Assessing the purity grade of lithium carbonate and lithium hydroxide using ICP-OES and ICP-MS

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Abstract

Purpose: Different approaches towards determining the purity grade of lithium salts using inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

Methods: Two separate methods were developed, one using ICP-OES and one using ICP-MS, for the highly sensitive analysis of elemental impurities in Li_2CO_3 and LiOH salts. Accuracy and precision measurements, and data stability checks, as well as uninterrupted sequences of circa twelve hours length were performed to validate the analytical methods.

Results: Reliable and accurate data was achieved, covering a large suite of target analytes with excellent detection limits at ppb ($\mu g \cdot L^{-1}$), sub ppb, and ppt ($ng \cdot L^{-1}$) levels. Both methods demonstrated excellent stability and robustness and data quality was not compromised by matrix effects.

Introduction

The superior energy density and high storage capacity of lithium-ion batteries has led to their rapid adoption in portable electronic devices, energy storage systems, and electric vehicle battery packs. The ongoing rapid growth of the electric vehicle market has increased the need for large quantities of high-quality lithium batteries that are safe to use and have long lifetimes. Therefore, the need for accurate, precise, and reliable battery material analysis is of utmost importance.

The two most important sources of lithium are lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH). This study describes two robust and reliable methods for the analysis of these lithium salts using either ICP-OES or ICP-MS. Modern day ICP-OES can meet the sensitivity requirements for most measured impurities for determining presently required purity levels. In the future it is likely that batteries with even higher efficiency and therefore, raw materials with lower impurities will be required, which will make a switch to a higher sensitivity technique like ICP-MS imperative. The targeted analytes includes common impurities, such as alkali and alkaline earth elements, transition elements, heavy metals – which may influence the performance efficiency of the final manufactured batteries. The ICP-MS method also covers the ultra-trace level lanthanide series rare earth elements (REE), which have an important use in high technology electrotechnical applications, as well as the highest concentration element in the salts – lithium (Li) itself.

Methods and materials

Test methods

A Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo and a Thermo Scientific™ iCAP RQ ICP-MS were used for the analysis of 45 and 60 elemental impurities in lithium salts, respectively (Figure 1). Both methods were optimized to enable the successful measurement of such samples with heavy matrices and high concentrations of easily ionized elements (EIE) such as Li. Each instrument was equipped with the highly chemical resistant and durable ceramic torches and the ICP-MS was further paired with AGD in order to avoid additional sample dilution steps that may have otherwise been necessary to minimize matrix effects (Instrument parameters in Table 1). These instrument modules/features enabled successful analysis in the presence of heavy matrices and high concentrations of easily ionizable elements (EIE) such as Li.

Table 1. Instrument parameters for the developed methods

Instrument Parameter	iCAP PRO XP Duo ICP-OES Setting - Method 1	iCAP RQ ICP-MS Setting - Method 2
Pump tubing	Sample: Tygon™ orange/white Internal standard: Tygon™ blue/white Drain: Tygon™ white/white	Sample: PVC orange/green Internal standard: PVC orange/green Drain: Santoprene™ gray/gray
Peristaltic Pump speed	45 rpm	40 rpm
Torch	Ceramic D-torch	Ceramic PLUS torch
Centre tube	2 mm i.d., ceramic	2.5 mm id., quartz
Spray chamber	Glass cyclonic	Quartz cyclonic
Nebulizer	Standard glass nebulizer	Glass concentric, MicroMist™
RF power	1350 W	1550 W
Auxiliary gas flow	1.5 L·min⁻¹	N.A.
Argon gas dilution flow	N.A.	62.6% (1000 mL·min⁻¹ MFC)
Nebulizer gas flow	0.55 L·min⁻¹	0.26 L·min⁻¹
Measurement mode	Axial view, iFR mode	He KED with high matrix 3.5 mm insert
Exposure/ acquisition time for each repeat	15 s for all analytes	0.05 s per analyte isotope
Autosampler	Teledyne™ CETAC™ ASX-560	Elemental Scientific™ ESI SC-4 DX
Uptake/wash times	25/30 s	35/10 s

Samples and standards

Two Li_2CO_3 samples (99% and 99.998% stated purities) and one LiOH·H₂O (98% stated purity) sample was analyzed in this study. A unified sample preparation method was adopted for both methods whereby 250 mg sample was dissolved in 50 mL of 2% nitric acid (v/v) and these solutions, containing ~0.5% (m/v) total dissolved solids (TDS), were directly introduced into the ICP-OES and ICP-MS systems (Figure 2).

Calibration standards were prepared in 2% (v/v) nitric acid, with analyte concentrations covering the range expected in the samples. For the ICP-OES method, the standards and blanks were matrix matched and fortified to a concentration of 1,000 mg·L⁻¹ of Li in the final solutions in order to overcome the easily ionized elements (EIE) effect. For the ICP-MS method, the use of AGD is sufficient to handle the matrix effects and no matrix match of standards to sample is required.

Results

Linearity and sensitivity

The linear dynamic range chosen for the ICP-OES method was 50 to 2000 µg·L⁻¹ for all analytes. This wide range enabled accurate quantitation at low trace levels as well as higher concentration impurities, if present.

The linearity range used for the ICP-MS method was closely aligned with expected low concentrations of impurities in the samples tested – from 0.1 to 100 µg·L⁻¹. By contrast to the quantitation of low-level impurities, the same ICP-MS method was simultaneously used to measure Li, the major elemental component of these samples. Thus, Li was calibrated at very high concentrations, over a range of 100 – 1000 mg·L⁻¹.

Low detection limits and wide linearity were obtained in this study for all elements and both methods. The intelligent full range (iFR) mode of the iCAP PRO XP DUO ICP-OES measured all analytes simultaneously within a single exposure, providing high sensitivities and interference free analysis in a short time. The ICP-MS method achieved even higher sensitivity, as expected, with detection limits for many elements in the ng·L⁻¹ range, typically lower by at least 3–4 orders of magnitude than those achieved by OES (Table 2). This assumes particular significance for the additional lanthanide group of elements or REEs that were covered exclusively by the ICP-MS method. Their presence in the target samples is expected to be in the sub µg·L⁻¹ levels or even lower.

Table 2. Limit of detections (LOD) of selected analytes from the two methods discussed in this study

Analyte	Method 1 using ICP-OES			Method 2 using ICP-MS		
	Wavelength (nm)	Coefficient of determination, R²	LOD (µg·L⁻¹)	Isotope (m/z)	Coefficient of determination, R²	LOD (µg·L⁻¹ or *ng·L⁻¹)
Ce	-	-	-	140	>0.9999	0.001
Co	238.892	0.9996	0.48	59	0.9999	0.022*
Cr	283.563	0.9999	0.42	52	0.9999	0.001
Cs	-	-	-	133	>0.9999	0.001
Gd	-	-	-	157	>0.9999	0.002
Mn	257.610	0.9999	0.05	55	>0.9999	0.004
Nd	-	-	-	146	>0.9999	0.001
Ni	221.647	0.9999	0.5	60	0.9999	0.005
Pr	-	-	-	141	>0.9999	0.444*
Sm	-	-	-	147	>0.9999	0.001

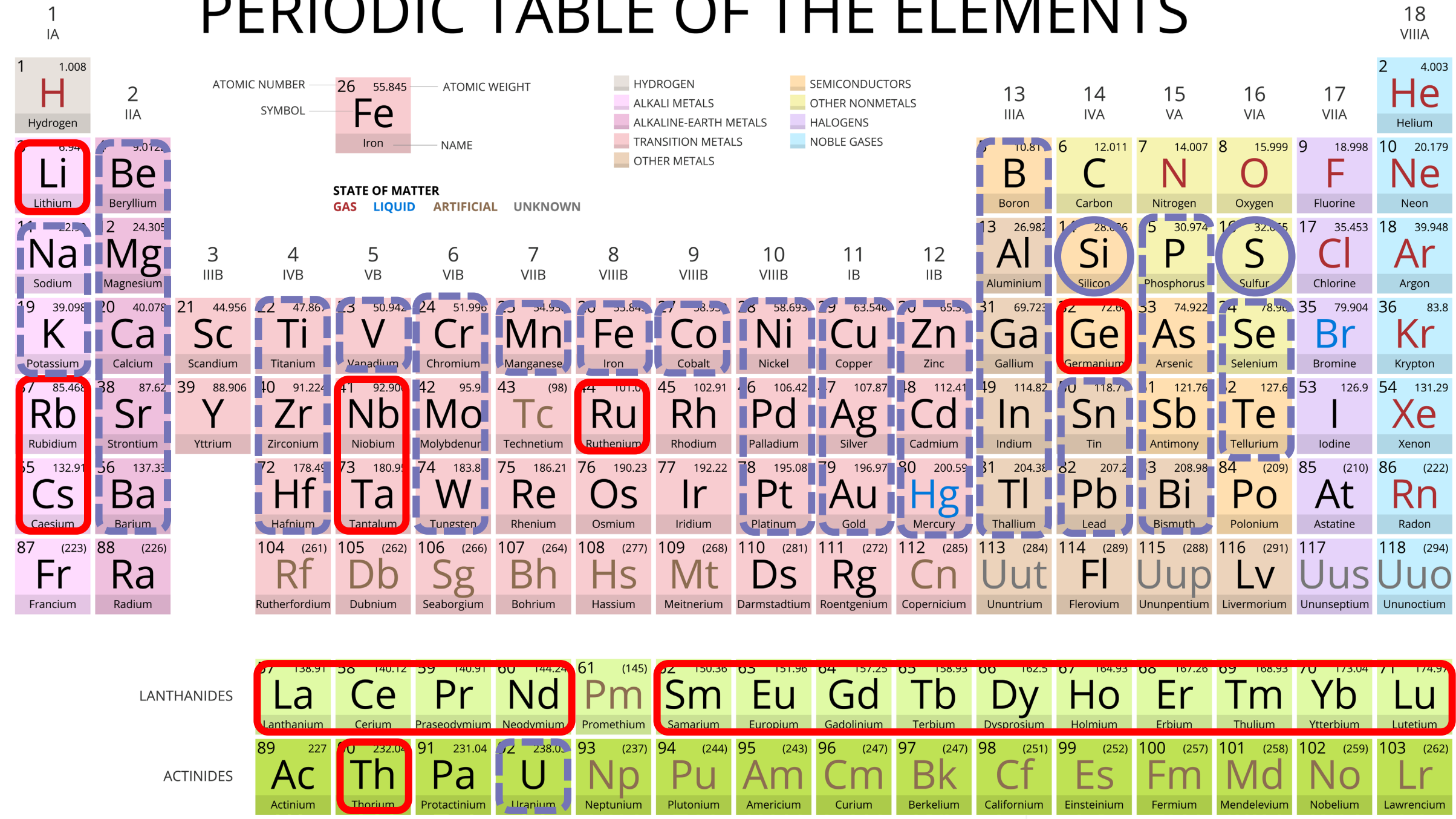LOD calculated as three times standard deviation of repeat blank runs

Figure 1. This study presents the analysis of Li salt samples with a total of 45 and 60 elements covered, using the ICP-OES and ICP-MS methods respectively, as marked in this figure of the periodic table of the elements.
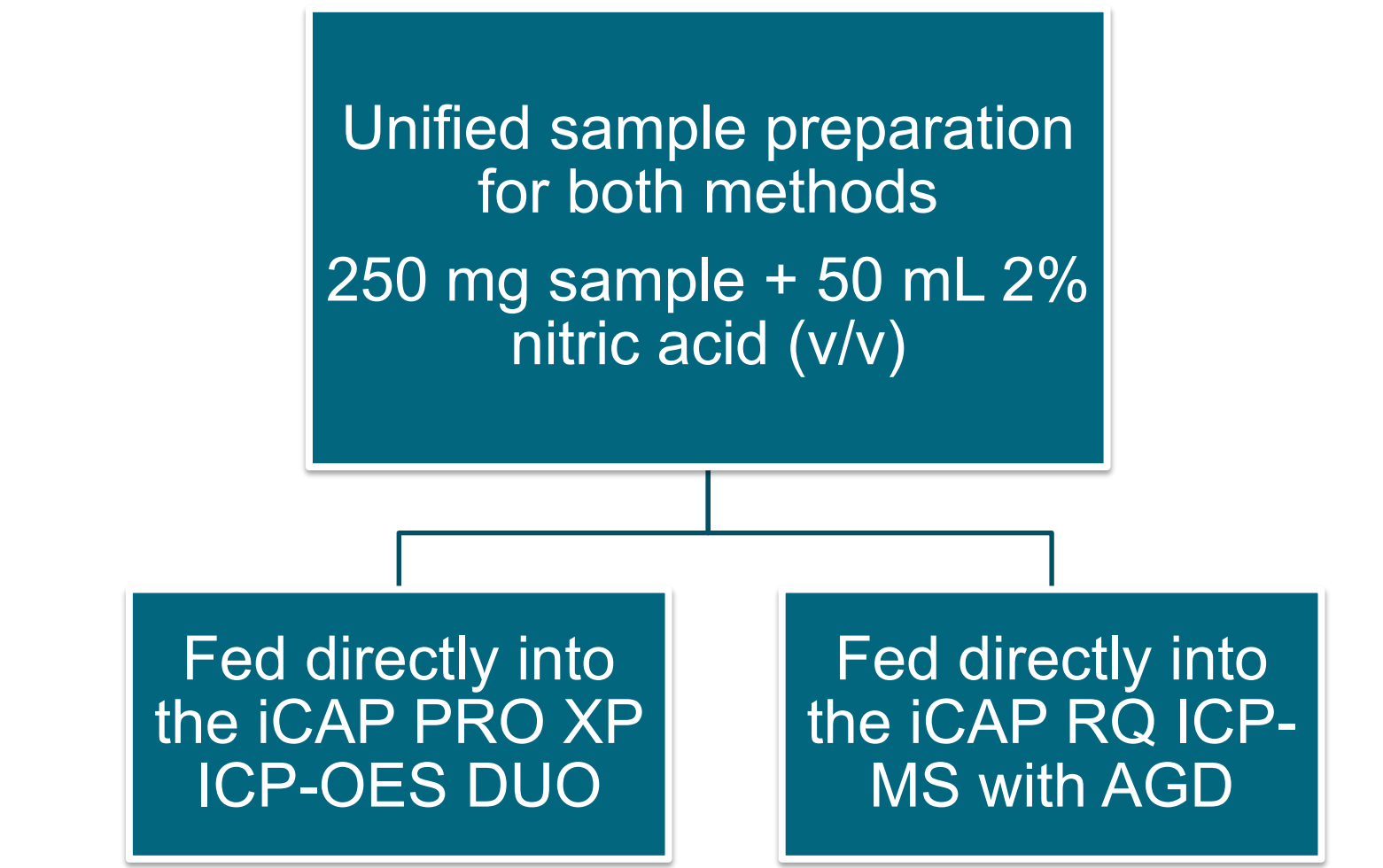
Elements that were covered by both ICP-OES and ICP-MS techniques

Elements that were covered by only ICP-OES method

Elements analyzed exclusively by the ICP-MS method

Unified sample preparation for both methods
250 mg sample + 50 mL 2% nitric acid (v/v)

Fed directly into the iCAP PRO XP ICP-OES DUO

Fed directly into the iCAP RQ ICP-MS with AGD

Figure 2. A single sample preparation method was adopted for measurements involving both techniques

Data analysis

All data acquisition and reporting in this study was carried out using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. All steps including plasma ignition, stabilization, instrument tuning, and performance check can be performed automatically from the Qtegra ISDS Dashboard without any user intervention.

Accuracy

The method accuracies were validated by spiking the salt samples with known amounts of the analytes at different concentrations and then monitoring these spike recoveries. Figure 3a shows the recovery results, using ICP-OES, of a 50 µg·L⁻¹ level spike of different analytes in LiOH. The recoveries are all within the acceptable 100±20% range.

Figure 3b shows a tight recovery range between 90 – 102% of a 0.1 µg·L⁻¹ spike of REEs in the same LiOH sample. More recovery data can be found in the full application notes[1,2].
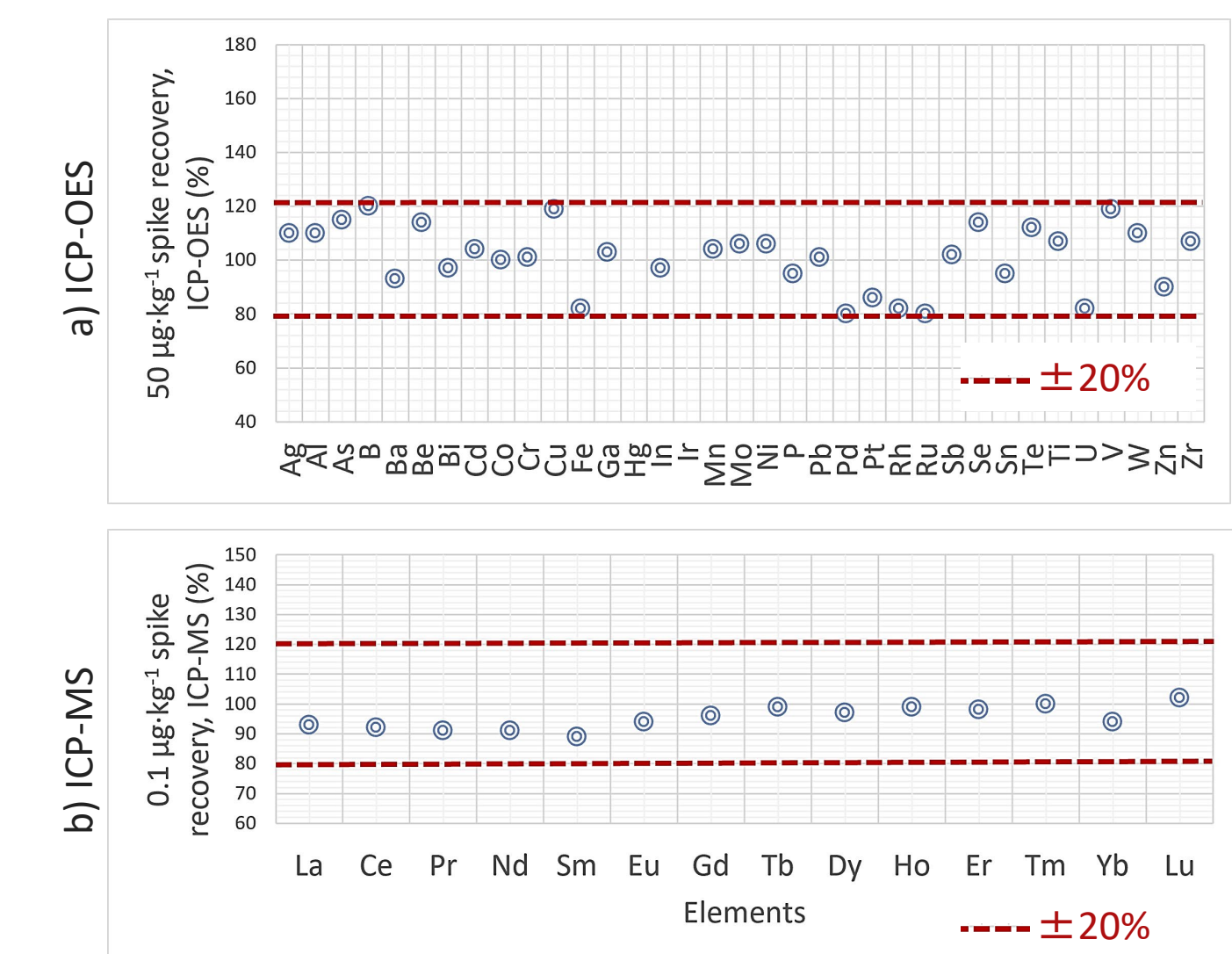

Figure 3. Spike recovery results on the LiOH salt sample. The dotted red lines show the acceptable ±20% range.

Raw material results - impurities and Li content

Three lithium salts were analyzed, and each sample prepared in duplicate for comparison. The results found the purity levels of the Li_2CO_3 and LiOH samples to match the label claims of the salts. The main impurities found were the alkaline and alkaline earth elements (few results listed in Table 3). The LiOH sample was found to contain much lower calcium and silicon contents and higher aluminum and sulfur amounts compared to the Li_2CO_3 samples. Such impurities may have significant effects on the next processing steps of the raw materials.

In addition to the impurities, the lithium content was also determined, using The [6]Li less abundant (7.50%) isotope of lithium. This was to avoid excessively large signals on the detector from the high Li concentration in the salt samples.

Table 3. Some results of Li_2CO_3 and LiOH analysis

	Concentration with ICP-OES - Method 1 (mg·kg⁻¹)			Concentration with ICP-MS - Method 2 (µg for Li, * in mg.kg⁻¹, rest in µg·kg⁻¹)		
	Li_2CO_3 99%	Li_2CO_3 99.998%	LiOH 98%	Li_2CO_3 99%	Li_2CO_3 99.998%	LiOH 98%
		Err		Err		Err		Err		Err		Err
Al	1.5	0.04	0.2	N/A	24.5	<0.01	0.7*	0.12	0.73*	0.12	32*	0.14
Ca	114.6	5.6	1.7	0.02	6.8	<0.01	15.6*	0.49	0.55*	0.16	1.24*	0.08
Cr	0.4	0.01	<DL	N/A	0.3	<0.01	375.0	26.87	74.0	2.83	372	2.83
Li	-	-	-	-	-	-	18.30	0.14	18.8	0.21	16.40	0.28
Mg	6.6	0.001	0.01	0.001	0.1	N/A	6.8*	0.35	0.28*	<0.01	0.43*	0.03
Mn	0.1	0.01	<DL	N/A	<DL	N/A	95.0	1.41	12.0	<0.01	17	1.41
S	<DL	N/A	<DL	N/A	16.4	<0.01	-	-	-	-	-	-
Si	112.7	0.06	<DL	N/A	12.4	0.001	-	-	-	-	-	-
Pb	<DL	N/A	<DL	N/A	<DL	N/A	173.0	4.24	-	-	77	4.24

Easily ionized element (EIE) effects

When using ICP-OES, the EIE effects from the presence of large proportion of Group I EIE in the samples, for e.g., Na, Li etc., was compensated by matrix matching the calibration solutions to the real samples. In absence of this matrix match the EIE effects shift the ionization equilibrium in the plasma. This leads to a disproportionate increase in the intensity of atomic emission lines and a decrease in ionic emission lines which may lead to inaccurate data. An addition of 1000 mg·L⁻¹ lithium in the calibration solutions helped to minimize the EIE effect, as indicated by excellent internal standard response discussed in the robustness section, and the accurate results obtained.

Robustness study

Twelve hours long analytical sequences were run on both instruments, to evaluate robustness and data stability. A calibration block was run only at the beginning of the LabBooks, followed by unknown samples and regular QC checks using continuing calibration verification (CCV) within the software. The QC recoveries from both methods remained stable and accurate throughout the 12 hours, within the range of 80-120% (Figure 4) for the ICP-OES and 98-115% for the ICP-MS methods. Very stable internal standard response was also observed throughout (Figure 5).
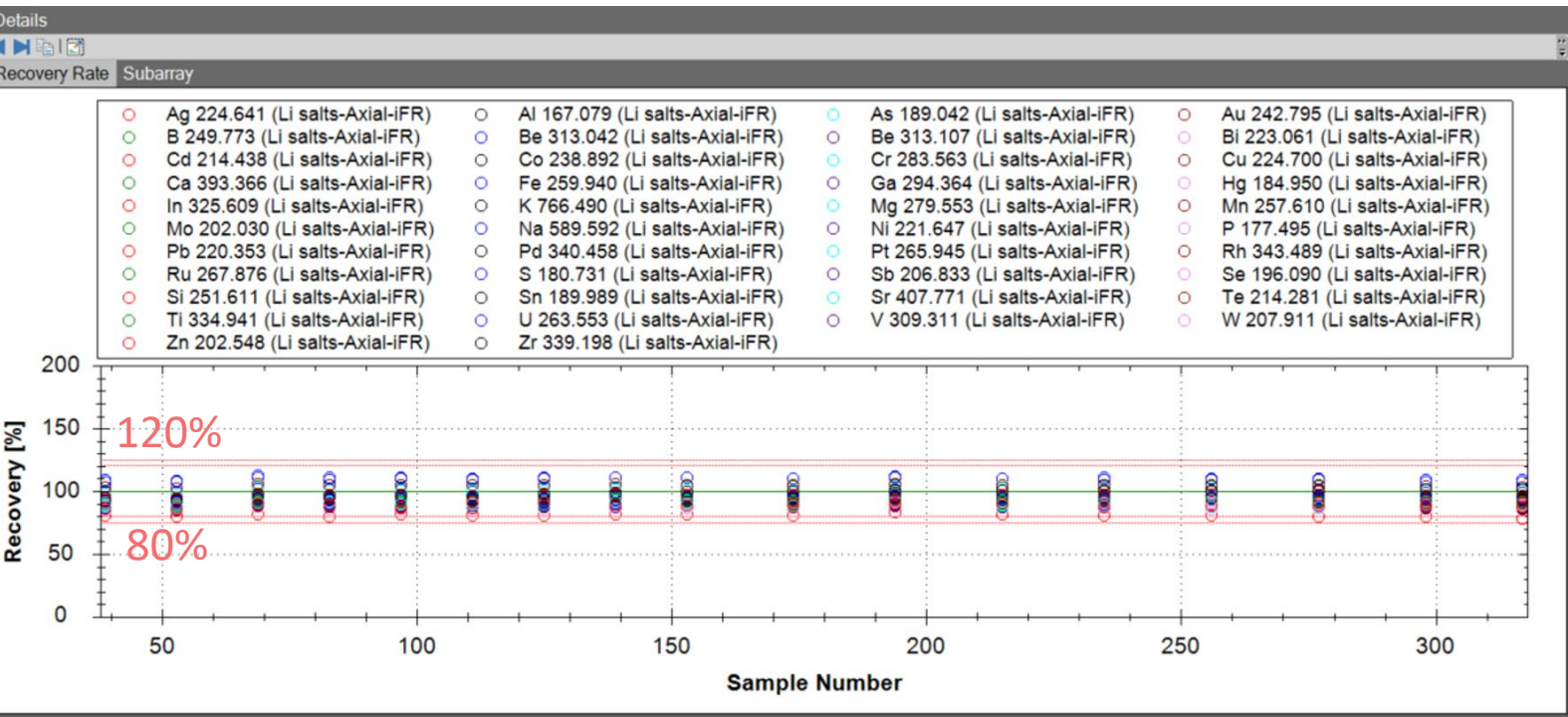

Figure 4. Stable QC CCV recoveries over twelve hours long uninterrupted ICP-OES sequence measuring Li_2CO_3 and LiOH samples. All 45 elements were measured simultaneously within the same exposure in Axial iFR mode.
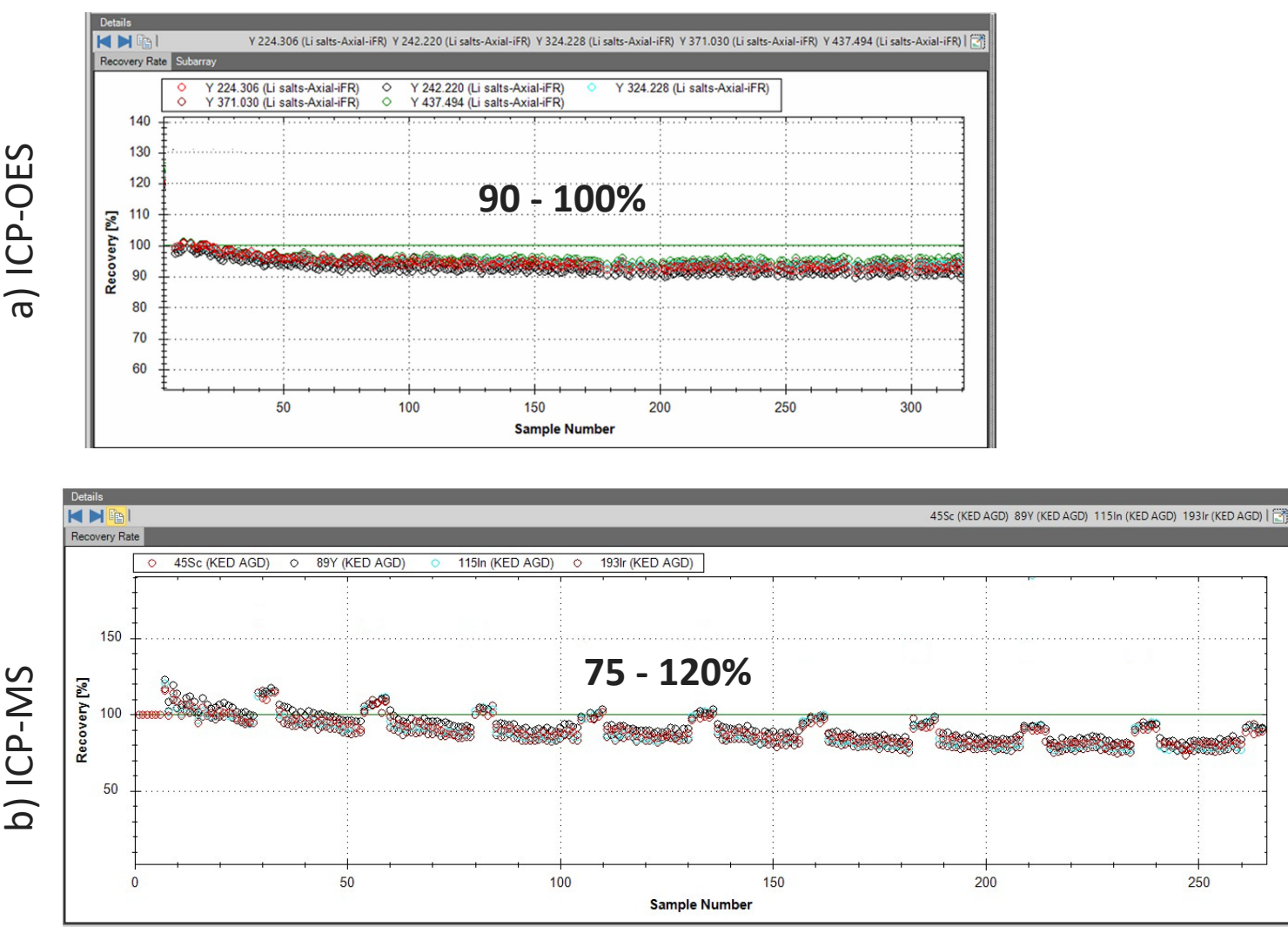

Figure 5. Internal standards response over the entire 12 hours duration of the robustness tests

Conclusions

The iCAP PRO XP ICP-OES Duo and the iCAP RQ ICP-MS with AGD instruments were used to analyze a total of 60 impurity elements in Li salt samples. The samples were prepared using a unified and simple sample preparation method which involved dissolving the samples in 2% nitric acid. The methods provided excellent results and reliable high-quality data.

- Both Li_2CO_3 and LiOH salts were analyzed applying a single method covering 45 elements with the iCAP PRO XP ICP-OES Duo and 60 elements with the iCAP RQ ICP-MS.
- Excellent sensitivity was achieved in both methods. The ICP-MS enabled the analysis of a higher number of elements at lower detection limits.
- All selected wavelengths were covered within a single mode in ICP-OES, in this case Axial iFR – the wavelengths could all be captured simultaneously in the same exposure (10 s in this study) saving valuable analysis time and costs. This allowed measurement of all analytes together, at multiple wavelengths, without increasing the analysis time.
- A single sample preparation step was adopted, and sample extracts were fed directly into both the ICP-OES and/or ICP-MS instruments, depending on the target analytes and the sensitivity levels required. In the case of the iCAP RQ ICP-MS no additional manual dilution steps are necessary as AGD is performed at the ICP-MS instrument directly
- Excellent spike recovery and QC results were obtained, and QC stability was demonstrated over 12 hours. The methods were found to be robust for up to a minimum of 12 hours and showed very stable internal standard responses, indicating minimum matrix effects for the salts.
- The AGD is fully incorporated into the Qtegra ISDS software and allows for easy and simple operation. Data acquisition, visualization and reporting is straightforward and simple using the software for both methods.

References

1.Thermo Scientific Application Note 001168: Assessing the purity grade of lithium carbonate and lithium hydroxide using ICP-OES.

2. Thermo Scientific Application Note 001179: Elemental analysis of lithium salts using ICP-MS combined with argon gas dilution (AGD).

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