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

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Keywords

Battery production, ICP-OES, robustness, method validation, sensitivity, limits of quantification, analytical testing

Goal

To demonstrate the capabilities of the Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo to measure Li_2CO_3 and LiOH materials in a robust and precise manner within the same analytical run

Introduction

The global demand for lithium salts has dramatically increased in recent years due to the fast-developing market for lithium-ion batteries (LIB), specifically for the automotive industry. The two most important compounds in which lithium is traded are lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH). Both compounds are produced by extracting lithium from natural repositories, such as geological ores and underground brines, and are ultimately used in different LIB components (Figure 1). While lithium carbonate extraction is typically less expensive, lithium hydroxide is popular because of its low temperature decomposition which helps establish a more sustainable battery cathode manufacturing process and also makes the final product more long lasting.
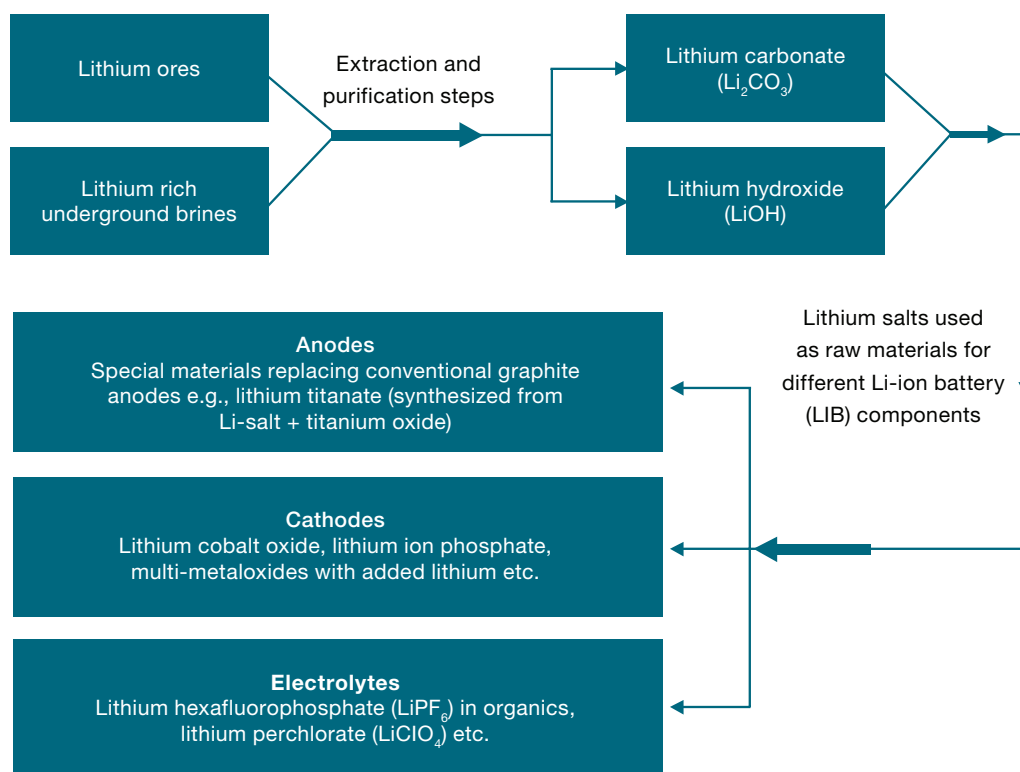
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Figure 1. Simplified schematic of lithium extraction – from ores to battery components

Battery and raw material manufacturers need to ensure that all substances used in the production of battery components are tested for the presence of elemental impurities, such as alkaline and alkaline earth elements and transition metals, so that the performance of the end products is not compromised. Purity is a key differentiator that increases material value and ultimately profitability so stringent and regular quality control is essential. Analysis of elemental impurities in battery grade lithium salts is often based on the methods described in Chinese standard GB/T-11064.16-2013 and International Electrotechnical Commission (IEC) 62321 standard where ICP-OES is a suggested technique in both. ICP-OES is considered a key technology for analytical testing of battery materials as it can perform full multi-elemental analysis in a short time and is able to handle a wide variety of potential sample types. This note relates to the requirement Li_2CO_3 and LiOH production facilities for purity checks of both salts, using a Thermo Scientific™ iCAP™ PRO Series ICP-OES to measure a suite of 45 elements. The robust and fast analysis method for the large list of analytes within both these lithium sources yields a method detection limit (MDL) of around 1 mg·L[1] for the majority of the elements analyzed.

Experimental
Instrument parameters and experimental conditions
An iCAP PRO XP ICP OES Duo instrument was used to measure 45 trace elements in Li_2CO_3 and LiOH to check the total concentration of impurities in the compounds, as well as the

composition of these salts. The instrument was operated using the intelligent full range (iFR) mode with axial plasma viewing, allowing measurement of wavelengths in both the UV and the visible part of the spectrum in a single exposure with high sensitivity. This leads to a reduced turnover time per sample, provides results faster, and helps laboratories to save costs. The sample introduction system was configured for standard aqueous analysis, with the exception of the torch. A ceramic D-torch was chosen to improve the tolerance against the sample matrix and to decrease the need for maintenance. A torch made from high purity quartz can show signs of damage and devitrification due to prolonged exposure to such sample types and would need more frequent replacement. The ceramic D-torch is capable of handling both the sample types with ease while consistently producing robust and reliable data.

Details of the sample introduction setup and typical instrument parameters are listed in Table 1. The simultaneous measurement of the entire wavelength range with the iCAP PRO Series ICP-OES enables rapid sample analysis, irrespective of the number of analytes and wavelengths measured in the sample. In this experiment, a total run time of 144 seconds per sample was achieved for the fully quantitative analysis of 45 analytes.

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Table 1. Instrument configuration and typical operating parameters

Instrument parameter	Setting
Pump tubing	Sample: Tygon™ orange/white Drain: Tygon™ white/white
Spray chamber	Glass cyclonic
Nebulizer	Standard glass nebulizer
Center tube	2.0 mm ceramic injector
Torch	Demountable ceramic D-torch
Pump speed	45 rpm
Flush pump speed	125 rpm
Uptake time	25 s
Pump stabilization time	10 s
Wash time	30 s
Nebulizer gas flow	0.55 L·min^{-1}
Auxiliary gas flow	1.5 L·min^{-1}
Coolant gas flow	14.5 L·min^{-1}
RF power	1,350 W
Repeats	3
Exposure time	15 s Axial iFR

Sample preparation

Two samples of Li_2CO_3 (with indicated purity grades of 99.9% and 99.998%) and one sample of LiOH (Monohydrate, of 98% purity) were analyzed. Aliquots of 250 ± 2 mg of each sample were weighed into sample tubes, and 1 mL of HNO_3 (Trace Metal™ grade, Fisher Scientific™) was carefully added to each. The samples were allowed to stand for 15 minutes to complete the neutralization reaction, followed by further dilution of the samples to final volume of 50 mL using ultra-pure water.

Standards and reference materials

A calibration blank and a set of calibration standards, covering a concentration range of three orders of magnitude, were prepared in 2% (v/v) HNO_3 using single element standards (1,000 mg·L^{-1}, SPEX CertiPrep™ Group, Metuchen, NJ, USA) of individual analytes. The individual concentrations of the standards were 50, 200, 500, 1,000, and 2,000 µg·L^{-1}.

To account for the interference of easily ionizable elements (EIE) due to the high lithium content of the samples, the calibration standards and the calibration blank were matrix matched and fortified to a concentration of 1,000 mg·L^{-1} of lithium in the final solutions.

To monitor and correct for any physical interreferences during analysis, an internal standard solution containing 5 mg·L^{-1} yttrium was added online via a T-piece throughout the experiment.

Quality control and method validation

The standard solution containing 200 µg·L^{-1} of all analytes was used as a quality control (QC) standard in the study to confirm the calibration quality. The method accuracy was further confirmed by spiking selected samples at concentration levels of 50 µg·L^{-1} and 1 mg·L^{-1}. All samples, spiked and native, were measured continuously over a period of more than 10 hours to verify the robustness of the proposed method.

Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software was used for data acquisition, processing, and reporting.

Results and discussion
Selectivity, sensitivity, and linearity

Table 2 provides an overview of all analytes investigated in this study, together with the selected wavelength based on relative sensitivity and absence of interferences, and the analytical figures of merit achieved. The coefficients of determination (R^2) obtained for all analyte wavelengths were found to be >0.9996 over the entire calibration range (examples of calibration curves are shown in Figure 1). The instrumental detection limit (IDL), calculated on the basis of three repeat measurements of blank and low concentration calibration standards, and the method detection limit (MDL) in the original solid sample, based on the IDL multiplied by the dilution factor applied during sample preparation are also listed in Table 2. Out of the 45 elements targeted, 43 elements had MDLs well below 1 mg·L^{-1}, thus showing very good sensitivity for the entire suite of analytes.

The total lithium content of the samples could also be monitored using this same method, if desired, using a different set of non-matrix matched standards and blank contained in a separate calibration block.

Accuracy

The samples were spiked with two different concentration levels for different analytes, as described previously, to test the accuracy of the method at similar concentrations at which these impurities are expected. All spike recoveries were in the range of ± 20% around the expected concentration.

Table 2. List of suitable wavelengths, lowest limits of detections (LOD), R^2 values, and method detection limits (MDL) for the individual elements

Element	Wavelength (nm)	R^2	IDL (µg·L⁻¹)	MDL (mg·L⁻¹)
Ag	328.068	0.9998	0.73	0.15
Al	167.079	0.9999	0.08	0.02
As	189.042	0.9997	2.33	0.47
Au	242.795	0.9999	1.30	0.26
B	249.773	0.9999	0.48	0.10
Ba	455.403	0.9998	0.10	0.02
Be	313.042	0.9999	0.02	0.00
Bi	223.061	0.9997	6.82	1.36
Ca	393.366	0.9999	0.08	0.02
Ca	422.673	0.9998	0.22	0.04
Cd	214.438	0.9999	0.20	0.04
Co	238.892	0.9998	0.48	0.10
Cr	283.563	0.9999	0.42	0.08
Cu	224.700	0.9999	0.77	0.15
Fe	259.940	0.9999	0.47	0.09
Ga	294.364	0.9998	3.19	0.64
Hf	339.980	0.9998	1.75	0.35
Hg	184.950	0.9999	1.04	0.21
In	325.609	0.9999	4.91	0.98
Ir	224.268	0.9999	2.79	0.56
K	766.490	0.9996	0.26	0.05
Mg	279.553	0.9999	0.01	0.00
Mn	257.610	0.9999	0.05	0.01
Mo	202.030	0.9998	1.07	0.21
Na	589.592	0.9997	1.36	0.27
Ni	221.647	0.9999	0.50	0.10
P	177.495	0.9998	2.64	0.53
Pb	220.353	0.9998	3.72	0.74
Pd	340.458	0.9998	1.55	0.31
Pt	265.945	0.9998	5.81	1.16
Rh	343.489	0.9997	4.70	0.94
Ru	267.876	0.9999	1.82	0.36
S	180.731	0.9999	2.53	0.51
Sb	206.833	0.9998	4.63	0.93
Se	196.090	0.9997	5.80	1.16
Si	251.611	0.9999	0.91	0.18
Sn	189.989	0.9999	1.30	0.26
Sr	407.771	0.9995	0.04	0.01
Te	214.281	0.9999	3.84	0.77
Ti	334.941	0.9999	0.19	0.04
U	263.553	0.9998	3.08	0.62
V	309.311	0.9998	0.29	0.06
W	207.911	0.9999	1.42	0.28
Zn	202.548	0.9999	0.14	0.03
Zr	339.198	0.9998	0.20	0.04

Table 3. Spike recoveries (N=8) on Li$_2$CO$_3$ and LiOH samples of 50 µg·L^{-1} and 1 mg·L^{-1} spikes. In case no results are given (denoted as - in the table), the spike recovery test was not performed due to the concentration levels found in the samples.

	Li$_2$CO$_3$ 99%, 50 µg·L^{-1} spike		LiOH, 50 µg·L^{-1} spike		LiOH, 1 mg·L^{-1} spike	
	Spike rec%	%RSD [N=8]	Spike rec%	%RSD [N=8]	Spike rec%	RSD% [N=8]
Ag	106	5.1	110	3.2	85	1.1
Al	112	3.0	110	2.6	101	0.6
As	118	2.1	115	1.3	91	0.3
B	108	0.9	124	0.6	92	0.2
Ba	91	0.8	93	0.8	94	0.3
Be	109	0.5	114	0.6	–	–
Bi	89	1.9	97	1.2	90	0.6
Ca	–	–	–	–	107	0.5
Cd	99	1.1	104	0.8	96	0.2
Co	96	0.6	100	0.6	96	0.1
Cr	101	0.4	101	0.7	94	0.4
Cu	113	2.2	119	0.7	109	0.9
Fe	102	2.8	82	0.8	94	0.2
Ga	93	1.5	103	1.6	91	0.2
Hg	99	1.8	110	1.3	–	–
In	98	3.2	97	1.2	92	1.0
Ir	101	1.4	36	0.5	–	–
K	–	–	–	–	86	0.2
Mg	–	–	–	–	96	0.2
Mn	102	0.9	104	0.7	94	0.9
Mo	104	1.3	106	0.8	93	0.7
Na	–	–	–	–	95	0.7
Ni	111	1.2	106	0.6	97	0.8
P	98	0.0	95	0.0	89	0.7
Pb	100	0.7	101	0.7	97	0.7
Pd	78	1.3	80	1.3	101	1.1
Pt	84	2.0	86	1.5	100	0.5
Rh	79	1.0	82	1.7	104	0.8
Ru	77	1.1	79	1.6	109	0.4
S	–	–	–	–	90	0.8
Sb	96	1.5	102	1.1	89	0.3
Se	109	1.5	114	2.4	92	0.2
Si	–	–	–	–	100	0.8
Sn	98	3.4	95	2.8	94	0.7
Sr	–	–	–	–	94	0.5
Te	108	1.3	112	1.6	103	0.3
Ti	110	0.7	107	0.8	92	0.7
U	78	1.1	82	1.0	103	0.8
V	108	1.1	119	0.9	93	0.2
W	102	1.4	110	1.3	94	0.7
Zn	86	3.6	90	1.0	107	0.2
Zr	106	0.7	107	0.8	92	0.9

Easily ionized element (EIE) effects

Easily ionized elements (EIE) or elements with low ionization potential, such as alkali elements sodium, potassium, or lithium, present in the sample can shift the ionization equilibrium in the plasma. The easily lost electrons from the EIE are then available for other elements in the plasma, causing an equilibrium shift between ions and atoms. As a result, there is an increase in the intensity of atomic emission lines and a decrease in ionic emission lines, so that the apparent concentration of certain analytes changes. This effect is considered a chemical interference and leads to inaccurate results when non-matrix matched standards are used (as shown in Figure 2). The use of matrix matching in this study prevented inaccurate results from being obtained.

Real sample composition/purity check of Li_2CO_3 and LiOH raw materials

The results of the quantitative analysis of the three lithium salts under investigation in this study are summarized in Table 4. The results indicate that the overall level of impurities in the salts are in good agreement with the purity claims. The main impurities detected in all samples were alkaline and alkaline earth elements (such as sodium, potassium, magnesium, and calcium), but common transition metals (i.e., chromium, iron, or zinc) were also found. However, it is noteworthy that the composition of the impurities may change significantly even for samples with the same purity grade. For example, the LiOH sample (with overall certified purity of >98%) contained significantly lower levels of calcium and silicon, compared with the Li_2CO_3 sample with certified purity of >99%, but higher levels of aluminium and sulfur. This may have implications to the workflows used for further processing the raw materials. For a wide range of analytes, the impurity levels are below the detection limit of ICP-OES. Here, an analytical technique with even higher sensitivity would be required, for example, inductively coupled plasma combined with mass spectrometry (ICP-MS).
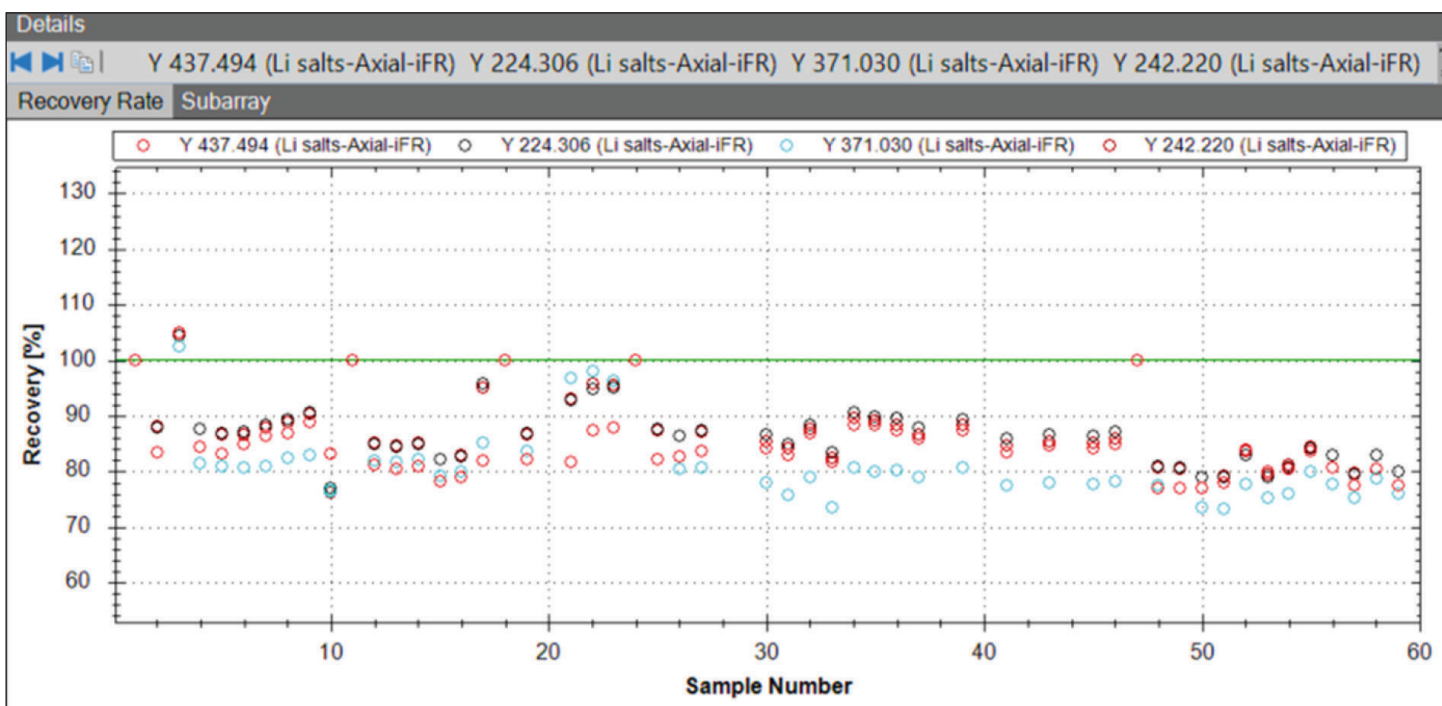

Figure 2. The easily ionized elements can cause poor and unstable internal standard recovery when calibration solutions and real samples are not matrix matched. The data points at 100% recovery are the calibration blanks that were run occasionally. In sequences extending for several hours, the recoveries are expected to further worsen. This study overcomes this effect by adopting matrix matching, which greatly improves data stability.

Table 4. Trace elemental composition of the raw material samples measured in this study

Sample	Li_2CO_3 99%		Li_2CO_3 99.998%		LiOH 98%	
Analyte	Avg (mg·kg⁻¹)	Stdev	Avg (mg·kg⁻¹)	Stdev	Avg (mg·kg⁻¹)	Stdev
Al	1.5	0.04	0.2	N/A	24.5	<0.001
B	<DL	N/A	<DL	N/A	1.4	<0.001
Ca	114.6	5.6	1.7	0.02	6.8	<0.001
Cr	0.4	0.01	<DL	N/A	0.3	<0.001
Fe	1.4	0.04	<DL	N/A	<DL	N/A
K	0.9	1.3	<DL	N/A	23.3	<0.001
Mg	6.6	0.001	0.01	0.002	0.1	N/A
Mn	0.1	0.01	<DL	N/A	<DL	N/A
Na	131.6	0.5	<DL	N/A	78.5	0.001
S	<DL	N/A	<DL	N/A	16.4	<0.001
Si	112.7	0.06	<DL	N/A	12.4	<0.001
Sr	1.4	0.04	<DL	N/A	<DL	N/A
Ti	0.2	0.002	<DL	N/A	<DL	N/A
V	<DL	N/A	<DL	N/A	0.6	<0.001
Zn	<DL	N/A	<DL	N/A	0.1	<0.001
Total traces	371.4		1.91		164.4	
% purity	99.96		99.9998		99.98	

Elements found to be <DL in all samples – Ag, As, Au, Ba, Be, Bi, Cd, Ce, Co, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, La, Lu, Mo, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Ta, Tb, Th, Te, Tl, Tm, U, W, Yb, Zr

Robustness validation over a typical working day

The developed method was tested and validated for accuracy over an extended period by setting up a robustness test for twelve hours of continuous measurements. This simulates a real-life setting in industry where hundreds of such samples need to be continuously measured to assure consistent product quality and homogeneity. All three samples of Li_2CO_3 and LiOH, both native as well as spiked aliquots, were included in the robustness test. The sequence started with the calibration block, including blanks and standards, followed by an initial QC check (ICV = Initial Calibration Verification). The QC sample was regularly analyzed after every 20 unknown samples.

The results show no significant signal drift or QC failures throughout the duration of the experiment. The recovery of the internal standard, QC sample concentration recovery, and spiked concentration recoveries all remained stable throughout the analysis. The internal standard recovery remained within 90–100% throughout (Figure 3). The QC recoveries were well within 80–110% for all analytes, with the majority within an even narrower range of 85–100% (Figure 4).
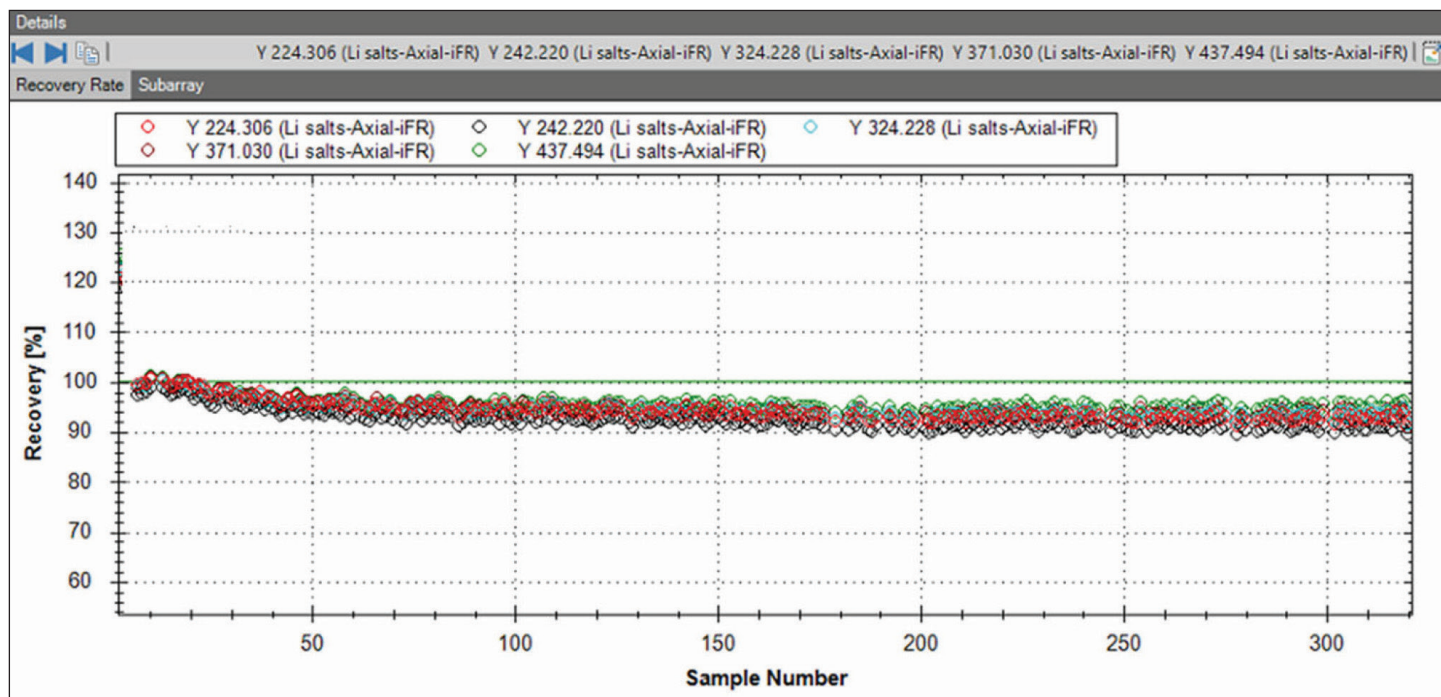

Figure 3. Excellent internal standard recovery throughout the 12-hour robustness test analysis, with calibration solutions matrix matched to the real samples
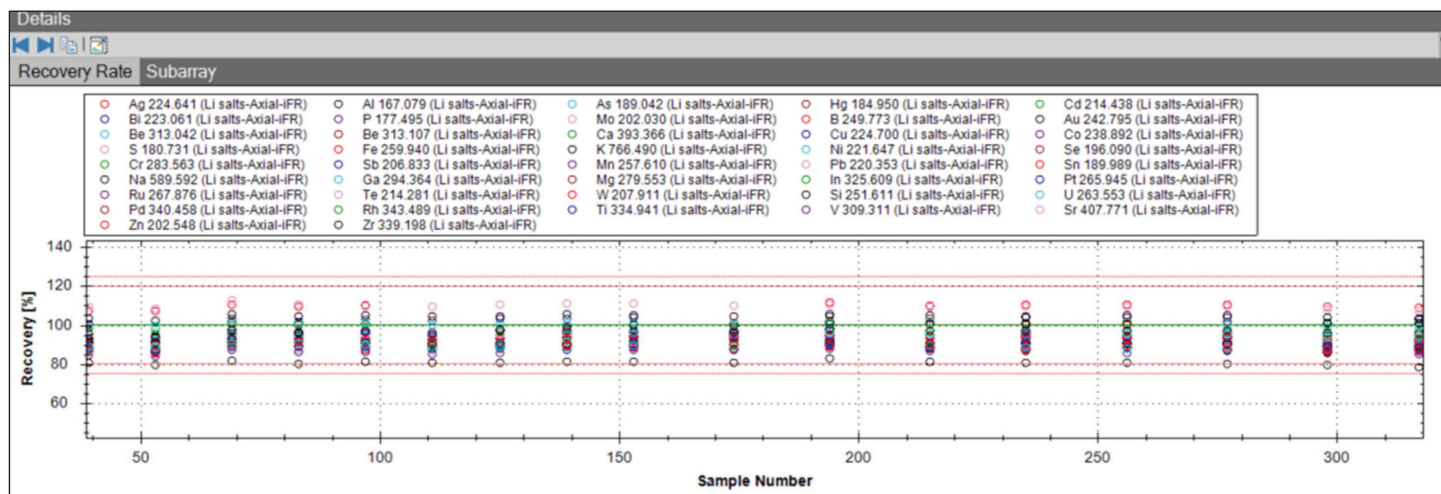

Figure 4. QC recoveries during the robustness test analysis. The red double line marks the 80–120 ± 5% interval.

Conclusions

This application note presents a method for the fast, sensitive, accurate, and robust analysis of different common lithium-ion battery raw materials, namely Li_2CO_3 and LiOH. Simultaneous measurement and characterization of 45 trace analytes in both sample types using the iCAP PRO XP ICP-OES Duo instrument provides the end-user with an elegant and effective technique for reliable measurement of hundreds of samples daily.

- Both Li_2CO_3 and LiOH salts were analyzed in this study applying a single method covering 45 elements simultaneously with the iCAP PRO XP ICP-OES Duo. The MDLs were below 0.01 mg·L^{-1} for 19 elements, below 0.1 mg·L^{-1} for 23 elements, and slightly above 1 mg·L^{-1} for the remaining 2 elements.

- The multi-element analysis was carried out quickly at only 2 min 24 s per sample (including three repeats, uptake, and wash) due to the simultaneous data acquisition for all analytes in a single exposure.

- The method accuracy and precision are demonstrated by precise spike recovery on real sample matrices as well as excellent QC recovery and stable internal standard recovery throughout a 12-hour robustness test. The EIE effect from the high lithium concentration in the matrix did not compromise data quality because of the matrix matching of calibration standards and blanks to the real samples.

- Uninterrupted analysis over twelve hours demonstrates the exceptional robustness of the iCAP PRO XP ICP-OES Duo for handling lithium salts of different compositions.

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