Elemental Analysis of Brine Samples used for Lithium Extraction

Sebastian Sannac[1], Marc-Andre Gagnon[2]
[1]Agilent Technologies, Inc., France
[2]Agilent Technologies, Inc., Canada

EWCPS 2023
We 20

Agilent
Trusted Answers

Introduction

Increasing demand for lithium

Lithium (Li) is a key raw material in the production of high density, rechargeable batteries and battery packs. To keep pace with increased production of Li-ion batteries (LIBs) more Li is needed.[1]

Sources of Li include:

- Mining solid lithium minerals from the ground in the form of spodumene, lepidolite, and petalite (Figure 1).
- Pumping lithium rich brine from underground aquifers.
- Extracting lithium from salt lake and seawater brines.

Brines are the focus of this study.

Fig. 1. Lithium mine.

Fig. 2. Undiluted brines.

Application aim and analytical challenge

Suppliers of battery-grade Li and Li-compounds need to determine a few key elements in brines before extraction of Li.

The analysis is challenging by ICP-based techniques, due to the high total dissolved solid (TDS) content, high density, and likely presence of algae and undissolved particles in the brine samples.

Solution

Fitting the Agilent 5800 Vertical Dual View (VDV) ICP-OES with an Advanced Valve System (AVS 7) switching valve provides stable measurements while reducing instrument exposure to solids in high TDS samples, reducing excessive maintenance and minimizing carry-over.[2]

Experimental

Instrumentation

In this study, B, Ca, Li, Mg, Mn, Si, K, and Sr were determined in supernatant brine samples containing 15-25% NaCl (Figure 2) using the 5800 VDV ICP-OES fitted with an AVS 7 and SPS 4 autosampler.
The 5800 ICP-OES sample introduction system consisted of a SeaSpray nebulizer, double-pass cyclonic spray chamber and a 1.8 mm I.D. demountable injector torch. Instrument operating conditions are given in Table 1.

Figure 3. Agilent 5800 ICP-OES and ICP Expert software.

Parameter	Setting	Parameter	Setting
Viewing Mode	Radial	Plasma Flow (L/min)	13.5
Read Time (s)	5	Nebulizer Flow (L/min)	0.7
Replicates	3	Viewing Height (mm)	8
Sample Uptake Delay (s)	0	Sample Pump Tubing	PVC white-white
Stabilization Time (s)	20	IS Tubing	PVC orange-green
Pump Speed (rpm)	12	Waste Pump Tubing	Blue-blue
RF Power (kW)	1.45	Background Correction	Fitted
Auxiliary Flow (L/min)	1.6		

Table 1. ICP-OES instrument operating conditions.

The instrument and software features beneficial to this application include:

- Early Maintenance Feedback (EMF) diagnostics that tracked instrument usage throughout and alerted the analyst when maintenance was required (Figure 4).
- Extended dynamic range with MultiCal: brine contains elements at high-ppb to percentage levels, so the ICP-OES needs a wide linear dynamic range (LDR) to avoid excessive sample dilution steps and avoid remeasurements. The Agilent Vista Chip III detector of the 5800 provides full wavelength coverage enabling many elements to be measured using more than one wavelength. Since different wavelengths have different sensitivities, a combination of wavelengths can be used for the same element.
- The IntelliQuant Screening function in ICP Expert software that was used to screen samples (Figure 5). Knowing the elemental composition of the samples helped determine the calibration range and dilutions required.[3]

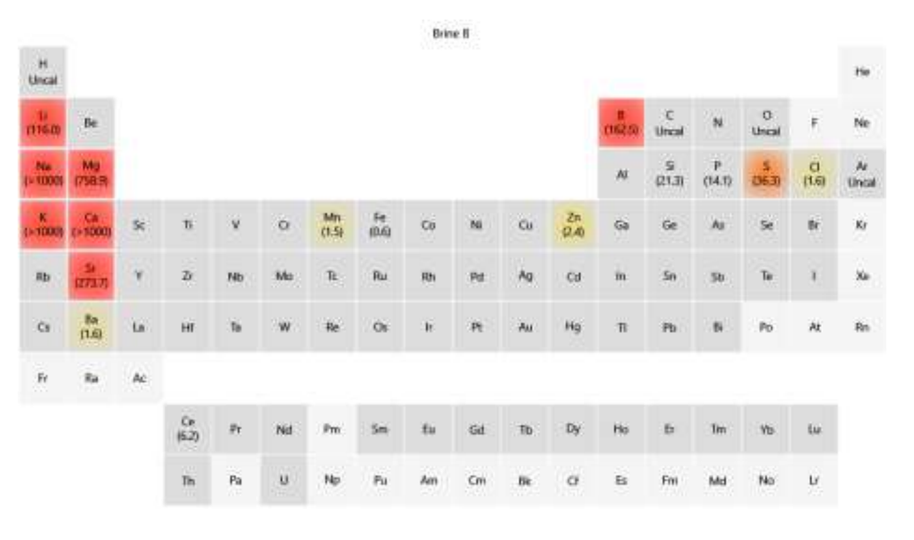

Figure 5. IntelliQuant heat map of a brine sample, showing semiquantitative concentrations of elements in the sample.

Experimental

Sample preparation

Seven supernatant brine samples were diluted 1:20 and 1:100 gravimetrically in 5% HNO_3. Typically, calibration standards are matrix-matched with high-concentration NaCl. However, this is time-consuming and cannot account for the variability of matrices encountered in real Li brine samples, where the concentration varies from 15-25%.

Internal standard mix

A carefully-selected internal standard (IS) mixture (Table 2) was used to correct for physical matrix interferences and was added in-line using the seventh port of the AVS 7.

Element	Concentration (mg/L)
Sc	5
In	25
Rb	75

Table 2. Concentration of elements in internal standard mix.

This IS mixture also corrects for ionization interferences, such as easily ionized element (EIE) effects, caused by the large amount of NaCl in the samples.

Radial view mode also reduces EIE interferences, so is typically used for the analysis of Li brines.

Calibration and linear dynamic range

Brine samples contain elements at high-ppb to percentage levels, so the method needs to provide a wide linear dynamic range (LDR).

The Vista Chip III detector of the 5800 allows full wavelength coverage, enabling many elements to be measured using more than one wavelength. As different wavelengths often have different sensitivities, a combination of wavelengths can be used for the same element.

The MultiCal function within the ICP Expert software was used to create multiple calibration ranges for Na, Mg, and Ca – a quick and effective way to extend the LDR without any trade-off in performance.

Results and Discussion

Method detection limits (MDLs)

MDLs were determined by 10 measurements of a 1% NaCl sample, spiked with the target analytes at 20 ppb. The MDL was calculated as three times the standard deviation of the concentration determined for each element, multiplied by the dilution factor (Table 3).

Element and Wavelength	MDL (mg/L)	Element and Wavelength	MDL (mg/L)
B 249.678	0.005	Mn 257.610	0.0006
*Ca	0.003	S 171.972	0.019
K 766.491	0.129	Si 251.611	0.008
Li 670.783	0.004	Sr 216.596	0.004

Table 3. MDLs for elements in a synthetic 1% NaCl solution spiked at 20 ppb. **Combination of wavelengths used for MultiCal calibration.*

Spike recovery test

A spike recovery test was conducted on a real brine sample diluted 1:20 and spiked with target elements at 1 ppm. Since Na, Ca, Cl, K, and S are present in brine at percentage levels, they were not included in the test. As shown in Table 4, all recoveries were within $\pm$10%, demonstrating the accuracy of the method for the determination of the target elements in brine.

Element and Wavelength	Conc in Li Brine (mg/L)	Li Brine + Spike (mg/L)	Recovery (%)
B 249.678	99.3	117.4	91
Li 670.783	70.0	88.2	91
*Mg	714	733	95
Mn 257.610	0.963	19.5	93
Si 251.611	0.958	21.1	101
Sr 216.596	340	361	105

Table 4. Spike recovery data in a Li brine sample.

Quantitative analysis

All elements of interest were quantifiable (above the MDL), as shown in Table 5. The resulting solutions had a TDS of about 1%.

	Brine 1 Concentration (mg/L)			Brine 2 Concentration (mg/L)			Brine 3 Concentration (mg/L)		
Element, Wavelength	1:20	1:100	RPD (%)	1:20	1:100	RPD (%)	1:20	1:100	RPD (%)
Li 670.783	108.3	105.0	3.0	48.5	49.5	2.2	28.8	28.8	0.3
Mn 257.610	0.920	0.883	4.1	0.411	0.388	5.7	0.655	0.641	2.1
Sr 216.596	573	545	4.9	117	117	0.6	71.1	69.7	2.1
Mg*	884	860	2.8	1118	1130	1.1	260	263	1.2
K 766.491	4567	4609	0.9	3533	3806	7.4	1499	1523	1.6
Ca*	25782	24812	3.8	4444	4495	1.1	1591	1577	0.9
B 249.678	175	165	5.6	47.1	47.2	0.2	36.5	36.7	0.6
Si 251.611	23.8	22.2	6.9	4.56	4.35	4.8	3.01	3.13	4.0

Table 5. Average quantitative data in three brine samples at two dilutions and relative percentage difference (RPD). **Combination of wavelengths used for MultiCal calibration.*

Results and Discussion

Long-term stability

To assess the stability of the 5800 ICP-OES, 360 solutions were measured over 10 hours without recalibration. A QC solution was measured every 10 samples.

Figure 6 shows the recovery of all elements to be within ±3%, with no QC failures.

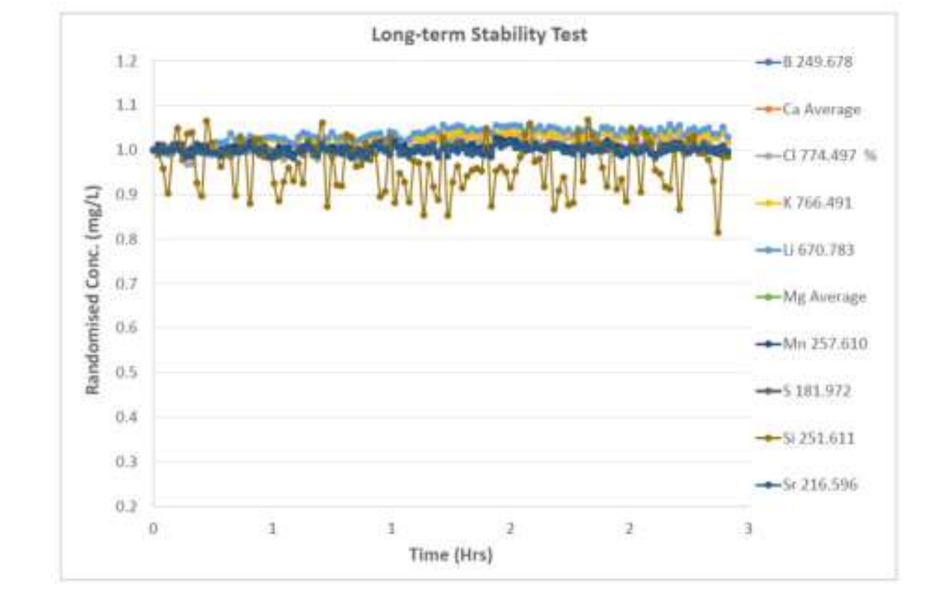

Figure 6. Long term stability data.

Conclusions

Accurate, robust measurements of elements in brines can be performed using the Agilent 5800 ICP-OES

The Agilent 5800 VDV ICP-OES fitted with an ASV switching valve was used for the quantitative analysis of multiple elements in Li brine samples, yielding excellent results.

Method development was greatly simplified and streamlined using smart tools included in the instrument software:

- IntelliQuant Screening
- MultiCal
- Early Maintenance Feedback (EMF)

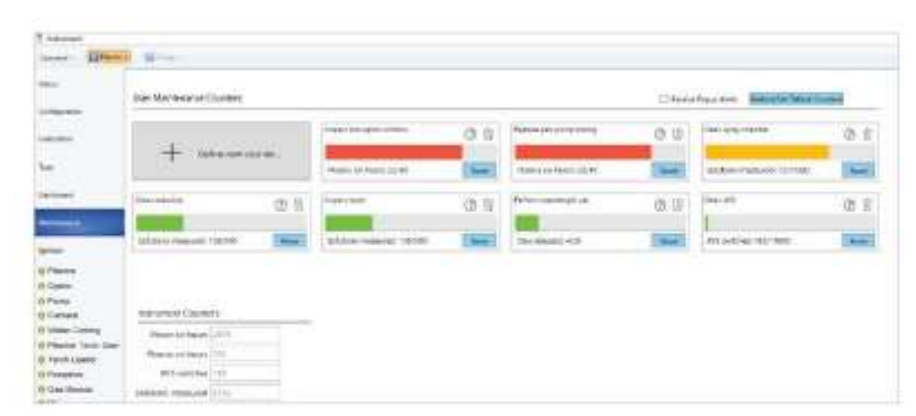

Figure 4. EMF uses a traffic light system to show which maintenance activities should be done immediately (red) and which can wait (green). EMF also ensures that consumables are only replaced when needed.

The study demonstrates that a good compromise between speed, detection limits, carryover management, and sample preparation can be achieved with real-life Li brine samples.

References

1. Xu, C., Dai, Q., Gaines, L. *et al.* Future material demand for automotive lithium-based batteries. Commun Mater, 1, 99 2020.
2. Reduce Costs and Boost Productivity with the Advanced Valve System (AVS) 6 or 7 Port Switching Valve System, Agilent publication 5991-6863EN
3. Agilent IntelliQuant Screening: Smarter and quicker semiquantitative ICP-OES analysis, 5994-1518EN
4. Quantification of Key Elements in Lithium Brines by ICP-OES, 5994-4868EN

DE91532041