

Industrial

# Determination of lithium and other elements in brine solutions using ICP-OES

## Authors

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## Keywords

iCAP PRO Series, ICP-OES, Li-ion battery, brine solutions, robustness, lithium extraction

## Goal

To develop a robust methodology for the determination of a wide concentration range of lithium together with trace level measurement of other critical elemental contaminants in brine solutions using the Thermo Scientific™ iCAP™ PRO Series ICP-OES.

## Introduction

As part of the global initiative on sustainability and green energy, battery electric vehicles (BEVs) are rapidly gaining in popularity and their share of the vehicle market is expected to increase at least 10-fold over the next decade. After a few years of rapid growth, there are now more than 10 million electric cars on the road globally, and this is anticipated to rise to about 40 million in 2030 and up to 300 million by 2050.<sup>1</sup>

Currently, electric vehicles most often use batteries based on lithium-ion technology because of the high energy density of such batteries relative to their weight, their ability to undergo multiple charge / discharge cycles before significantly losing performance, and their relatively low cost. Since the late 1990s, advances in the performance of lithium-ion battery technology have mainly been driven by demand from portable electronics, laptop computers, mobile phones, and power tools. However, the rapid rise of BEVs and hybrid electric vehicles (HEVs) has intensified research and development of a new generation of batteries with greater robustness and higher charge capacity to significantly increase the achievable range of these vehicles between each charging cycle.

The rapidly increasing demand for Li-ion batteries has led to a critical need for exploration and development of additional natural resources of lithium as well as other commonly used elements in battery manufacturing, such as manganese, nickel, and cobalt. In addition to mineral sources, such as spodumene ore, underground brine reserves are also rich sources of lithium. There are various methods for extracting lithium from brine, including precipitation, liquid-liquid extraction, selective membrane separation, electrodialysis, and ion exchange adsorption.<sup>2</sup> With cost and efficiency taken into consideration, extraction of lithium ions from solutions by ion exchange adsorption is one of the most effective methods. The abundance of lithium in brine solutions can vary significantly in the concentration range of 10 mg·L<sup>-1</sup> or less to about 4,000 mg·L<sup>-1</sup> or more depending upon the geography of the source.

To assess the quality of brine solutions from the perspective of their lithium content and to determine the cost-effectiveness and efficiency of the extraction process, it is important to accurately measure lithium concentrations in brine extracts prior to establishing the extraction process. The concentration of other trace impurity elements present in the original brine itself, the lithium salts extracted from the brine, and the waste brine once the lithium has been extracted must also be determined, as these have an adverse impact on the quality of the material extracted during the process and can also have negative environmental impacts.

In this work, a comprehensive analytical method was developed and tested for analysis of brine solutions using the Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo instrument, operated using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. The main objective of this application note is to present the performance of the method developed in the study for laboratories working in the lithium extraction area or otherwise involved in measuring concentrated salt solutions such as brine.

## Experimental

### Instrument parameters and experimental conditions

In this study, an iCAP PRO XP ICP-OES Duo instrument equipped with a ceramic D-Torch and operated in axial Intelligent Full Range (iFR) and Radial iFR modes was used to analyze 19 analytes including lithium. Lithium was measured using radial viewing mode while the other trace elements were measured using the higher sensitivity axial view of the ICP-OES. Details of the sample introduction system components and instrument parameters used are given in Table 1. Automated sample introduction was carried out using a Teledyne CETAC ASX-560 autosampler.

A 10 mg·L<sup>-1</sup> yttrium internal standard solution, prepared in a matrix of 0.5% (v/v) nitric acid, was added online to correct for any drift or physical interferences such as signal suppression.

**Table 1. Instrument configuration and operating parameters**

Instrument parameter	Setting
Spray chamber	Baffled cyclonic
Nebulizer	Burgener Mira Mist
Pump tubing	Sample uptake: Tygon™ orange/white Drain: Tygon™ white/white
Torch injector tube	2.0 mm (ceramic)
Torch	Ceramic D-Torch Duo
Pump speed	45 rpm
Flush pump speed	100 rpm
Nebulizer gas flow	0.55 L/min
Auxiliary gas flow	1.5 L/min
Coolant gas flow	12.5 L/min
Additional argon gas flow	0.15 L/min
Plasma RF power	1,350 W
Replicates	3
Exposure time	Axial iFR – 10 s Radial iFR – 10 s
Radial viewing height	6 mm

Brine solutions containing 25% (w/w) sodium chloride were analyzed in this study. The analysis of samples containing high dissolved solids is often a challenge for ICP-OES instruments, and particularly so for dual view systems, because of problems such as salting up (leading to a blocked nebulizer or torch injector) and sample deposition on optical components (leading to signal drift and the need for increased instrument maintenance). However, innovative hardware adaptations for the iCAP PRO Series ICP-OES Duo instrument, such as its optimized vertical torch configuration, offer significantly improved matrix tolerance with an achievable robustness that is similar to that of radial view only instruments. The ability to also optimize the radial plasma viewing height for radially viewed elements enables accurate and precise measurement of analytes in the presence of high amounts of easily ionizable elements such as sodium in the sample matrix. Deposition of salts at the nebulizer tip during long analytical runs was avoided by using a Burgener Mira Mist™ nebulizer, and to prevent salting up of the torch injector, an additional flow of argon gas was introduced at a flow rate of 0.15 L·min<sup>-1</sup> around the sample aerosol with the help of a sheath gas adaptor (for more information on the instrument configuration used, please refer to application note AN44470).<sup>3</sup>

## Sample and standard preparation

The samples used in this study were prepared using commercially available sodium chloride salt. To simulate the typical matrix of brine solutions, a 25% (w/w) solution of sodium chloride was prepared by dissolving 25 g of salt in 100 g of distilled water. All samples were then acidified at 0.5% (v/v) using nitric acid prior to analysis.

To tackle matrix-related challenges and avoid physical and spectral interferences, the approach of matrix-matched calibration standards was followed in the study. All calibration standards were prepared in the same matrix as the samples using a 25% (w/w) solution of pure sodium chloride. A mixed stock solution of 10 mg·L<sup>-1</sup> of the trace level analytes was prepared in 2% (v/v) nitric acid, which was then gravimetrically diluted to yield calibration standards with the concentrations given in Table 2. A lithium standard stock solution of 10,000 mg·L<sup>-1</sup> concentration was added appropriately in the same calibration solutions to prepare lithium standard solutions

with the concentrations given in Table 2. Trace level analytes were calibrated in the concentration range of 0.01 to 1 mg·L<sup>-1</sup>, while lithium was calibrated in the range of 10 mg·L<sup>-1</sup> to 5,000 mg·L<sup>-1</sup>.

## Calibration linearity and instrument detection limits

Instrument detection limits and calibration line correlation coefficients for all the measured analytes obtained during the linearity study are given in Table 3, together with the wavelength and plasma viewing mode used for each analyte. Instrument detection limits were calculated based on 10 replicate measurements of the calibration blank solution and the slope achieved for each individual analyte calibration line. Excellent detection limits and calibration linearity were achieved for all the analytes measured, as shown in Table 3. In this case, all brine samples were analyzed directly without any sample preparation steps or any sample dilution performed prior to analysis. Hence, the instrument detection limits achieved also represent the method detection limits (MDLs).

Table 2. List of target elements and their concentrations in the calibration standards (mg·L<sup>-1</sup>)

Elements	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6	Standard 7
Al, As, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, Si, Sr, S, Zn	0.01	0.05	0.1	0.25	0.5	1	-
Li	10	100	1,000	2,000	3,000	4,000	5,000

Table 3. List of analytes, wavelengths, measurement mode, correlation coefficients, and method detection limits (mg·L<sup>-1</sup>)

Element	Wavelength (nm)	Plasma view	R <sup>2</sup>	MDL (mg·L <sup>-1</sup> )
Al	167.079	Axial	0.9998	0.0011
As	189.042	Axial	0.9995	0.0141
Ba	455.403	Axial	0.9996	0.0001
Cd	226.502	Axial	0.9994	0.0010
Ca	393.366	Axial	0.9993	0.0011
Cr	267.716	Axial	0.9998	0.0014
Co	228.616	Axial	0.9999	0.0041
Cu	324.754	Axial	0.9995	0.0017
Fe	238.204	Axial	0.9996	0.0003
Pb	220.353	Axial	0.9997	0.0151
Mg	279.553	Axial	0.9996	0.0014
Mn	257.610	Axial	0.9997	0.0005
Hg	184.950	Axial	0.9999	0.0023
Ni	231.604	Axial	0.9997	0.0066
Si	251.611	Axial	0.9995	0.0061
Sr	421.552	Axial	0.9998	0.0001
S	80.731	Axial	0.9999	0.0981
Zn	213.856	Axial	0.9997	0.0008
Li	610.362	Radial	0.9994	0.0578

## Method accuracy

The accuracy of the entire analytical setup was assessed by measuring an independently prepared QC standard containing  $0.5 \text{ mg}\cdot\text{L}^{-1}$  of the trace level analytes and  $3,000 \text{ mg}\cdot\text{L}^{-1}$  of Li. The QC sample was analyzed every 10 samples throughout the entire analytical run of 11 hours. Figure 1 shows the percentage accuracy level for all the measured trace level analytes, and Figure 2 presents the accuracy of the Li measurement in the periodically analyzed QC samples. As can be seen, the accuracy observed for all analytes was found to be in the range of 90% to 110% throughout the whole analytical run.

To check the method performance against its intended purpose of accurate Li measurement over a wider range of concentrations, Li was spiked into unknown brine samples at relatively low concentration levels of  $10 \text{ mg}\cdot\text{L}^{-1}$  and  $100 \text{ mg}\cdot\text{L}^{-1}$

and the percent recovery calculated. Accurate measurement of Li at lower concentrations in brine is as important as being able to measure high Li concentrations, as the ability to achieve lower-level detection is vital for ensuring that efficient Li extraction has been achieved after processing the brine solutions. Extraction efficiency can be easily assessed by analyzing the original brine solution after the extraction process. Table 4 shows spiked concentrations and percent recovery observed for lithium in this additional study. The recovery presented is the average value calculated from six replicate measurements of each spiked sample analyzed at different intervals over the 11-hour duration of the analytical run. The observed average recovery for Li was found to be in the range of  $100\pm 5\%$  with a relative standard deviation of less than 5%.

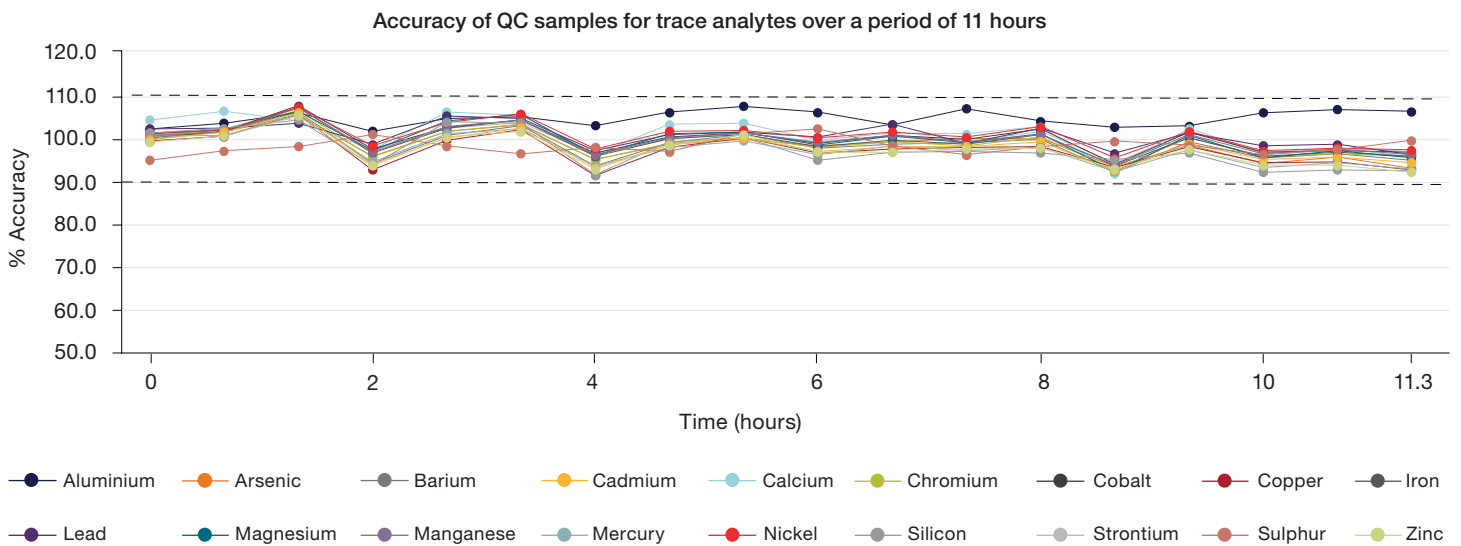


Figure 1. Percent accuracy observed for QC standards containing  $0.5 \text{ mg}\cdot\text{L}^{-1}$  of the trace level analytes

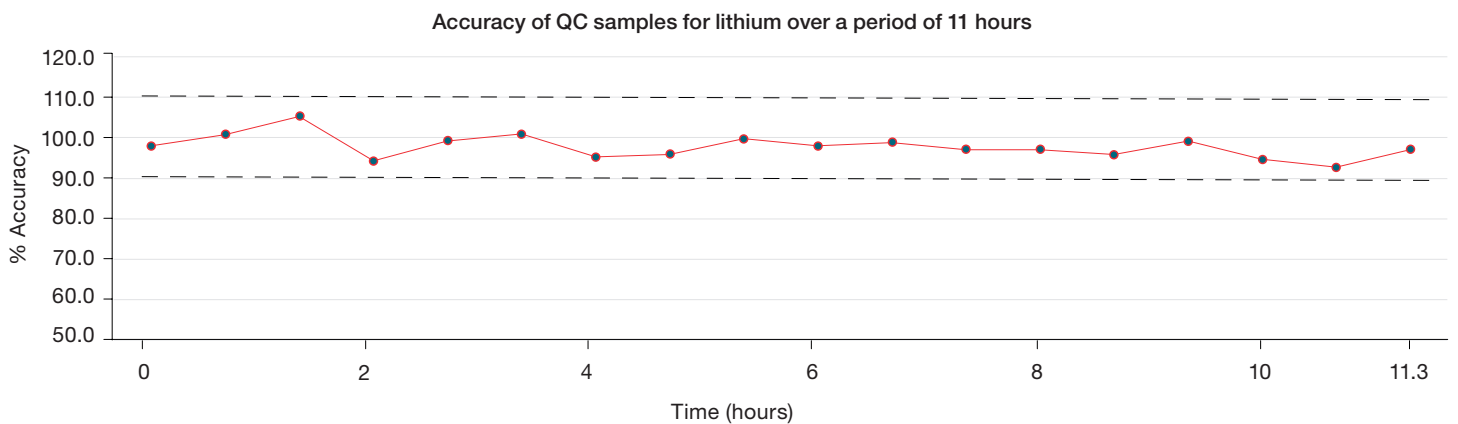


Figure 2. Percent accuracy observed for QC standards containing  $3,000 \text{ mg}\cdot\text{L}^{-1}$  of lithium

Table 4. Spiked concentrations of Li and average percent recovery (n=6)

Spiked concentration of Li (mg·L <sup>-1</sup> )	Recovered concentration (mg·L <sup>-1</sup> )	%Recovery	%RSD
10	10.5	105.0	4.0
100	100.3	100.3	2.2

### System robustness

Since analysis of high dissolved solids containing samples such as brine solutions with ICP-OES is a challenge, the proposed method was assessed thoroughly for matrix tolerance and its performance robustness. An internal standard solution containing 10 mg·L<sup>-1</sup> of yttrium (Y) was added online throughout the analytical batch of over 11 hours of continuous measurement where more than 200 brine samples were analyzed. Three different wavelengths of Y were measured in both axial and radial view, and their response was monitored against the initial intensity of each wavelength recorded at the beginning of the analytical batch. Figure 3 shows a graphical representation of the internal standard response directly taken from the Qtegra ISDS

Software. This figure shows that all internal standard wavelengths read back in the range of between 90% and 115% of their initial values, indicating that the proposed analytical setup has excellent robustness and is suitable for longer batch analysis containing these types of challenging matrices.

Upon completion of the long-term measurement, sample introduction system components such as the nebulizer, spray chamber, injector, and torch were examined carefully for salt deposition or any possible damage. There was no significant salt deposition observed anywhere in the sample introduction components and no damage or deterioration of these components was visible.

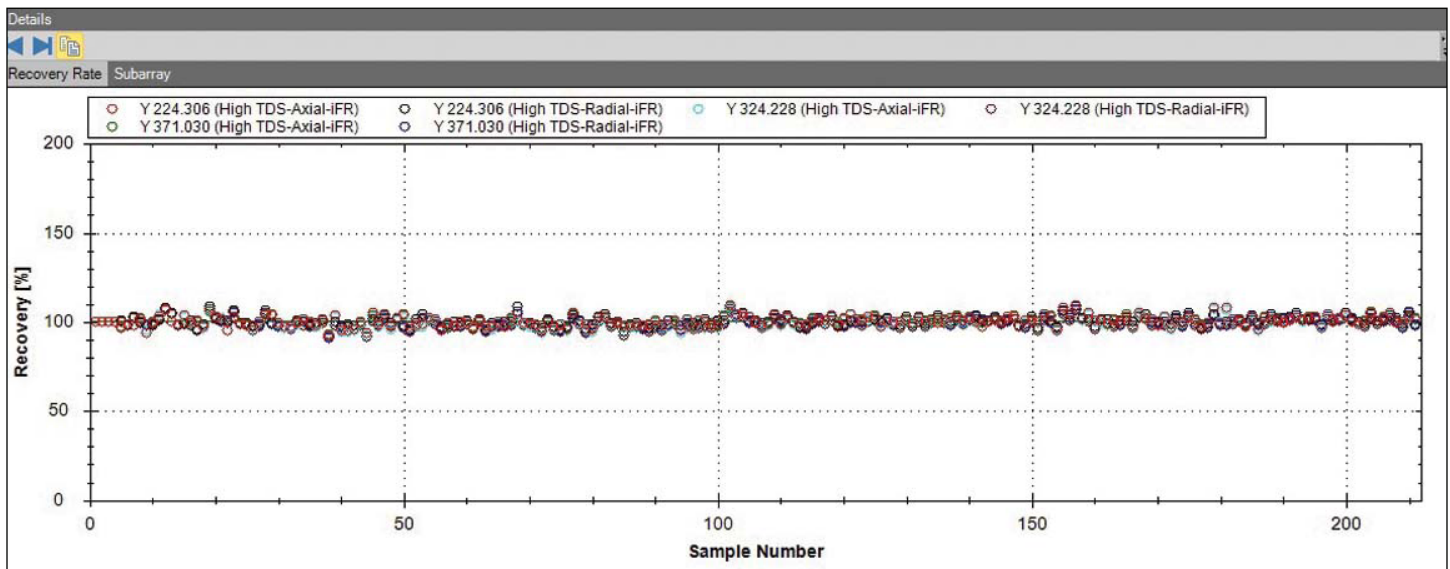


Figure 3. Signal stability of the internal standard wavelengths during the more than 11-hour analytical run

## Summary and conclusions

- The quality of the analytical data observed in this study shows that the iCAP PRO XP ICP-OES equipped with a Burgener Mira Mist nebulizer and sheath gas adaptor is a reliable and robust analytical solution for the analysis of brine solutions and similar, equally challenging samples.
- The wide linear dynamic range established for lithium (up to 5,000 mg·L<sup>-1</sup>) together with the high degree of accuracy and precision across this linear range enables reliable quantification of lithium with varying concentrations, without the need for sample pre-treatments such as dilution. This enables quick sample turnaround, increasing the overall productivity of analytical laboratories involved with analysis of brine and other similar high matrix samples.
- The iCAP PRO series ICP-OES Duo instrument, with its vertical torch configuration and sheath gas adaptor, offers great flexibility for analyzing a wide range of analytes at both higher concentrations and trace levels in a single analytical measurement with robustness equivalent to that of radial ICP-OES instruments.
- The axial mode of the iCAP PRO Series ICP-OES provides significantly lower detection limits and consistently accurate analytical data while analyzing samples with high dissolved solids, enabling reliable measurement of analytes with emission wavelengths distributed across the entire wavelength range.
- The Qtegra ISDS Software simplifies method optimization through various available auto-tune options and provides useful analytical information with customizable report templates, reducing the manual effort required for data evaluation, re-processing, and results reporting.

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