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Application News

No. HPLC-047

Ion Chromatography

Brine Analysis Pt. 1: Determination of Commonly Found Cations in Geological Brine Samples

■ Introduction

Brine, or high-concentration salt water (>100,000 mg/L TDS), contains common salts such as sodium chloride, calcium chloride and magnesium chloride. Natural brines may occur from a variety of sources such as in ground water, in salt lakes, or as seawater. Brine samples from natural sources are often analyzed and used to determine environmental and human health impacts as well as in understanding mineral commodities. This study utilizes a non-suppressor ion chromatography method using the Prominence IC to successfully separate common cations and detect their presence in geological brine samples.

■ Experimental

Equipment

Experiments were performed using a modular Shimadzu LC system consisting of:

- CBM-40 lite system controller
- DGU-403 degassing unit
- LC-20Ai pump with automatic rinsing kit
- SIL-20AC autosampler with inert kit
- CTO-40S column oven
- CDD-10Avp conductivity detector
- LabSolutions chromatography software

Prominence Ion Chromatograph

Columns

- Shodex IC YS-50, 4.6 x 125mm (Part number: 220-91524-06)
- Guard column, IC YS-G, 4.6 x 10mm (Part number: 220-91524-07)

Materials

Methane sulfonic acid was obtained from Sigma-Aldrich. A mixed standard containing 50ppm Lithium (Li+), 200ppm Sodium (Na+), 400ppm Ammonium (NH4+), 200ppm Potassium (K+), 200ppm Magnesium (Mg2+), and 1000ppm Calcium (Ca2+) was obtained from Inorganic Ventures. Three different geological brine samples were provided by Aquatech International LLC. Deionized water with resistivity equal to or greater than 18 megaohm (MΩ) per cm was obtained from an in-house lab water purification system.

Eluent Preparation

Preparation of 1 L of 5mM methane sulfonic acid was prepared by pipetting 324µL of 99% methane sulfonic acid in deionized water and dilute to 1L.

Sample and Standards Preparation

All samples were filtered through 0.45 µm PES syringe filters, discarding the first 1 mL of the effluent. Samples were diluted 1000x using deionized water with resistivity equal to or greater than 18.0 megaohm (MΩ) per cm and prepared in a final volume of 1mL. Working standards at different concentrations were prepared by diluting from the commercial stock standard using degassed deionized water with resistivity equal to or greater than 18 megaohm (MΩ) per cm.

Method Conditions

Column:	Shodex IC YS-50, 4.6 x 125mm
Eluent:	5mM methane sulfonic acid
Flow rate:	1.0mL/min
Oven:	40C
Inj. Vol.:	10µL
System Backpressure:	~1102psi
Conductance:	< 40µs/cm

■ Results and Discussion

In this study, cations were detected by non-suppressed conductivity. Figure 1 shows the separation results of six cation standards using the method conditions outlined in the previous section. As shown by the figure, this method can be used to effectively separate six cations. The system backpressure remained constant at approximately 1102 psi over 200 injections at 1mL/min flow rate.

Figures 2-4 show sample chromatogram data for the detection of lithium, sodium, potassium, magnesium, and calcium in geological brine samples. All cations are eluted in less than 12 minutes following the outlined method conditions.

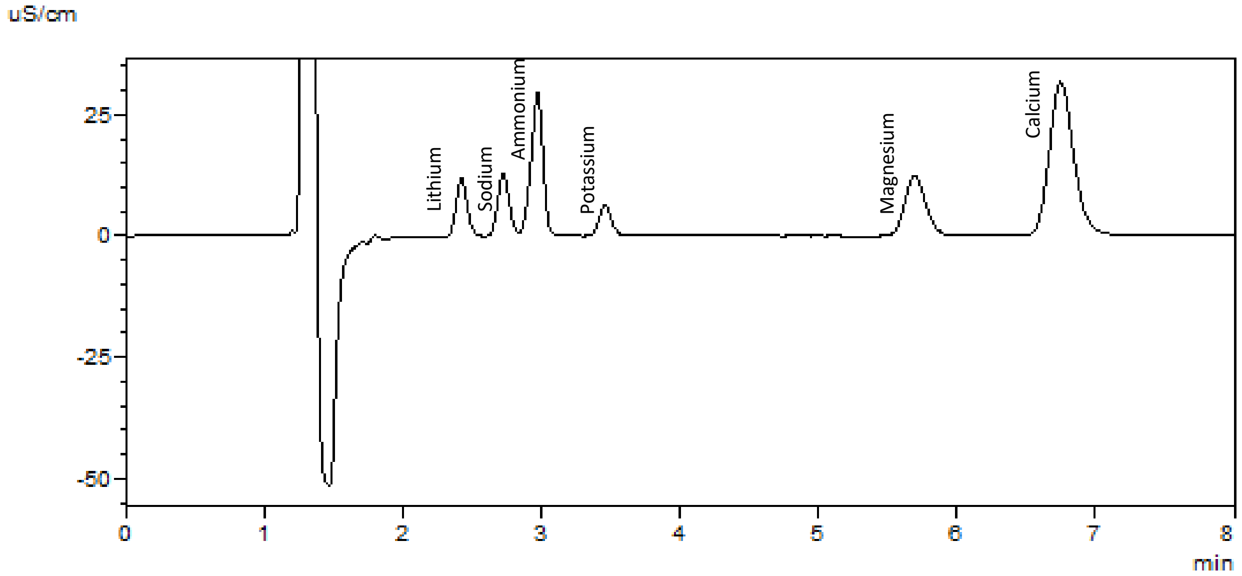

Figure 1: Separation of six common cation standards using the Shodex IC YS-50 column.

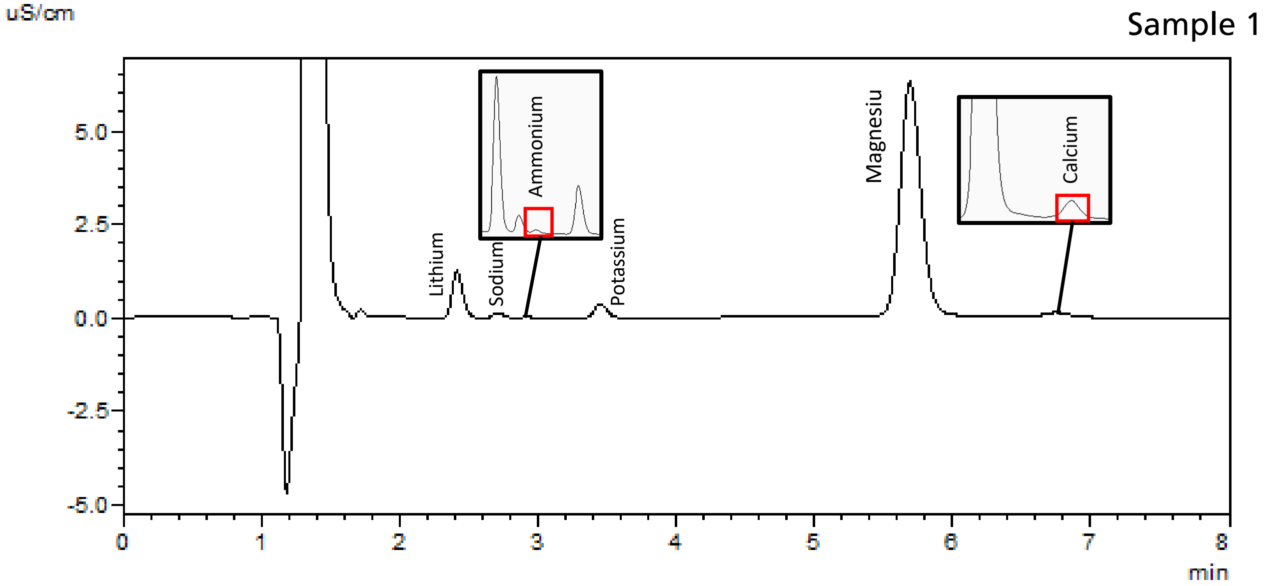

Figure 2: Detection of common cations in geological brine sample 1 (injection volume 10 µL). Additional sample chromatograms using sample volume of 100 µL are shown (inset) for the detection of ammonium and calcium.

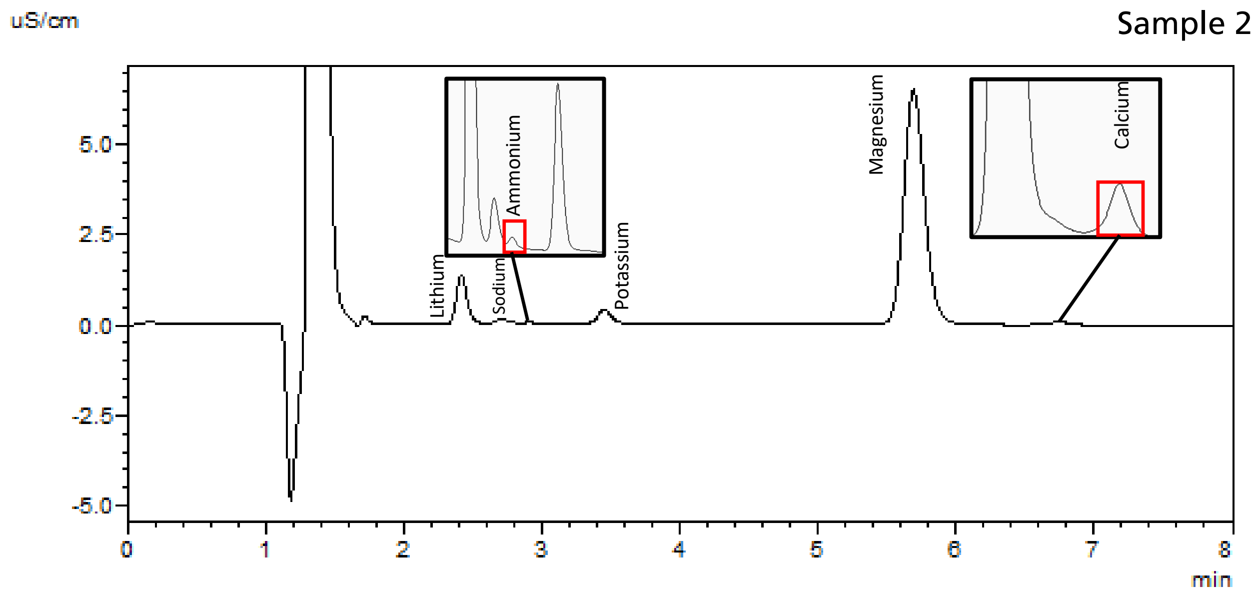

Figure 3: Detection of common cations in geological brine sample 2 (injection volume 10 µL). An additional sample chromatogram using sample volume of 100 µL is shown (inset) for the detection of ammonium.

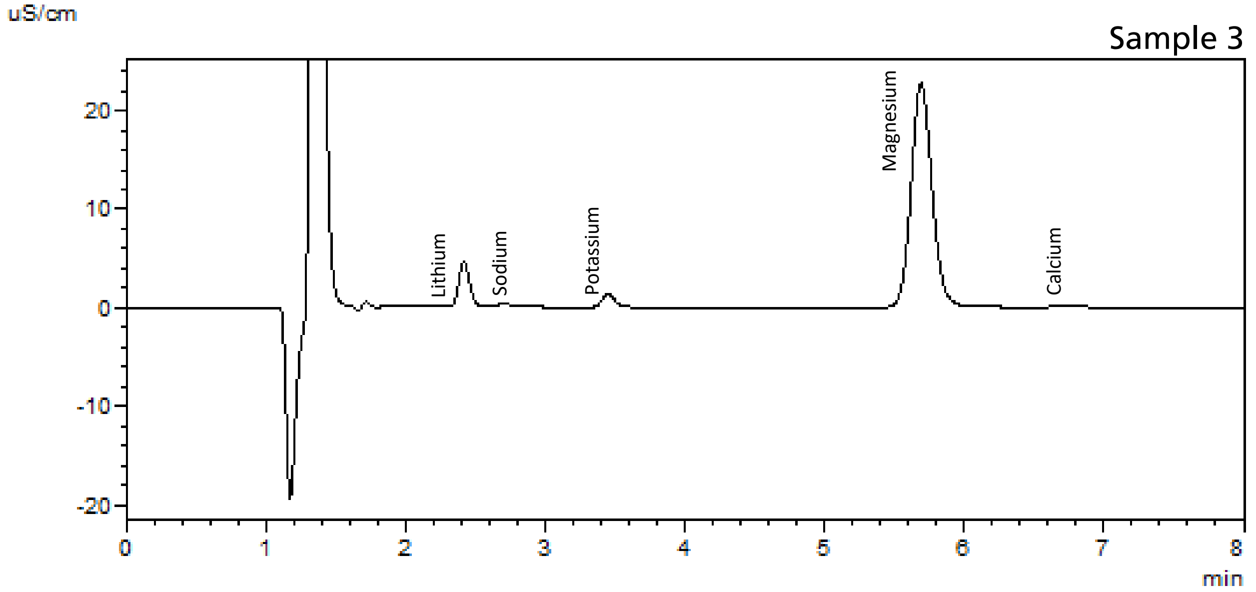

Figure 4: Detection of common cations in geological brine sample 3 (injection volume 10 µL). An additional sample injection of 100 µL was done for ammonium but no ions were detected.

Linearity, Limit of Detection, and Limit of Quantitation

A series of seven calibration standards across the concentration range of 0.025-3.75 ppm for lithium, 0.1-10 ppm for sodium, 0.2-20 ppm for ammonium, 0.1-15 ppm for potassium and magnesium, and 0.5-75 ppm for calcium respectively were used for a linearity study. As shown in Figure 5 and Table 1, excellent linear response with coefficient of determination (R^2) greater than 0.999 was obtained for all six cations. The next part of the application note will show the analysis of anions in the same brine samples.

LOD was calculated as 3.3s/m and LOQ as 10s/m where s is the standard deviation from three injections and m is the slope of the calibration curve linear equation. The linear calibration range, linearity, LOD, and LOQ are shown in table 1.

Repeatability

Method precision was performed using a mixed standard with a concentration of 2.5 ppm for lithium, 50 ppm for sodium, ammonium, and magnesium, 15 ppm for potassium and 25 ppm for calcium. Tables 1 and 2 show peak area precision of six cations from five injections of the mixed standard. As shown in the table, excellent reproducibility was achieved for peak area.

The concentration of cations present in brine samples shown in table 2 was determined using the calibration data and accounting for the dilution factor.

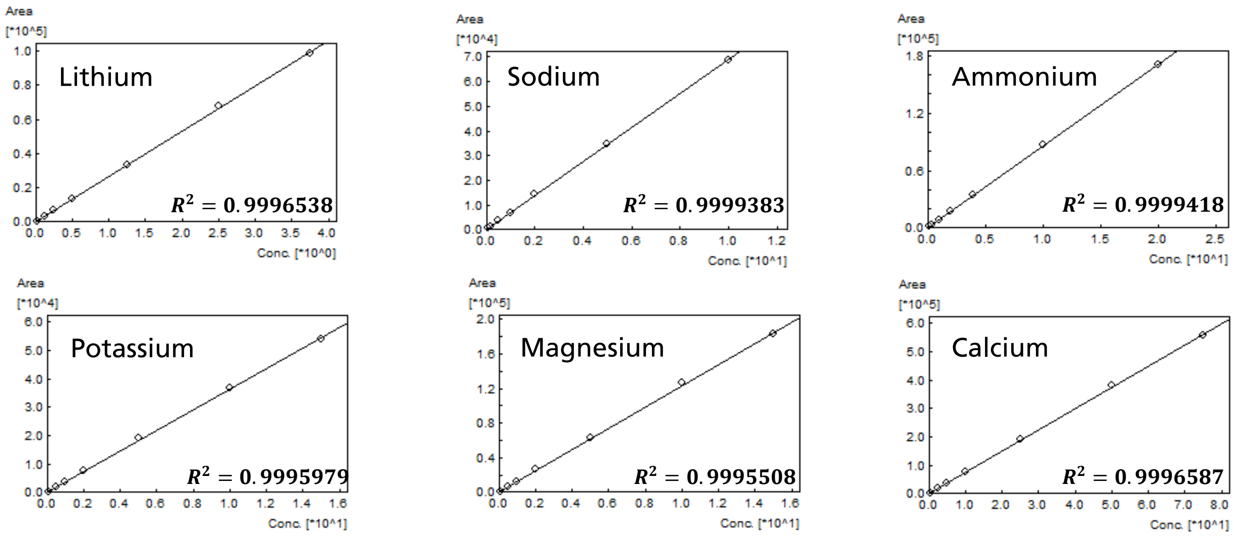

Figure 5: Calibration curves for 6 cations commonly found in brine samples.

Table 1: Linear calibration range, linearity (coefficient of determination), LOD, and LOQ

Cations	Calibration Range (ppm)	Linearity (R^2)	LOD (ppm)	LOQ (ppm)	%RSD Peak Area
Lithium	0.025-3.75	0.9996538	0.01	0.02	0.038401
Sodium	0.1-10	0.9999383	0.01	0.02	0.207603
Ammonium	0.2-20	0.9999418	0.01	0.02	0.118427
Potassium	0.1-15	0.9995979	0.03	0.08	0.235862
Magnesium	0.1-15	0.9995508	0.01	0.04	0.060162
Calcium	0.5-75	0.9996587	0.06	0.17	0.071696

Table 2: Concentration of cations present in brine samples

Cations	Cation Conc. (ppm)		
	Sample 1	**Sample 2**	**Sample 3**
Lithium	246	257	920
Sodium	72	56	246
Ammonium	72*	57*	Not detected
Potassium	601	602	2231
Magnesium	5243	5435	19296
Calcium	1647*	220	174

*Sample injection volume of 100µL to be within LOQ range.

■ Conclusion

This study demonstrates precise and reliable performance of Shimadzu's high-resolution IC system using a non-suppressor method for the determination of common cations, including lithium, sodium, ammonium, potassium, magnesium, and calcium, in geological brine samples.

Acknowledgement

We would like to thank Aquatech International LLC for agreeing to have us use their brine samples for this study.

First Edition: September 2023

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