



### Challenge

Direct and fast online analysis of brine samples (up to 300 g/L NaCl)

### Solution

HR ICP-OES equipped with high salt kit with exceptional matrix tolerance towards high salt matrices, high sensitivity, and industry leading high-resolution optical system

### Intended audience

Lithium exploration, mining and refining companies working with brine

## Online Analysis of Lithium in Brine Samples by HR-ICP-OES

### Introduction

Lithium-ion batteries are rechargeable batteries that use lithium ions as the main component of their electrolyte. Over the past two decades, the lithium-ion battery (LIB) has transformed the use of metals and minerals. The landscape is expected to change further as the LIB evolves from portable applications such as the mobile phone with a small 10 watt hour (Wh) pack, to the electric vehicle with a battery capacity of 50-100 kWh, to the monster energy storage system (ESS) with up to 100 MWh battery banks. The origin of lithium is thought to be the Big Bang, which is believed to have created the first atoms of hydrogen, helium, and lithium. Lithium is a relatively rare element in the Earth's crust and is typically found in mineral deposits such as spodumene, lepidolite, petalite, brine lakes, or even in groundwater and seawater. It is estimated that there are approximately 39 million tons of lithium on earth. Lithium brine is a type of saline solution containing high concentrations of lithium ions. Lithium brine deposits can be found in various parts of the world, including South America, North America, and Asia. The largest known deposits are

in the so-called lithium triangle, a region in South America around the borders of Argentina, Bolivia, and Chile. The process of extracting lithium from brine involves pumping the brine to the surface and allowing it to evaporate in large evaporation ponds. As the water evaporates, the concentration of lithium increases, and the lithium can then be extracted using various chemical processes. Lithium brine has therefore become an increasingly important source of lithium and is essential to meet the growing demand for batteries.

The continuous monitoring of lithium concentration in brine solutions by inductively coupled plasma optical emission spectroscopy (ICP-OES) provides very useful information about the performance of these materials in terms of adsorption capabilities but also about the kinetic adsorption of lithium. The online analysis gives a better understanding of the real-time monitoring of lithium concentration and therefore minimizes the risks of wrong assessment. Major challenges in the continuous measurement of lithium in brine samples include the high amount of total dissolved

solids (TDS), the speed of analysis required to have as much data as possible over long term runs (>24h), and the wide range of lithium content that can occur during each run. In order to successfully run high TDS samples over a long period of time with excellent accuracy, highly robust plasma and sample introduction systems are required. Otherwise, plasma-based fluctuations can lead to poor precision and blockages can occur in the nebulizer and torch injector tip. Sample throughput can be increased substantially by use of an injection valve. The presented methodology describes a

direct online analysis of brine samples for the continuous determination of lithium by the use of the high-resolution ICP-OES PlasmaQuant 9100 Elite system. The exceptionally high resolution allows for interference-free analysis of lithium in the demanding matrix of undiluted brine samples, up to 300 g/L NaCl. The dedicated introduction kit for high matrix samples, combined with the highly robust plasma of the high-frequency generator enable precise and accurate measurements of demanding matrices with LODs in the sub-ppb range.

## Materials and Methods

### Samples and reagents

The samples were lithiated bayerite extrudates specifically developed for lithium recovery in brine. The brine was an aqueous solution, containing several elements including Li, B, Na, Ca Mg, S, and Cl. This solution was injected into the column containing extrudates with a controlled flow rate and then pumped into a sampling station located on the autosampler to be constantly renewed. A measurement of lithium concentration every 30 seconds including the uptake, analysis, and rinse steps could be achieved using these conditions.

### Sample preparation

No sample preparation was required, the brine samples with 300 g/L NaCl were analyzed directly.

### Instrument settings

The PlasmaQuant 9100 Elite ICP-OES was used to carry out the measurements. It was combined with a 6-port injection valve (ASXPress Plus, Teledyne Cetac) to speed up the analysis and achieve the highest throughput. The salt kit, comprising a SeaSpray™ concentric nebulizer and a double pass cyclonic spray chamber, in combination with an alumina/Syalon torch, were mounted. The brine samples (300 g/L NaCl) were diluted 5-fold using a combination of various pump tubing inner diameters. A solution containing 1% (v/v) HNO<sub>3</sub> was used as a carrier solution, as the diluent and for the rinse (Figures 1–2). An external peristaltic pump was connected to the column and was utilized to constantly renew the sampling station located on the autosampler. An argon humidifier was connected to the nebulizer to avoid any potential blockage from the brine sample.

### Calibration

A matrix-matched calibration was used to avoid matrix effects. The standard solutions were prepared from a single standard solution (Li, 1 000 mg/L, Inorganic Ventures) and added to the brine solution. To cover the widest dynamic range and improve the accuracy over the full concentration range, two separate calibration curves were made, the first one ranging from 0.05 to 0.5 mg/L, the second one ranging from 10 to 100 mg/L. The same wavelength of Li (670.971 nm) with two different views, axial and attenuated radial (table 1) were used for this purpose.

Table 1: Concentration of calibration standards

Element	Line [nm]	Plasma View	Concentrations [mg/L]
Li	670.971	Axial	0.05 – 0.1 – 0.5
		Attenuated radial	10 – 20 – 100

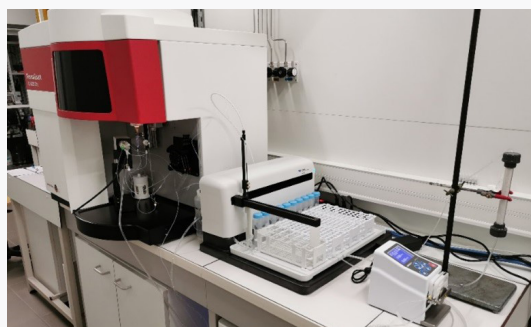


Figure 1: PlasmaQuant 9100 Elite and the accessories

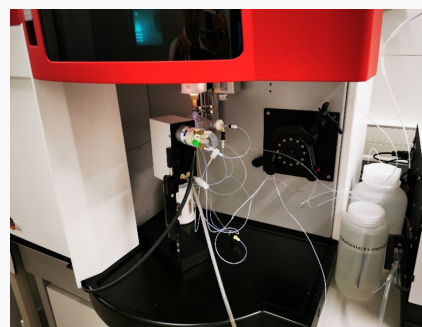


Figure 2: PlasmaQuant 9100 Elite and the accessories

The detailed system configuration and method settings are shown in table 2.

Table 2: Instrument settings

Parameter	Specification
RF power	1,400 W
Plasma gas flow	15 L/min
Auxiliary gas flow	1 L/min
Nebulizer gas flow	0.6 L/min
Pump rate	1 mL/min
Nebulizer	Concentric, SeaSpray™, 1.0 mL/min, borosilicate
Spray chamber	Cyclonic spray chamber with dip tube, 50 mL, borosilicate
Injector	2 mm, alumina
Outer tube/Inner tube	Syalon/alumina
Pump tubings	PVC, Orange/Green for the carrier solution (0.38 mm ID), Black/Black for the diluent (0.76 mm ID), Red/Red for the drain (1.14 mm ID)
Injection valve	Cetac ASXPress Plus
Sample loop volume	0.7 mL
Argon humidifier	Yes
Rinse delay	0 sec
External peristaltic pump	Yes, with adjustable flow rates
Torch position <sup>1</sup>	-2 mm

<sup>1</sup> Increasing distance between injector and plasma which reduces deposits at the injector tip

## Method and evaluation parameters

Table 3: Evaluation parameters

Element	Line [nm]	Plasma view	Integration	Read time [s]	Evaluation		
					Pixel	Baseline fit	Correction
Li	670.971	Axial	Peak	2	7	ABC <sup>1</sup>	auto
Li	671.971	Radial attenuated	Peak	2	7	ABC	auto

<sup>1</sup> Automated Baseline Correction

## Results and Discussion

The configuration put in place allows continuous measurements of the brine sample every 30 seconds. This time includes the sample uptake, analysis, and rinse spans. Before measuring the brine sample, calibration curves were made, both in axial and attenuated radial views (Figures 3 and 4). Besides the common radial and axial plasma observation modes, the PlasmaQuant 9100 Elite ICP-OES offers the options axial plus and radial plus, which attenuate the signal in the respective observation mode so that the linear dynamic range can be extended even further.

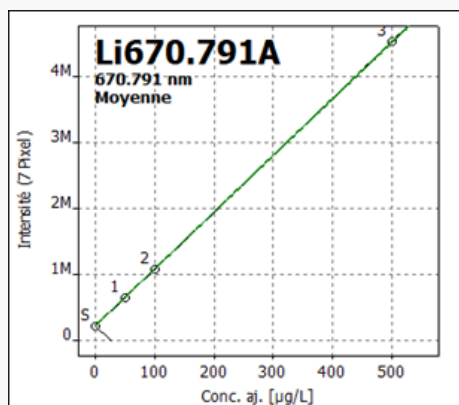


Figure 3: Calibration curve for Li using the axial view

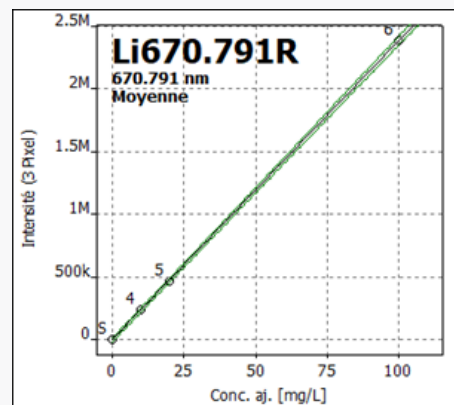


Figure 4: Calibration curve for Li using the attenuated radial view

The precision was evaluated by measuring the lithium concentration nine consecutive times in the brine samples. The data is shown in Table 4.

Table 4: Evaluation of the precision of the method

Measurement number	Lithium concentration [mg/L]
1	0.0287
2	0.0287
3	0.0283
4	0.0285
5	0.0284
6	0.0284
7	0.0284
8	0.0286
9	0.0286
<b>Mean [mg/L]</b>	<b>0.0285</b>
<b>RSD [%]</b>	<b>0.51</b>

An excellent repeatability (0.51% RSD) was achieved with a very short analysis time. The method limit of detection (MDL) was determined by running a brine sample at 300 g/L several times ( $n=11$ ), using 3 times the standard deviation of the measured value. An MDL value 0.3  $\mu\text{g/L}$  was calculated, showing the high sensitivity and the plasma robustness of the PlasmaQuant 9100 Elite in high salt matrices. Therefore, very precise lithium adsorption kinetics can be obtained for trace and higher concentrations of lithium.

In addition, the high resolution of the PlasmaQuant 9100 Elite provides a powerful tool for obtaining information regarding the isotopic composition of lithium. Indeed, the shape of the peak at 670.971 nm can provide useful information about the natural abundance state of Li or its potential enrichment in  $^6\text{Li}$  (Figure 5).

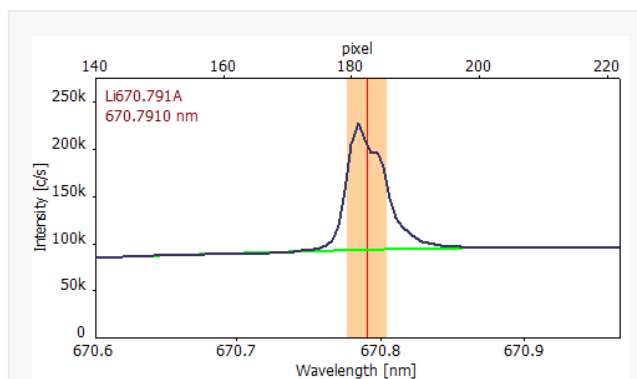


Figure 5: Lithium peak at 670.971 nm in a brine sample. The shape of the peak can provide information about the isotopic composition of the sample

## Summary

The analysis of samples such as brines is a highly demanding challenge. The high concentration of total dissolved solids (TDS) has a negative impact on signal stability and is a challenge for most instrumentation. Therefore, dilution is often required on such systems in order to guarantee signal stability, which is crucial if the small analyte signals are to be detected.

In contrast to other instrumentation, the PlasmaQuant 9100 Elite HR ICP-OES can run undiluted saline samples. Moreover, its industry-leading optical resolution and sensitivity allows for unmatched matrix specific limits of detection among ICP-OES instrumentation. The applied configuration allowed for the direct analysis of brine sample at 300 g/L with a lithium limit of detection of 0.3  $\mu\text{g/L}$ . The specific configuration that was mounted for this application and the very short integration times (2 sec) allowed a fast online measurement of the constantly renewed brine sample with a single analysis every 30 seconds, giving real-time information about the kinetic adsorption of lithium in such matrices.

The PlasmaQuant 9100 Elite's high spectral resolution (2 pm @ 200 nm) can provide very useful information about the isotopic composition of lithium in brine samples. Low and high contents of lithium can be analyzed during the same run by exploiting the wide working range offered



Figure 6: PlasmaQuant 9100 Elite

as DualView Plus by the PlasmaQuant 9100 Elite. Its high sensitivity, exceptional plasma robustness, and wide working range make it the ideal tool for the analysis of highly saline samples. The same setup can potentially be used for other elements in a wide range of applications, like wastewater monitoring, online process control, etc.

## Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9100 Elite	818-09101-2	High resolution ICP-OES
Salt Kit	810-88009-0	Kit included concentric nebulizer SeaSpray™
Teledyne Cetac ASX 560	810-88015-0	Next generation autosampler with integrated rinse function
Teledyne Cetac ASXPress Plus	810-88120-0	Fully automated and easy-to-install 6 port injection valve and vacuum pump unit
Argon humidifier	810-88033-0	Recommended for aqueous samples with high salt contents

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.

Trademark notice: The brand names of the third-party products specified in the application protocol are usually registered trademarks of the respective companies or organizations.

### Headquarters

Analytik Jena GmbH+Co. KG  
Konrad-Zuse-Strasse 1  
07745 Jena · Germany

Phone +49 3641 77 70  
Fax +49 3641 77 9279

info@analytik-jena.com  
www.analytik-jena.com

Version 1.0 · Author: PeRi, FISc  
en · 04/2023

© Analytik Jena | Picture © p. 1: Adobe Stock/Henner Damke