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Short communication

Determination of inorganic cations in brine solutions by ion chromatography

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Abstract

The method for analysis of inorganic cations in brine solutions was developed. Ion chromatography is a well-established and accepted technique in the determination of a variety of inorganic ions. However, there are significant complications when ion chromatography is used to determine trace concentrations of inorganic ions in brine matrices. The brine solution in our study was made to simulate the solution from the Waste Isolation Pilot Plant. Instrumental parameters such as eluent composition, flow-rates, and sample loop volumes were investigated to arrive at the optimum condition for the determination of the cations with minimal dilution. Separation was carried out in a Dionex CG12A/CS12A with 8.25 mM H₂SO₄ as eluent at 1.2 ml/min flow-rate. Our results indicated that ion chromatography is an accurate and a good alternative method for the analysis of cations in brine solution. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Brine; Inorganic cations

1. Introduction

More than 20 years ago, the US National Academy of Science recommended the disposal of radioactive wastes in deep geologic salt beds and as a result US Congress authorized the Waste Isolation Pilot Plant (WIPP). WIPP is a full-scale pilot plant designed to demonstrate the safe, cost-effective and permanent disposal of transuranic radioactive wastes [1]. The facilities include excavated rooms, 266 meters underground in an ancient stable salt formation. The US Department of Energy (DOE) is using laboratory tests together with computer modeling to demonstrate WIPP's validity as a permanent disposal solution. Los Alamos National Laboratory (LANL) and Sandia National Laboratories were selected to conduct an actinide source-term waste test program (STTP) to predict actinide concentrations. Analytical

results obtained from STTP will provide an understanding of the chemical behavior of the actinides under conditions similar to those found in the WIPP disposal rooms.

Ion chromatography (IC) has been shown to be a reliable method for the determination of cations in water samples [2]. In the presented work IC was used for determination of trace ammonium and the alkali/alkaline-earth metal cations in brine solution. The brine solutions have high concentrations of Na⁺ and Mg²⁺, lower quantities of K⁺ and Ca²⁺, and trace amounts of Li⁺, Cs⁺, Rb⁺, NH₄⁺, and Sr²⁺. Simulated brine solutions from the Salado (Brine A) and Castile (Brine B) formation at WIPP were the pertinent brine solutions used in this research. Brine A is 7 M in ionic strength (MgCl₂) and Brine B is 5 M in ionic strength (NaCl). Method development investigated the effects of the different sample loop volumes and eluent concentrations in the determination of the cations. A target detection limit of

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0.02–0.05 mg/l was also a part of the focus in this investigation.

The aim of this work was to establish the optimum conditions for the successful determination of the nine cations (Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , and Sr^{2+}) in brine solution.

2. Experimental

2.1. Instrumentation

The experiments were conducted with a Dionex DX500 ion chromatographic system (Dionex, Sunnyvale, CA, USA). The system consisted of GP40 gradient pump with automated membrane eluent degassing, a conductivity detector (EG40) and an automated sampler (AS40). Five milliliter sample vials with filter caps with no pre-treatment were used throughout the experiment. A cation self-regenerating suppressor (4 mm CSRS) was used to minimize background conductivity and enhance analyte conductance in the recycle mode. The separations were carried out on an IonPac CS12A cation-exchange column (250 mm \times 4 mm I.D.) with an IonPac CG12A guard column (50 mm \times 4 mm I.D.) at a flow-rate of 1.2 ml/min. All the instrument control,

data collection and data processing were performed with the PeakNet Chromatography station.

2.2. Reagents

Solutions were prepared from analytical-grade reagent chemicals in 18 M Ω water, obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Dilute working solutions were prepared from commercially available (SPEX) 1000 mg/l stock standards of sodium, ammonium, potassium, cesium, rubidium, calcium, magnesium, strontium, and lithium. Seawater standard solution was prepared from commercially available (high purity) standards. Sulfuric acid (J.T. Baker) was used for eluent preparation. All standards, samples, and reagents were prepared and stored in polyethylene containers that were previously rinsed with millipore water.

3. Results and discussion

3.1. Injection volume and eluent concentration

In the initial stages, the effect of the injection volume or the sample loop size and eluent concentration were investigated. Results indicated that

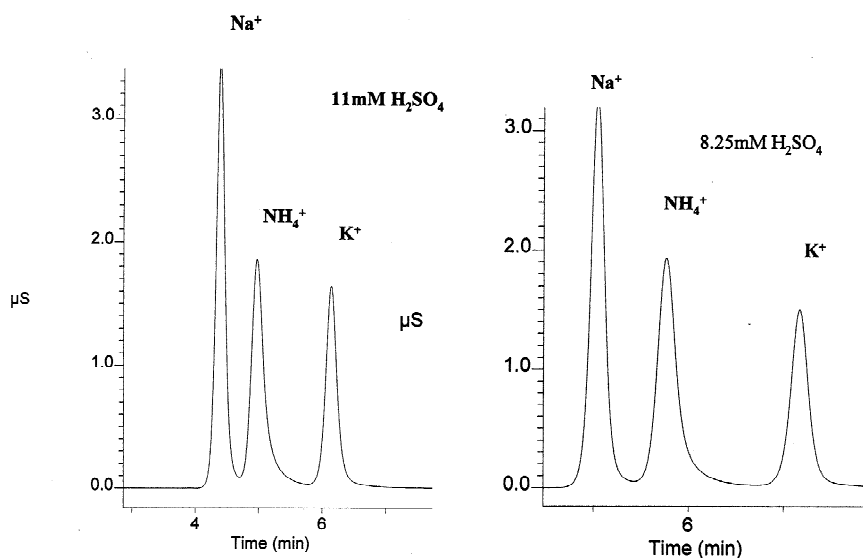


Fig. 1. Separation of ammonium and sodium at different eluent concentration.

Table 1
Effect of eluent concentration on retention time

Eluent conc. (mM)	Retention time (min)				
	Na	NH ₄	K	Mg	Ca
11	4.21	4.8	6.03	8.72	10.56
10.5	4.32	4.91	6.19	9.36	11.36
9.9	4.45	5.07	6.37	10.19	12.4
9.35	4.59	5.25	6.8	10.69	13.25
8.25	4.93	5.68	7.36	13.17	16.4

the 50 μl loop has 2.1 times greater sensitivity over the 25 μl loop. The loop sizes did not seem to have an effect on the limit of detection (LOD). A slight co-elution was observed between the Na⁺ ion and NH₄⁺ ion. We expected a high Na⁺ ion concentration and a low NH₄⁺ ion concentration. The resolution between the two peaks was increased by varying the concentration of the eluent and this result is shown in the plot of concentration of eluent vs. retention time in Fig. 1. Table 1 shows the different retention times obtained when the concentration of the eluent was varied. The 11 mM concentration of the eluent was the manufacturer's suggested concentration to obtain

the different separations. There was an increase in retention time when the eluent concentration was decreased from 11 mM H₂SO₄ to 8.25 mM H₂SO₄. This resulted in a better separation between the Na⁺ ion and the NH₄⁺ ion (Fig. 1) and also between the Mg²⁺ and the Ca⁺ ions (Fig. 2). We came to the conclusion that 8.25 mM H₂SO₄ was the optimum condition to obtain a better separation and better resolution for all the cations within less than 20 min.

A gradient elution technique is an effective way of separating ions of diverse affinities. Divalent cations are very strongly retained during cation-exchange chromatography. The nine standards (0.1 to 1.0 mg/l) and samples were analyzed by a suppressed gradient elution method using 8.25 mM to 11 mM H₂SO₄ gradient in 20 min (Fig. 3). A linear least-squares best-fit regression analysis was used in the multilevel calibrations. The NH₄⁺ ion did not fit the regression model thus it was necessary to use a second order polynomial fit. Approximate limits of detection (defined as three times the signal-to-noise ratio) obtained were in the range of 0.02–0.2 mg/l and percent recoveries between 95% and 102%. Table 2 contains the summary of calibration results.

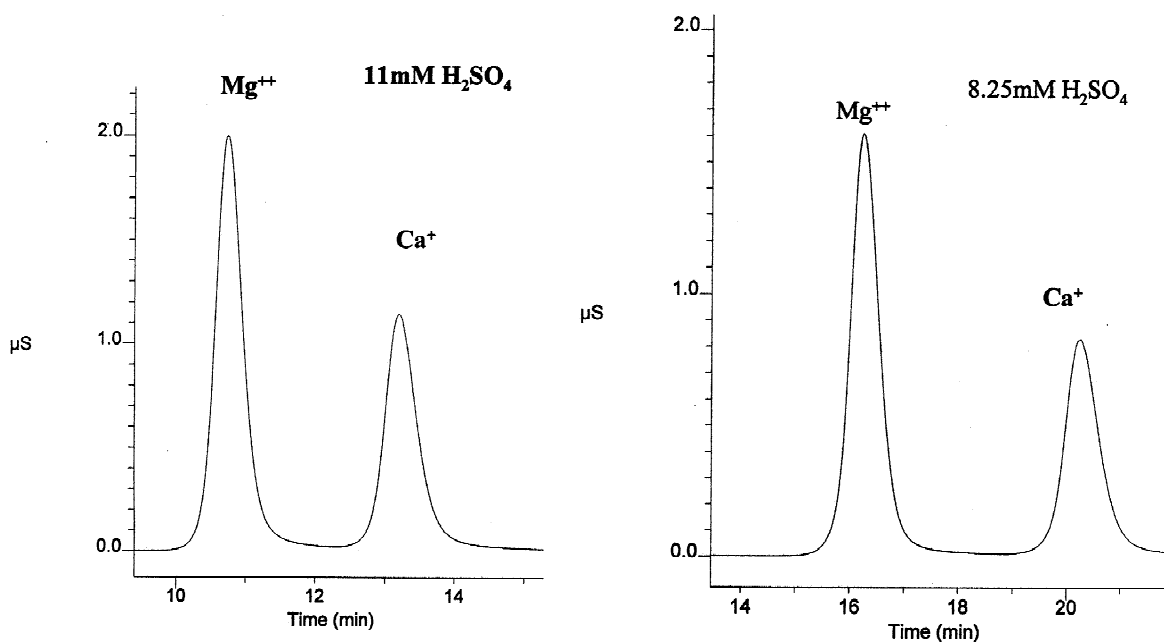


Fig. 2. Separation of magnesium and calcium at different eluent concentration.

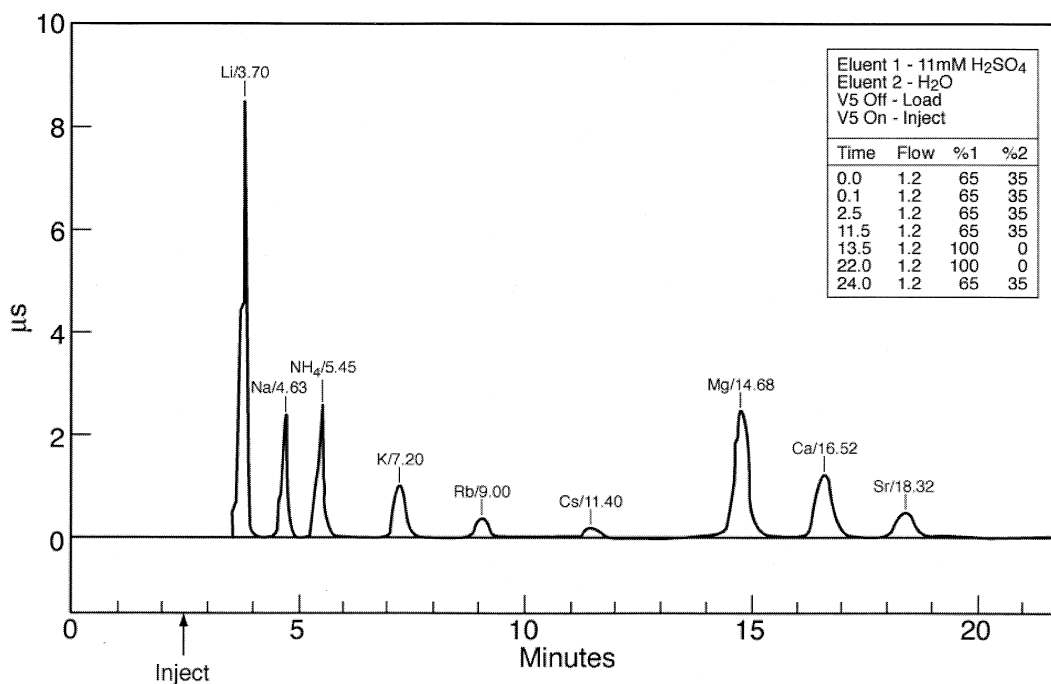


Fig. 3. Chromatogram of gradient analysis.

3.2. Brine results

Under the conditions selected, the brine solutions were analyzed and seawater was used for comparison. No additional sample pretreatment, other than dilutions (v/v) was required. Inductively-coupled plasma optical emission spectroscopy (ICP-OES) has been the predominant technique for trace

metal analysis [3]. A comparison of results obtained by IC and ICP-OES is shown in Table 3. Table 4 shows the results obtained using different sample loop volumes. The recoveries of all cations are comparable to each other at each sample loop size. The 1 μ l sample loop required the most minimal dilution.

Table 2

Calibration results

Li, Na, K, Rb, Cs, Mg, Ca, and Sr

Linear range (mg/l)	0.1–1.0
Approx. LOD (mg/l)	0.02–0.2
Recoveries (%)	95–102

NH₄⁺

Second order polynomial fit	
Calibration range (mg/l)	0.1–1.0
Approx. LOD (mg/l)	<0.1
Recoveries (%)	95–102

4. Conclusions

A successful method for the simultaneous determination of lithium, sodium, ammonium, potassium, rubidium, cesium, calcium, magnesium and strontium in brine solution is reported. The results indicated a good recovery of the different cations by ion chromatography. Even though ICP-OES has been the predominant technique for trace metal analysis, IC gave a comparable result and a good alternative method. This method enabled accurate and reliable analysis of cations in brine solutions. With this investigation, the recovery of sodium, potassium,

Table 3
Comparison of IC results with ICP-OES

	Mg		Ca	
	IC	ICP-OES	IC	ICP-OES
Brine A	<i>n</i> =4	<i>n</i> =6	<i>n</i> =4	<i>n</i> =6
Average conc (mg/l)	33815	34237	704	489
Standard deviation	77	342	4	20
True value	34860	34860	601	601
Brine B	<i>n</i> =8	<i>n</i> =6	<i>n</i> =4	<i>n</i> =6
Average conc (mg/l)	510	435	477	361
Standard deviation	26	9	55	19
True value	462	462	470	470
Seawater	<i>n</i> =13	<i>n</i> =4	<i>n</i> =10	<i>n</i> =4
Average conc (mg/l)	1267	1360	401	431
Standard deviation	68	9	25	4
True value	1254	1254	401	401

Table 4
Recoveries of cations with different sample loop sizes

	Recovery (%)			
	Na	K	Mg	Ca
1 μ l Sample loop				
Brine A (<i>n</i> =8)	100.0 \pm 5.5	90.6 \pm 6.2	90.0 \pm 4.2	108.6 \pm 3.8
Brine B (<i>n</i> =8)	99.6 \pm 6.0	103.0 \pm 3.9	103.2 \pm 3.6	102.8 \pm 4.9
Seawater (<i>n</i> =12)	99.1 \pm 4.6	103.8 \pm 5.3	101.4 \pm 5.5	100.3 \pm 6.2
3 μ l Sample loop				
Brine A (<i>n</i> =2)	118.7 \pm 0.1	109.9 \pm 0.1	93.2 \pm 0.6	93.2 \pm 0.6
Brine B (<i>n</i> =2)	117.5 \pm 0.1	109.1 \pm 0.4	102.5 \pm 0.1	107.2 \pm 0.5
Seawater (<i>n</i> =7)	103.7 \pm 1.5	108.0 \pm 2.2	104.7 \pm 2.2	106.3 \pm 1.1
5 μ l Sample loop				
Brine A (<i>n</i> =2)	101.2 \pm 0.1	97.3 \pm 0.1	83.0 \pm 0.4	126.9 \pm 2.2
Brine B (<i>n</i> =2)	102.9 \pm 0.4	112.0 \pm 0.1	98.1 \pm 0.4	101.5 \pm 0.4
Seawater (<i>n</i> =5)	101.8 \pm 0.8	113.8 \pm 1.1	104.5 \pm 1.3	105.0 \pm 2.7

calcium and magnesium was excellent using a small sample volume and minimal dilution of the brines.

Acknowledgements

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