Application Brief

Mining, Energy and Chemicals

Agilent
Trusted Answers

Quantification of Key Elements in Lithium Brines by ICP-OES

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

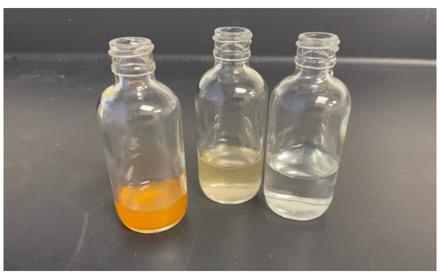

Figure 1. The lithium content of brine samples of varying concentrations was determined. Shown here are the undiluted samples.

Importance of lithium for battery technology

Countries are increasing investment in renewable electric power generation and high-capacity battery storage solutions as they move away from using fossil fuels for energy production. Lithium (Li) is a key raw material in the production of high density, rechargeable batteries and battery packs. To keep up with demand for Li-ion batteries, more Li will need to be extracted from new or existing sources. Due to its solubility as an ion, Li is present in seawater and is commonly obtained from salt-rich brines.

To improve the performance of batteries, manufacturers are demanding higher purity raw materials. So, suppliers of Li and Li-compounds need to determine a few key elements before extraction of Li. However, the application is challenging by ICP-based techniques, due to the high total dissolved solid (TDS) content, high density, and likely presence of algaes and undissolved particles in the brine samples. Any undissociated matrix in high TDS samples may deposit on the sample introduction system or quench the plasma, impacting the long-term stability of the instrument.

Evaluation of real brine samples using robust ICP-OES

Supernatant brine samples containing 15 -25% NaCl (shown in Figure 1) were diluted 1: 20 and 1:100 in 5% HNO_3. B, Ca, Li, Mg, Mn, Si, K, and Sr were then determined in both sets of samples using an Agilent 5800 Vertical Dual View (VDV) ICP-OES fitted with an AVS 7 switching valve and SPS 4 autosampler. To avoid time consuming preparation of matrix matched calibration standards containing a high amount of NaCl (similar to the sample), attention was given to the selection of the internal standard mixture. Internal standards are used to correct for physical matrix and non-spectral (easily ionized element (EIE)) interferences. 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.

Reduce instrument maintenance

Analyzing high matrix brine samples can be tough on the sample introduction system of ICP instrumentation. The AVS 7 introduces less sample to the ICP-OES, meaning that fewer solids in high TDS samples reach the instrument. The AVS therefore greatly reduces the frequency of cleaning and extends the lifespan of parts and consumables. The AVS also minimizes carry-over from Na and torch devitrification.

Early Maintenance Feedback (EMF) diagnostics alert the analyst when maintenance is required, using counters to track instrument usage (Figure 2). When using the 5800 ICP-OES with the AVS 7, the counters can be adjusted to allow more samples to be measured before the analyst receives a maintenance-alert.

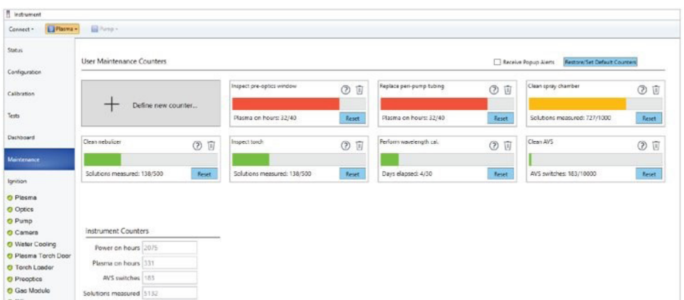

Figure 2. EMF uses a traffic light system to show which maintenance activities should be done immediately (red) and which can wait (green). EMF also ensures that consumables are only replaced when needed.

Extend the 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 often have different sensitivities, a combination of wavelengths can be used for the same element. The MultiCal function within the Agilent ICP Expert software was used to create multiple calibration ranges for Mg and Ca—a quick and effective way to extend the LDR without any trade off in performance.

Reproducible data in real samples

Three brine samples were diluted 1:20 and 1:100 and analyzed using the 5800 ICP-OES with AVS 7. The results for all elements were reproducible, with relative percentage differences between 0.2 and 7.4%, confirming the efficiency of the internal standard elements to compensate for viscosity differences between the samples and EIE effects. The reproducibility of the data also confirmed the accuracy of the method and the absence of matrix effects.

Table 1. Average quantitative data for Li, Mn, Sr, Mg, K, Ca, B, and Si in three representative brine samples at two dilutions and relative percentage difference (RPD) of the results.

	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

Combination of wavelengths used for MultiCal calibration.

Benefits of the Agilent 5800 ICP-OES in radial view mode for the analysis of real brine samples used for Li-extraction:

- The vertical ICP plasma and RF system handled samples with high TDS, enabling reproducible results for brines.
- The AVS 7 reduced maintenance and cleaning requirements of the torch, as less sample passed through the sample introduction system.
- Fast analysis times were achieved—73 s sample-to-sample, which is relatively rapid for a sample type notorious for carry-over.
- The extensive wavelength range of the Vista Chip III detector enabled MultiCal to increase the LDR of major elements by combining multiple calibration ranges.
- All samples were diluted and the entire concentration range was covered using MultiCal.
- No drift, clogging, or plasma quenching occurred measuring continuously 120 samples.

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.

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

DE27517618

Printed in the USA, July 19, 2022
5994-4868EN