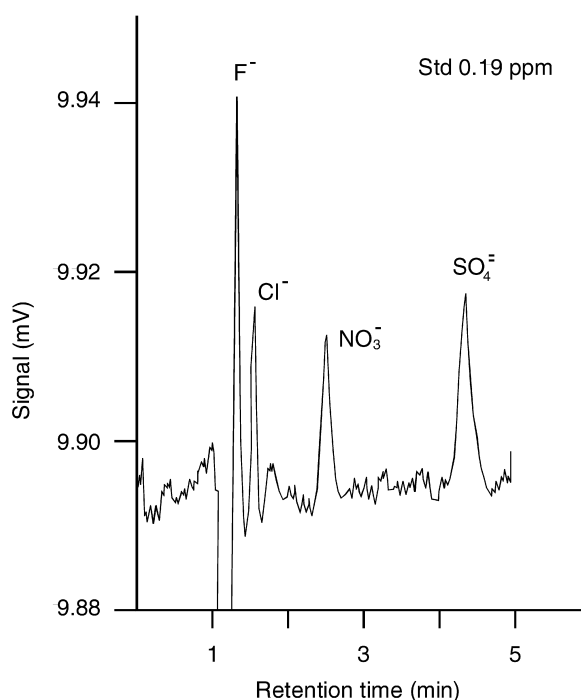


Fig. 2. Separation of inorganic anions of a standard mixture (0.19 mg/L). Conditions: suppressed conductivity detection at 0.1 μ S (signal sensitivity); column, IonPac AS4A-SC; suppressor, AMMS II; eluent, 1.8 mM sodium carbonate–1.7 mM sodium hydrogencarbonate, pH 9.39, at a flow-rate of 1.5 mL/min; other chromatographic operating conditions are described in Table 1.

3.2. Precision and calibration tests

Reproducibility tests based on five injections of an anion standard (0.39 mg/L) consisting of F^- , Cl^- , NO_3^- and SO_4^{2-} were performed (Table 2). Reproducibility data for retention times and peak areas

were calculated with an anion standard of 0.39 mg/L and using the operation parameters described in Table 1. The relative standard deviations (RSDs) of retention times and peak areas were less than 2.2 and 4.4%, respectively.

Five concentrations of each anion and five replicates of each concentration were used for evaluating the linearity response (Table 2). All the calibration curves of the anions showed good linear correlations ($r^2 > 0.9810$; $n=5$) for concentrations ranging from 0.19 to 3.125 mg/L (Table 2). Such linear correlations are statistically satisfactory (at the 99% confidence level), considering the high degree of probability $P_c(r,n) > 0.01$ [25].

Accuracy was checked continuously by the analysis of a standard test sample containing a mixture of anions with a known concentration of 0.78 mg/L. Satisfactory accuracy results were obtained when the test concentration was evaluated (Table 3). All samples collected were analyzed at the field geochemical laboratory. The concentrations were additionally verified by use of a Model 2010i ion chromatograph (Dionex, Sunnyvale, CA, USA) which was installed at the geochemical laboratory (GL) of the Electrical Research Institute (IIE, Cuernavaca, Mexico). Anion concentration ratios between field geochemical laboratory and GL results were close to unity, which confirms the validity of the results obtained with the implemented IC methodology at the geothermal power plant.

3.3. Limits of detection (LODs)

The LODs for all chromatographic analyses were

Table 2

Reproducibility results for retention time and peak area, limits of detection (LODs) and linearity data obtained for the determination of inorganic anions using the IonPac AS4A-SC separation column

Inorganic anion	Retention time (% RSD)	Peak area (% RSD)	LOD ^a (mg/L)	Slope	Intercept	Linearity ^b (r^2)
Fluoride, F^-	1.1	3.7	0.184	30 401.9	13 902.2	0.9860
Chloride, Cl^-	1.9	3.4	0.084	16 709.3	9682.9	0.9810
Nitrate, NO_3^-	2.2	3.6	0.040	10 310.4	29.7	0.9994
Sulfate, SO_4^{2-}	0.7	4.4	0.053	13 772.9	-90.7	0.9998

^a LODs were determined using the “ 3σ method” [26].

^b Linearity correlation coefficients were estimated from five calibration levels ($n = 5$).

Table 3

Suppressed ion chromatography results obtained during the analysis of condensed steam samples collected from steam pipelines of a geothermal power plant

Anion	Concentration ($\pm\sigma_c$) (mg/L)								
	U-5B	U-5A	U-7B	U-7A	A-9	A-22	A-41	A-56	STD-T
Fluoride	<LOD	0.110 (± 0.004)	0.071 (± 0.003)	0.089 (± 0.003)	0.174 (± 0.006)	0.116 (± 0.004)	n.d.	n.d.	0.77 (± 0.03)
Chloride	1.71 (± 0.06)	2.62 (± 0.090)	0.57 (± 0.02)	2.51 (± 0.09)	1.13 (± 0.04)	1.08 (± 0.04)	2.17 (± 0.07)	2.41 (± 0.08)	0.78 (± 0.03)
Nitrate	n.d.	n.d.	n.d.	<LOD	<LOD	<LOD	n.d.	n.d.	0.78 (± 0.03)
Sulfate	0.50 (± 0.02)	1.19 (± 0.05)	0.99 (± 0.04)	1.08 (± 0.05)	0.50 (± 0.02)	0.50 (± 0.02)	0.49 (± 0.02)	0.49 (± 0.02)	0.78 (± 0.03)

σ_c , standard deviation values calculated from triplicate injections; n.d., not detected.

calculated by use of the well-known “ 3σ method” [26]. This statistical method can determine a LOD based on a trace-level standard. To determine the precision, five replicates of the lowest-level anion standard (0.19 mg/L) were injected. The standard deviation of these replicates was divided by the slope of the calibration curve to estimate the standard deviation value (SDV) in concentration units. This SDV was finally multiplied by the corresponding Student's t -value (for a 99% confidence level and for $n - 1$ degrees of freedom) to calculate the LOD of the anion. Table 2 reports all the LODs obtained in these IC experimental runs. Although the LODs achieved with the present IC instrument were higher than expected, they were generally suitable for most of the analyzed samples.

3.4. Application: determination of anion impurities in condensed steam samples

The proposed suppressed IC procedure was applied as a monitoring analytical tool for the in-situ analysis of the inorganic anion composition of steam samples collected from geothermal power plants. Most of these samples were strategically selected for collecting steam before it goes through the turbines (U-5B, U-7B, A-9, A-22, A-41, and A-56). Likewise, two condensed steam samples were additionally collected at the exit of the turbines (U-5A and U-7A). Such samples were selected for evaluating the background anion composition of steam in the entire power production cycle. Examples of the application of the IC procedure using an IonPac HPIC-AS4A column for measuring major anions in

samples A-9 and A-22 are presented in Figs. 3 and 4, respectively. These figures present typical expanded chromatograms showing efficient separation of all anions for their detection at trace levels. In these figures, the peaks of F^- , Cl^- and SO_4^{2-} were well resolved within 5 min and successfully quantified by means of their corresponding calibration curves (Table 3).

All the sample chromatograms (Figs. 3–5) show an anomalous displacement (to a longer retention time) of the F^- peak from the water dip signal, in comparison with the chromatograms of the anion standard samples (Figs. 1 and 2). This behavior could create an uncertainty in the identification of the F^- peak of the condensed steam samples because there is the possibility that organic compounds could also be eluted at the same retention time. However, to the best of our knowledge, organic compounds in geothermal fluids have never been reported before in the literature. The consideration of both the geological nature of these matrices and the F/Cl geochemical ratios, $F/Cl > 0$, typically observed for most of the geothermal fluids enables the presence of the fluoride peak to be confirmed [27].

The NO_3^- peak was near background noise levels and was therefore reported as below the LOD (see Table 2). An interesting monitoring case was found when steam samples collected at the entrance of the turbine (U-7B) and at its exit (U-7A) were analyzed separately. The corresponding IC chromatograms are shown in Fig. 5a and b, respectively. An increase in the Cl^- and SO_4^{2-} peaks was detected in sample U-7A. Such small increases could probably be attributed to the effect of steam separation in the condenser section of the geothermal power plant.

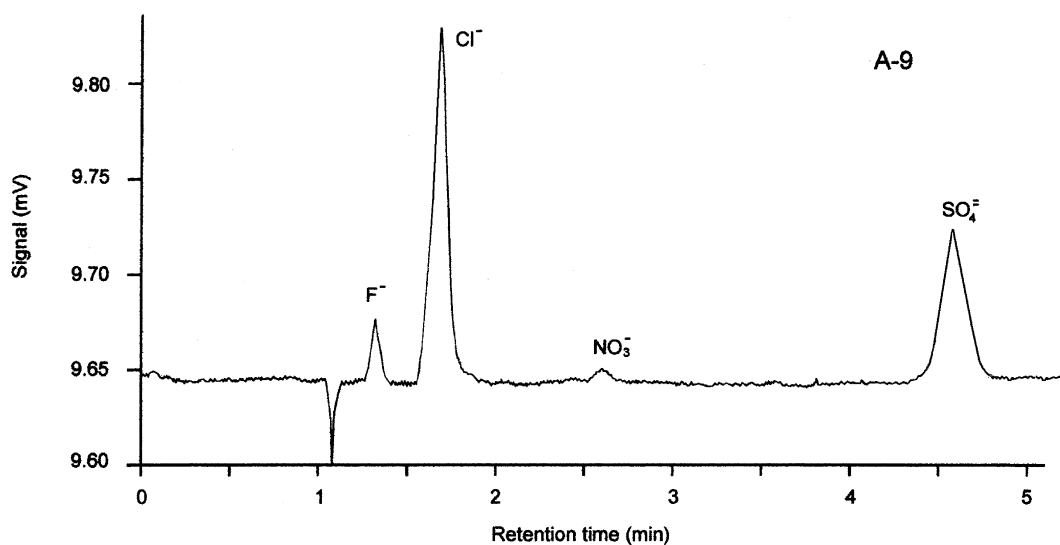


Fig. 3. Ion chromatogram of anions corresponding to suppressed IC analysis of a condensed steam sample (A-9). Chromatographic operating conditions as for Fig. 1.

This separation process tends to slightly concentrate the resulting condensed steam phase at that sampling site. A summary of the concentration results for all

geothermal condensed steam samples is presented in Table 3. Standard deviation values related to triplicate analyses are also reported in the same table.

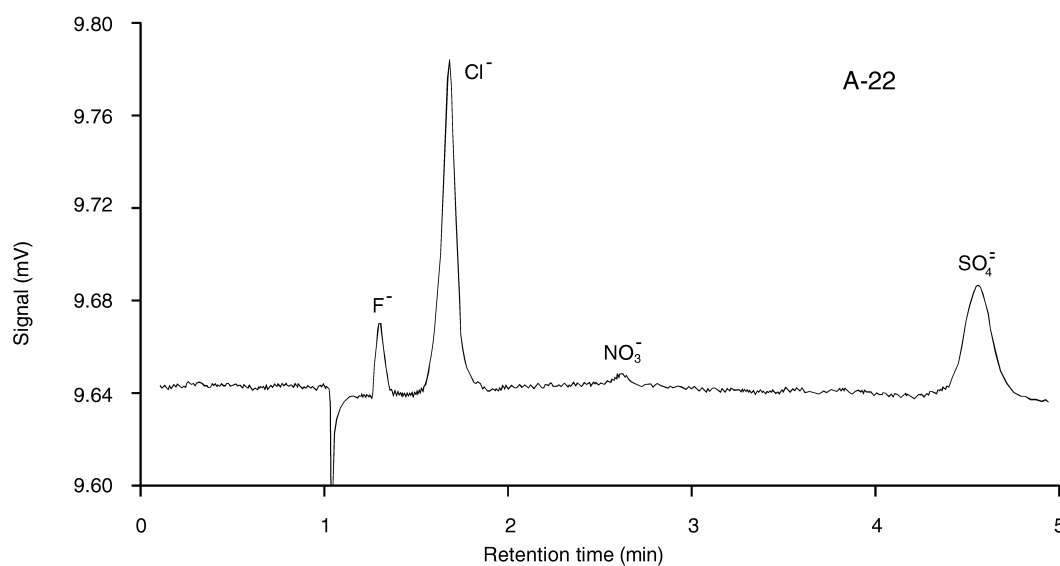


Fig. 4. Ion chromatogram of anions corresponding to suppressed IC analysis of a condensed steam sample (A-22). Chromatographic operating conditions as for Fig. 1.

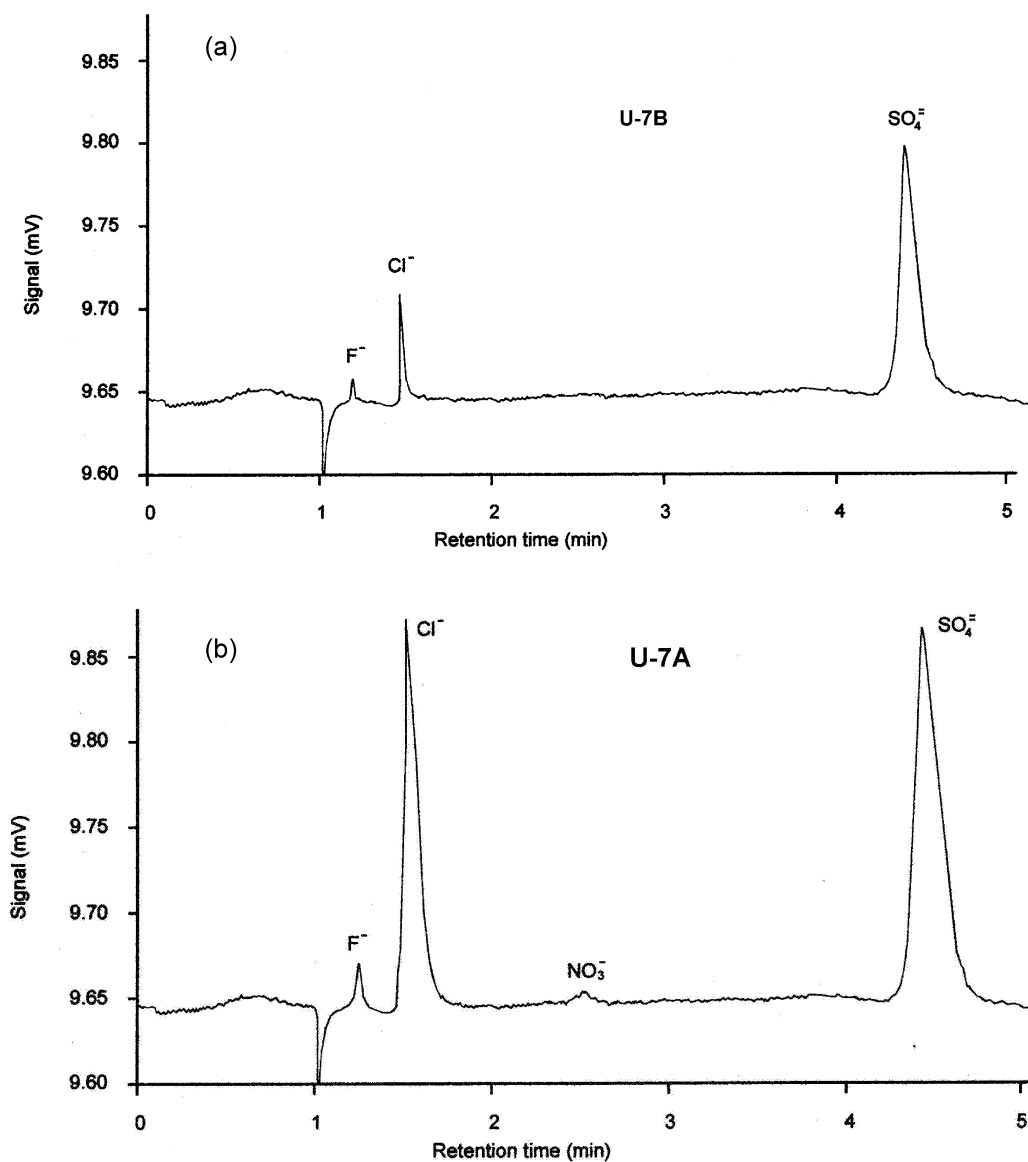


Fig. 5. Analysis of inorganic anions in (a) condensed steam sample U-7B collected at the turbine entrance and (b) condensed steam sample U-7A collected at the turbine exit. Chromatographic operating conditions as for Fig. 1.

3.5. Interferences

The displacement observed in the F^- peaks in all sample chromatograms may be associated with matrix effects, the origin of which should be studied in the future.

4. Conclusions

A simple suppressed IC procedure for the efficient separation and quantification of anions under isocratic eluent flow-rate conditions was evaluated. This method was used for the chemical analysis of

inorganic anions at concentrations ranging from 0.19 to 3.125 mg/L. The use of anion-exchange chromatography with an IonPac AS4A-SC separation column, a working eluent containing 1.8 mM Na₂CO₃–1.7 mM NaHCO₃, and suppressed conductivity detection provided a simple, cost-effective, fast, accurate, and highly sensitive technique for the determination of F⁻, Cl⁻, and SO₄²⁻ (NO₃⁻ was below its LOD) in geothermal condensed steam samples. The method was linear ($r^2 > 0.9810$) over the concentration working range. The detection limits were found to be 0.184, 0.084, 0.040, and 0.053 mg/L for F⁻, Cl⁻, NO₃⁻, and SO₄²⁻, respectively. With the suppressed IC technique, it was possible to measure the anion composition in geothermal condensed steam samples. The present method, therefore, constitutes an appropriate analytical tool for monitoring the chemical impurities of steam in geothermal power plants. Such monitoring should be considered essential for extending the life-time of power generation equipment in the geothermal industry. This new application clearly shows the great potential of the suppressed IC technique.

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References

- [1] G. Hiriart, J.I. Andaluz, in: Proceedings of the World Geothermal Congress, Kyushu-Tohoku, 2000, p. 799.
- [2] J.L. Quijano-León, L.C.A. Gutiérrez-Negrín, in: Proceedings of the World Geothermal Congress, Kyushu-Tohoku, 2000, p. 355.
- [3] H.C.H. Armstead, *Geothermal Energy: Its Past, Present and Future Contributions to the Energy Needs of Man*, E. Spon, London, 1983.
- [4] K.A. Lichti, L.G. Bacon, *Corros. Rev.* 17 (1999) 219.
- [5] S. Arnórsson, *Isotopic and Chemical Techniques in Geothermal Exploration, Development and Use*, International Atomic Energy Agency, Vienna, 2000.
- [6] P.J. Potts, *Geostandards Newsl.* 22 (1998) 57.
- [7] K. Anazawa, T. Tomiyasu, H. Sakamoto, *Anal. Sci.* 17 (2001) 217.
- [8] D.T. Gjerde, J.S. Fritz, *Ion Chromatography*, 2nd ed., Hüthig, Heidelberg, 1987.
- [9] P.R. Haddad, P.E. Jackson, *Ion Chromatography: Principles and Applications*, Journal of Chromatography Library, Vol. 46, Elsevier, Amsterdam, 1990.
- [10] J. Weiss, *Ion Chromatography*, 2nd ed., VCH, Weinheim, 1995.
- [11] W.W. Buchberger, P.R. Haddad, *J. Chromatogr. A* 789 (1997) 67.
- [12] H.T. Lu, S.F. Mou, R. Deng, J.M. Riviello, *Microchem. J.* 64 (2000) 1.
- [13] B. López-Ruiz, *J. Chromatogr. A* 881 (2000) 607.
- [14] P.E. Jackson, C. Weigert, C.A. Pohl, C. Saini, *J. Chromatogr. A* 884 (2000) 175.
- [15] D.T. Gjerde, J.S. Fritz, G. Schmuckler, *J. Chromatogr.* 186 (1979) 509.
- [16] K. Ohta, K. Tanaka, J.S. Fritz, *J. Chromatogr. A* 731 (1996) 179.
- [17] W.W. Buchberger, *J. Chromatogr. A* 884 (2000) 3.
- [18] W.Z. Hu, K. Tanaka, P.R. Haddad, K. Hasebe, *J. Chromatogr. A* 884 (2000) 161.
- [19] C.A. Pohl, J.R. Stillian, P.E. Jackson, *J. Chromatogr. A* 789 (1997) 29.
- [20] T. Jauhiainen, J. Moore, P. Peramaki, J. Derome, H. Derome, *Anal. Chim. Acta* 389 (1999) 21.
- [21] H.S. Amoli, M. Rabbani, P. Simpson, *Ind. J. Chem. A* 39 (2000) 1101.
- [22] *Standard Test Method for Anions in Water by Chemical Suppressed Ion Chromatography*, Annual Book of ASTM Standards, Part 31: Water, American Society for Testing Materials (ASTM), Philadelphia, PA, 1991.
- [23] K. Nicholson, *Geothermal Fluids: Chemistry and Exploration Techniques*, Springer, Berlin, 1993.
- [24] *The Determination of Inorganic Anions in Water by Ion Chromatography*, Method 300.0, US Environmental Protection Agency (EPA), 1993.
- [25] P.R. Bevington, *Data Reduction and Error Analysis for Physical Sciences*, 1st ed., McGraw-Hill, New York, 1969.
- [26] L.E. Vanatta, D.E. Coleman, *J. Chromatogr. A* 770 (1997) 105.
- [27] W.A.J. Mahon, in: *Proceedings of the United Nations Symposium on the Development and Utilization of Geothermal Resources*, Pisa, 1970.