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Elemental Analysis of Brine Samples used for Lithium Extraction

Fast, robust analysis of high matrix samples using the Agilent 5800 ICP-OES with AVS 7 switching valve

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Introduction

The demand for lithium (Li) is increasing rapidly due to its importance in the production of high density, rechargeable batteries (*1*).

Li-ion batteries are used in consumer electronics, such as laptops, mobile phones, game consoles, tools, and drones, and electric vehicles (EVs), motorcycles, bicycles, and wheelchairs. And, as countries move away from reliance on fossil fuels for energy production, large-scale battery storage is needed to store the energy produced by renewable energy plants. To meet the expected rise in demand for higher-purity Li, more will need to be extracted from existing or new sources, including seawater brines and lithium-containing underground brines.

To improve the performance of batteries, manufacturers are demanding higher purity raw materials. Suppliers of Li and Li-compounds need to determine the content of some key elements in seawater brine before extraction, in order to manage the extraction process and the quality of the final product. However, the measurement is challenging for ICP-based analytical techniques, due to the high total dissolved solids (TDS) content, high density of the solutions, and likely presence of algae and undissolved particles in the brine. Any undissociated matrix in high TDS samples may deposit on the sample introduction system or quench the plasma, impacting the long-term stability of measurements.

Robust instrumentation is needed for the routine elemental analysis of large numbers of high matrix brine samples. The Agilent 5800 ICP-OES uses a vertical plasma torch and a solid-state radio frequency (SSRF) generator operating at 27 MHz to create a plasma with the stability needed for the analysis of brines.

Fitting the ICP-OES with an Agilent Advanced Valve System (AVS 7) switching valve reduces instrument exposure to solids in high TDS samples. The accessory also minimizes carry-over from sodium and prevents excessive torch devitrification. The AVS greatly reduces the frequency of instrument cleaning and extends the lifespan of parts. The switching valve also delivers fast analysis times—only 73 s sample-to-sample in this study—which is relatively rapid for sample types that are notorious for carry over.

In this study, a 5800 Vertical Dual View (VDV) ICP-OES was used to measure key elements (B, Ca, Cl, K, Li, Mg, Mn, Na, S, Si, Sr) in supernatant 15–25% NaCl brine samples, with the samples being diluted with 5% HNO_3 before measurement.

Experimental

Instrumentation

All measurements were performed using a 5800 VDV ICP-OES fitted with a SeaSpray glass concentric nebulizer, double-pass cyclonic spray chamber, and an Agilent easy-fit demountable VDV torch with a 1.8 mm injector. The instrument was configured with an integrated AVS 7 seven-port switching valve and an Agilent SPS 4 autosampler. The AVS 7 uses a high-speed positive displacement pump to rapidly fill the sample loop, speeding up the analysis, and reducing argon consumption (2). The valve also reduces the maintenance and cleaning requirements of the torch and nebulizer, as lower sample volume passes through the sample introduction system compared to conventional sampling.

The Agilent Vista Chip III detector of the 5800 provides high-speed continuous wavelength coverage from 167 to 785 nm, ensuring that a suitable, interference-free line can be found for most analytes. There is no time penalty when adding extra wavelengths for an element to the analysis. The wide range of the detector enables both major (e.g., Mg and Ca) and trace elements (e.g., Mn and Si) to be analyzed at the same time, within the same sample, avoiding the need to perform multiple dilutions.

An internal standard mixture containing Sc (5 ppm), In (25 ppm), and Rb (75 ppm) was added in-line using the seventh port of the AVS 7. The internal standards were used to correct for the matrix and non-spectral interferences caused by the large amount of NaCl in the samples.

Agilent ICP Expert software with IntelliQuant Screening and Early Maintenance Feedback (EMF) was used to provide valuable insights into the samples and track instrument operational performance (3–5). Instrument and method parameters are given in Table 1 and the AVS 7 settings are given in Table 2.

Table 1. Agilent 5800 VDV ICP-OES instrument and method parameters.

Parameter	Setting
Viewing Mode	Radial
Read Time (s)	5
Replicates	3
Sample Uptake Delay (s)	0
Stabilization Time (s)	20
Pump Speed (rpm)	12
RF Power (kW)	1.45
Aux Flow (L/min)	1.6
Plasma Flow (L/min)	13.5
Nebulizer Flow (L/min)	0.70
Viewing Height (mm)	8
Sample Pump Tubing	PVC white-white
Internal Standard Pump Tubing	PVC orange-green
Waste Pump Tubing	Blue-blue
Background Correction	Fitted

Table 2. Agilent AVS 7 switching valve parameters.

Parameter	Setting
Sample Loop Size (mL)	1
Pump Rate - Uptake (mL/min)	25
Pump Rate - Inject (mL/min)	10
Valve Uptake Delay (s)	7.7
Bubble Inject Time (s)	2.5
Pre-emptive Rinse Time (s)	2
Rinse Time (s)	20

IntelliQuant Screening was used during method development to determine the approximate concentration of elements in some of the brine samples. This information helps determine the calibration range and any dilutions required. The software generates a periodic table heat map to visually represent the relative concentration of elements present in a sample. Elements present at low concentrations are shown in yellow, medium concentrations are shown in orange, and high concentrations are shown in red. Figure 1 shows a heat map for a diluted brine sample.
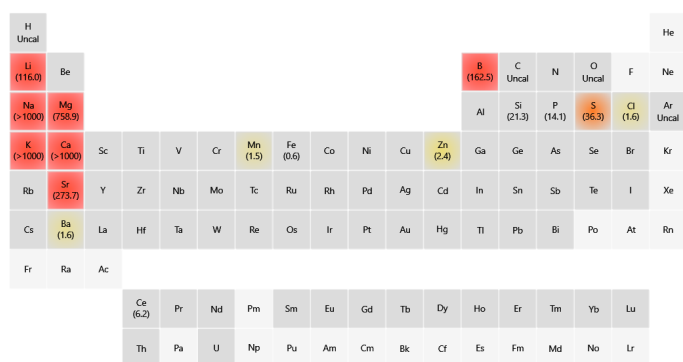
Figure 1. IntelliQuant heat map of a brine sample, showing the relative concentrations of elements in the sample.

Sample preparation

Seven supernatant brine samples were diluted 1:20 and 1:100 gravimetrically in 5% HNO_3 to avoid accuracy issues arising from performing volumetric dilution of high-density samples. Typically, matrix-matched calibration standards that contain a high-concentration of NaCl (similar to what is found in the sample) are recommended when dealing with brine solutions. However, this approach is time-consuming and cannot efficiently account for the great variability of matrices encountered in real Li brine samples, where the NaCl concentration varies from 15 to 25%. The strategy adopted in this work relies on the careful selection of an internal standard (IS) mixture to correct for physical matrix interferences. The IS mixture also corrects non-spectral interferences, such as easily ionized element (EIE) effects, caused by the large amount of NaCl in these samples. Also, radial view mode reduces the EIE interferences, so is typically used for the analysis of Li brines.

Calibration and linear dynamic range

Calibration standards were prepared in 5% HNO_3 from Agilent stock solutions:

– Agilent multi-element calibration mix 2 and majors mix.

– Agilent 1000 ppm single element stock solutions for Li, Sr, B , and Si.

– Agilent 1% single element stock solutions for Na, Ca, and S.

For the quantification of chlorine, two NH_4Cl calibration standards were prepared at 1.25 and 5% (w/v) in 5% HNO_3. Details of the calibration standards for each element and calibration correlation coefficients are given in Table 3.

Table 3. Concentration of calibration standards mg/L, (except for Cl, which is %), the calibration correlation coefficients, and the internal standard used for each element.

Element	Concentration of Standard															Correlation Coefficient	Internal Standard
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		
B						1	10									1.00000	In 325.609
Ca				10			100	250	500	1000	2000					0.99999	Sc 361.383
Cl														0.75%	1.25%	0.99989	-
K				10			100	250	500							0.99989	Rb 780.026
Li	0					1	10									1.00000	Rb 780.026
Mg				10	100											1.00000	In 230.606
Mn	0	1	5													1.00000	Sc 361.383
Na				10	100		100	250	500	1000	2000					0.99996	Rb 780.026
S												10	100			1.00000	In 325.609
Si						1	10									0.99999	In 325.609
Sr						1	10	50								1.00000	In 230.606

Brine samples contain 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 sample remeasurements. The Vista Chip III detector of the 5800 provides 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. For example, calcium has emissions of different intensities at the wavelengths: 317.933, 315.887, and 318.127 nm, with corresponding sensitivities of 0–100, 0–1000, and 0–2000 ppm, respectively. 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

Both Na and Cl were initially quantified in all brine samples and the equivalent NaCl concentration was estimated from these results. It was found that the median brine concentration was of the order of 20%. Therefore, a 1% NaCl solution is representative of the brine sample matrix upon a 20-fold dilution in 5% HNO_3.

Method detection limits (MDLs) were determined by ten measurements of a 1% NaCl sample, spiked with the target analytes at 20 ppb. The MDL was calculated as three standard deviations of the concentration determined for each element, multiplied by the dilution factor (Table 4).

Table 4. Method detection limits for elements in a synthetic 1% NaCl solution spiked at 20 ppb.

Element and Wavelength (nm)	MDL (mg/L)
B 249.678	0.005
*Ca	0.003
K 766.491	0.129
Li 670.783	0.004
*Mg	0.0007
Mn 257.610	0.0006
S 171.972	0.019
Si 251.611	0.008
Sr 216.596	0.004

Combination of wavelengths used for MultiCal calibration.

Quantitative analysis

Seven real brine samples were diluted 1:20 and 1:100 and then analyzed by the 5800 ICP-OES equipped with an AVS 7. A 1:20 dilution was used to attenuate any matrix effects, as well as the viscosity differences between samples. Even under such conditions, all elements of interest can still be quantified (above the MDL), as shown in Table 5. The resulting solutions had a TDS of about 1%.

Table 5. Average quantitative data for B, Ca, Cl, K, Li, Mg, Mn, Na, S, Si, and Sr in seven representative brine samples.

Element, Wavelength (nm)	Brine Sample Concentration (mg/L)						
	1	2	3	4	5	6	7
B 249.678	175	47.1	36.5	50.1	129	126	125
*Ca	25782	4444	1591	24812	7993	7550	7578
Cl 774.497	56 929	48 900	54 454	45 522	75 166	70 574	72057
K 766.491	4567	3533	1499	5586	2479	2347	2346
Li 670.783	108.3	48.5	28.8	64.8	76.2	72.3	71.8
*Mg	884	1118	260	1943	827	790	786
Mn 257.610	0.920	0.411	0.655	0.077	0.804	1.23	0.746
*Na	67 411	40 264	73 664	66 957	75 166	92 193	93560
S 181.97	420	80.8	789	982	150	143	149
Si 251.611	23.8	4.56	3.01	2.94	0.673	0.977	1.38
Sr 216.596	573	117	71.1	151	413	394	392

Combination of wavelengths used for MultiCal calibration.

The Na levels in brine samples is typically >5%, and the concentration is still in the high range after a 20-fold dilution. For this reason, a 1:100 gravimetric dilution was used to quantify Na, as well as all other elements of interest, in the brine samples. Viscosity and matrix effects are greatly minimized at high dilution. Therefore, comparison with the 1:20 data is a good indicator of how efficient the internal standard is to compensate for these effects at high TDS. The results for all elements were reproducible, with relative percentage differences (RPD) mostly between 0.2 and 8% (*6*). Therefore, the RPD data confirmed the efficiency of the internal standard elements to compensate for viscosity differences between the samples and EIE effects as well as the accuracy of the method at 1% TDS.

The design of the AVS 7 contributed to the performance of the method at 1% TDS. In-line introduction of an internal standard is typically carried out by merging two peristaltic pump tubings using a "Y" fitting. This approach can sometimes be problematic when dealing with high TDS samples because of a viscosity mismatch between the sample and the internal standard solution. The mismatch prevents proper mixing of the internal standard elements with the sample solution preventing adequate correction. To overcome this challenge, the AVS 7 has a premix chamber that enables proper mixing of the internal standard solution with the sample before it reaches the nebulizer.

Spike recovery test

To further evaluate the 5800 VDV ICP-OES method, 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 6, all recoveries were within ±10%, demonstrating the accuracy of the method for the determination of the target elements in brine.

Table 6. Spike recovery data in a Li brine sample.

Element and Wavelength	Concentration 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

*Combination of wavelengths used for MultiCal calibration.*

Stability test

To demonstrate the robustness of the 5800 ICP-OES, 120 samples were measured continuously over 2.5 hours (73 s per sample). A 1:20 diluted synthetic 20% NaCl sample containing all elements at concentrations that are representative of real brines was used for the measurements. The mean, standard deviation, and %RSD of the measurements were calculated, as shown in Table 7 and Figure 2. The results show the excellent stability of the method for the analysis of high matrix brine samples over an extended period. The most challenging scenario would be Si, as its concentration typically ranges from 0.05–1 ppm in brine samples. At a 20-fold dilution, the concentration is in the low range (still above MDL). Measurement conditions were not especially optimized for a trace amount of Si as this element isn't typically commercially important. Therefore, the 6% variability of a trace element over 2.5 hours at 1% TDS is still considered satisfactory.

Table 7. Stability of the measurement of elements in 120 synthetic 20% NaCl (1:20) samples, analyzed over 2.5 hours (73 s per sample) by the Agilent 5800 ICP-OES and AVS 7 switching valve.

Element and Wavelength	Mean Concentration (mg/L)	Standard Deviation	RSD (%)
B 249.678	95.2	0.77	0.8
*Ca	6629	40	0.6
K 766.491	1246	14	1.1
Li 670.783	69.3	1.02	1.5
*Mg	681	5.3	0.8
Mn 257.610	0.9	0.01	0.7
Si 251.611	1.10	0.07	6.2
Sr 216.596	324	2.5	0.8

Combination of wavelengths used for MultiCal calibration.
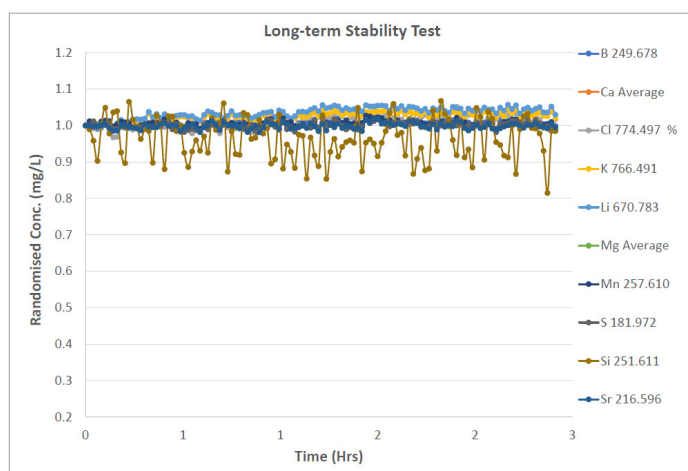
Figure 2. Stability of the measurement of elements in 120 synthetic 20% NaCl (1:20) samples analyzed over 2.5 hours (73 s per sample) by the Agilent 5800 ICP-OES fitted with an AVS 7 switching valve.

Conclusion

The Agilent 5800 VDV ICP-OES fitted with an Agilent AVS 7 sampling valve was used to analyze key elements in real brine samples.

Rather than prepare matrix-matched calibration standards, an internal standard was used to compensate for the physical matrix and non-spectral interferences at the high TDS levels present in brine samples. The matrix tolerance, robustness, and accuracy of the method was demonstrated by the excellent recoveries of key elements as well as a long-term stability experiment.

The 5800 ICP-OES method provides a practical compromise between sample preparation, speed, sensitivity (DLs), and matrix carryover management for the analysis of real 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**. https://doi.org/10.1038/s43246-020-00095-x

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 Software: For greater sample insight and simplified method development, Agilent publication 5994-1516EN

4. Agilent IntelliQuant Screening: Smarter and quicker semiquantitative ICP-OES analysis, Agilent publication 5994-1518EN

5. Early Maintenance Feedback for ICP-OES: Programmed notifications of instrument maintenance requirements, Agilent publication 5994-2164EN

6. Quantification of Key Elements in Lithium Brines by ICP-OES, Agilent publication 5994-4868EN

Agilent part numbers

G8010-60236	Easy-fit 1.8mm semi-demountable torch for 5000 series VDV/SVDV ICP-OES.
G8010-60256	Double-pass spray chamber, glass cyclonic design with ball joint socket and UniFit drain outlet, for Agilent 5000 series ICP-OES.
G8010-60255	Seaspray concentric glass nebulizer for 5000 series ICP-OES.
3710034400	Peristaltic pump tubing, white/white, 12/pk.
3710034600	Peristaltic pump tubing, blue/blue, 12/pk.
G8010-60305	Sample loop for AVS switching valve, 1.0 mL volume
6610030600	Agilent multi-element calibration mix 2 stock solution
6610030700	Agilent multi-element calibration majors mix stock solution
5190-8477	Agilent 1000 ppm single element stock solution for Li
5190-8527	Agilent 1000 ppm single element stock solution for Sr
5190-8254	Agilent 1000 ppm single element stock solution for B
ICP-314	Agilent 1000 ppm single element stock solution for Si
5190-8206	Agilent 1% single element stock solution for Na
5190-8369	Agilent 1% single element stock solution for Ca
5190-8433	Agilent 1% single element stock solution for S

www.agilent.com/chem/5800icp-oes