Challenge
Sensitive and accurate analysis of trace elements in challenging matrices containing high amounts of easily ionizable elements (EIE)

Solution
High-resolution ICP-OES with high sensitivity and high plasma robustness providing the best limits of detection

Target Audience
Scientists and researchers in materials science, battery manufacturers, mining and resource industries

Analysis of Lithium Carbonate for Lithium-Ion Battery Applications using HR ICP-OES

Introduction

Until the 1990s, the classic use of lithium was in the glass and ceramics industry as well as in the production of lubricants. At present, the main application of the metal is in lithium-ion batteries (LIBs). It is used in the electrolyte, anode, and cathode of the accumulators. The global trends of renewable energies and e-mobility are leading to the need for ever new Li materials with ever greater quality control requirements.

The tri-border area (also called the lithium triangle) between Bolivia, Chile, and Argentina, more than half of all lithium reserves are stored. With the help of water pumps, saline groundwater (brine) is pumped to the surface. There it is stored in artificially created lakes and the water is evaporated due to the hot and dry climate. What remains is a viscous lithium concentrate with a lithium content of about 6%, which is then further processed into lithium carbonate (Li_2CO_3).

Currently two major classes of rechargeable lithium batteries exist - those using lithium-ions and those using thin film polymer electrolyte-lithium metal. In the case of the lithium-ion battery, purified lithium carbonate is used for the cathode. Here, impurities such as sodium (can cause overheating) can affect performance and lifespan of the battery. In the case of thin film batteries, lithium metal is obtained by chlorinating lithium carbonate to form lithium chloride and subsequent electrolysis to metallic lithium. The key to obtaining lithium of the grade required for lithium batteries is to use purified lithium chloride and to minimize impurities such as calcium, magnesium, and sulfur in the initial raw material Li_2CO_3. Otherwise, these elements will reduce the purity or interfere with the electrolysis step. Therefore, the monitoring of impurities in lithium battery materials is crucial to ensure quality and performance of the final battery products.

The determination of trace impurities in lithium battery materials nowadays is largely carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES) and is described in numerous methods of international standards (e.g., Chinese Standard: GB/T 11064.16-2013 [1]; International Electrotechnical Commission (IEC) standard 62321-2013 [2]). The demands on Li-ion batteries are constantly increasing in terms of its lifetime and capacity. Therefore, the requirements of the raw materials are also constantly increasing. Currently, Li_2CO_3 with a purity of 99.5% is referred to as battery grade. However, the trend in the industry is clearly moving towards ever purer raw materials with purities greater than or equal to 99.9%. This also changes the technical specification on the ICP-OES technology. As the requirements for the battery material increase, the sensitivity and matrix compatibility of the analytical technique must be guaranteed.
In this study, a high-resolution (HR) ICP-OES, the PlasmaQuant 9100 Elite, was used for the trace elemental analysis in Li_2CO_3. The exceptionally high resolution in combination with high sensitivity and high plasma robustness of the instrument allows for interference-free analysis of all investigated analytes in the low to sub-ppb range. Since large amounts of lithium ions in the plasma can cause ionization interferences and thereby lead to false-positive results, especially for easily ionizable elements (EIE), the calibration standards were matrix-matched. Analyte recovery and long-term stability tests were performed to verify the suitability of the analytical method and instrument performance.

Materials and Methods

Sample preparation

All laboratory equipment was washed with deionized (DI) water from a PURELAB system (18.2 MΩ cm, ELGA LabWater, High Wycombe, England). Besides Li_2CO_3 ($w = 99.999\%$, Acros Organics), all chemicals were of analytical reagent grade. The working standards were prepared by serial volume/volume dilution in polypropylene of a multi-element standard solution (Sigma Aldrich, 10 mg/L). The blank solution and all calibration standards (see table 2) were matrix-matched (5.0% (w/v) Li_2CO_3) and acidified ($pH < 1$) with concentrated ($w \geq 65\%$) nitric acid. A spiked (0.1 mg/L) blank solution served both as sample and quality control.

The first step of preparing the blank solution was dissolving 2.5 g of Li_2CO_3 to 10 mL DI water. Then 6 mL of concentrated nitric acid was added dropwise to avoid vigorous foaming. Finally, the solution was filled up to 50 mL with DI water and sonicated (5 min) to remove residual carbon dioxide.

Calibration

The calibration levels for each element were chosen based on their typical concentration range. At least six calibration points were used for each element, as described in Table 1. Selected calibration curves are shown in Figure 1.

Table 1: Concentration of calibration standards

Element	Unit	Cal. 0	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6
Al, Ca, Cu, Fe, K, Mg, Mn, Ni, Pb, Si, Zn	mg/L	0	0.01	0.05	0.2	0.5	1.0	-
Na, S	mg/L	0	-	0.05	0.2	0.5	1.0	5.0

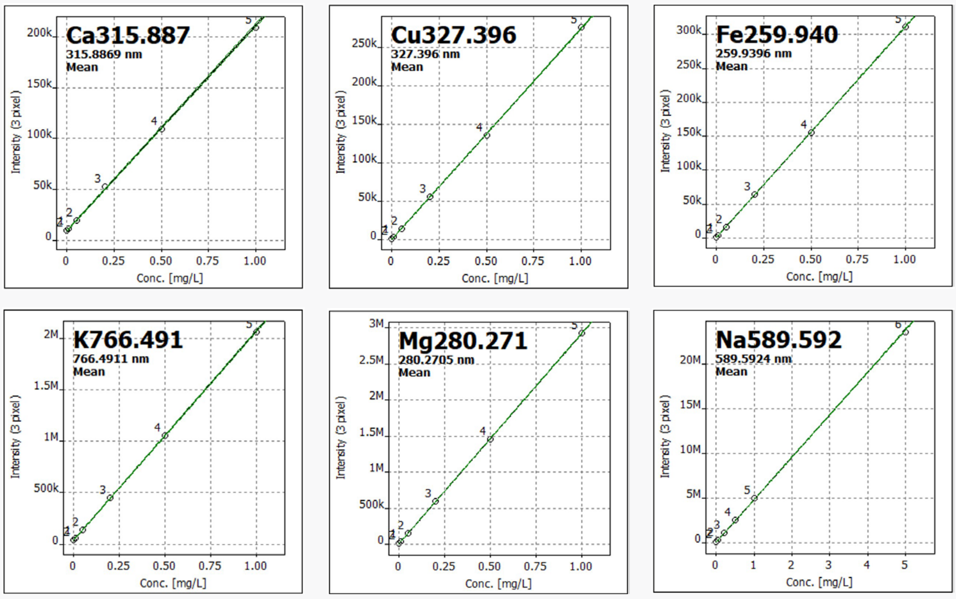


Figure 1: Selected calibration curves

Instrument settings

The analysis was performed on a PlasmaQuant 9100 Elite ICP-OES. The sample introduction components as well as the instrumental settings were selected to achieve low detection limits for trace elements in high salt containing matrices. The instrument was equipped with a glass concentric SeaSpray™ nebulizer, a cyclonic spray chamber with dip tube, and a 2.0 mm inner diameter injector tube. In conjunction with this instrument, a Teledyne CETAC ASX-560 autosampler was used. The distance between the injector and plasma was increased to reduce the probability of salt deposits at the injector tip.

Table 2: Instrument settings

Parameter	Setting
Plasma power	1,350 W
Plasma gas flow	14 L/min
Auxiliary gas flow	1.0 L/min[1]
Nebulizer gas flow	0.6 L/min
Nebulizer	Concentric, SeaSpray™, 2.0 mL/min, Borosilicate
Spray chamber	Cyclonic spray chamber with dip tube, 50 mL, Borosilicate
Outer tube / Inner tube	Quartz/Quartz
Injector	Quartz, ID: 2 mm
Sample tubing	PVC (black/black)
Pump rate	1.00 mL/min
Fast pump rate	2.0 mL/min
Measuring delay / Rinse time	60 s/30 s
Torch position	-1 mm[1]

1 … increasing distance between injector and plasma which reduces deposits at the injector tip

Method and evaluation parameters

Table 3: Method parameters

Element	Line [nm]	Plasma View	Integration	Read Time [s]	Evaluation		
					Pixel	Baseline fit	Poly. deg.
Al	396,152	axial	Peak	1	3	ABC[1]	auto
Ca	315,887	axial	Peak	1	3	ABC	auto
Cu	327,396	axial	Peak	1	3	ABC	auto
Fe	259,940	axial	Peak	1	3	ABC	auto
K	766,481	axial	Peak	1	3	ABC	auto
Mg	280,271	axial	Peak	1	3	ABC	auto
Mn	259,372	axial	Peak	1	3	ABC	auto
Na	589,592	axial	Peak	1	3	ABC	auto
Ni	221,648	axial	Peak	1	3	ABC	auto
Pb	220,353	axial	Peak	3	3	ABC	auto
S	180,672	axial	Peak	1	3	ABC	auto
Si	251,611	axial	Peak	1	3	ABC	auto
Zn	206,200	axial	Peak	1	3	ABC	auto

1 ... **A**utomated **B**aseline **C**orrection

Results and Discussion

Sensitivity and spectral resolution

The limits of detection (LODs) were calculated following the equation 1:

$$\mathrm{LOD} = 3 \times \sigma_0 \qquad (1)$$

where σ_0 is the standard deviation of 11 replicates of the blank. The instrumental and method detection limits, which consider the dilution factor of the dilution step, are shown in Table 4. Additionally, specifications for different purity grades of Li_2CO_3 are listed.

Table 4: Instrumental (IDL), method detection limits (MDL), and technical specifications for high purity Li_2CO_3 samples

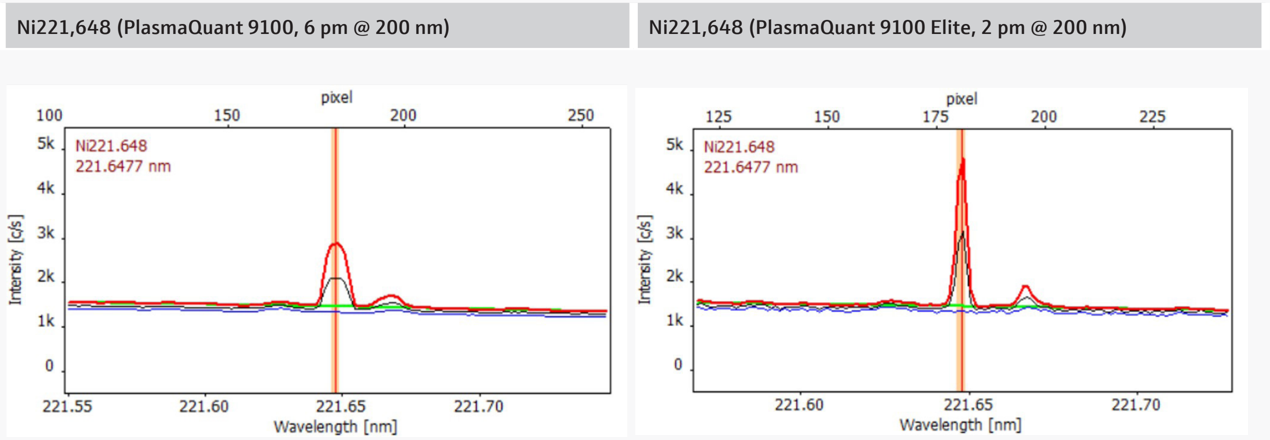
Element	Line [nm]	IDL* [µg/L]	MDL [mg/kg]	Li_2CO_3 > 99.90% purity requirement [mg/kg]	Li_2CO_3 > 99.95% purity requirement [mg/kg]
Al	396,152	0.9	0.018	≤ 2	≤ 2
Ca	315,887	1.1	0.022	≤ 25	≤ 20
Cu	327,396	0.5	0.010	≤ 2	≤ 1.5
Fe	259,940	0.3	0.006	≤ 2	≤ 1
K	766,481	0.7	0.014	≤ 10	≤ 10

Continuation of table 4: Instrumental (IDL), method detection limits (MDL), and technical specifications for high purity Li_2CO_3 samples

Element	Line [nm]	IDL* [µg/L]	MDL [mg/kg]	Li_2CO_3 > 99.90% purity requirement [mg/kg]	Li_2CO_3 > 99.95% purity requirement [mg/kg]
Mg	280,271	0.1	0.002	≤ 10	≤ 5
Mn	259,372	0.1	0.002	≤ 5	≤ 3
Na	589,592	0.6	0.012	≤ 20	≤ 15
Ni	221,648	0.1	0.002	≤ 30	≤ 10
Pb	220,353	2.2	0.044	≤ 5	≤ 3
S	180,672	7.9	0.158	≤ 10	≤ 8
Si	251,611	1.8	0.036	≤ 40	≤ 20
Zn	206,200	0.2	0.004	≤ 10	≤ 10

* determined in 5% (w/v) Li_2CO_3 solution [3]

The PlasmaQuant 9100 Elite offers a high sensitivity which is based on a multitude of technical features. The four-wind coil in combination with counter gas technology provides an elongated analytical zone in axial observation mode to provide as much signal as possible in ICP-OES. On top of this, the spectral resolution of 2 pm @ 200 nm (Figure 2) makes the use of laborious correction algorithms, such as inter-element correction, obsolete. This allows for a reliable and interference-free quantification of trace elements by granting access to most sensitive emission lines and high-definition peak shapes with extra sensitivity. This improved detectability enables the user to easily meet requirements for battery grade Li_2CO_3 and even allows to further dilute the sample to minimize instrument maintenance and downtime.


Ni221,648 (PlasmaQuant 9100, 6 pm @ 200 nm)

Ni221,648 (PlasmaQuant 9100 Elite, 2 pm @ 200 nm)

Figure 2: Comparison of PlasmaQuant 9100 (6 pm @ 200 nm) and PlasmaQuant 9100 Elite (2 pm @ 200 nm) illustrating the application advantage of high-resolution spectra (*red*: sample, *blue*: blank, *black*: Cal. Std., *green*: baseline correction (ABC))

Analyte recovery

To test the accuracy of the measurements, a spike recovery test was carried out in blank solution at a spike level of 0.1 mg/L. All analyte recoveries were within a ± 3% range illustrating the applicability of the analytical method for the determination of trace level impurities in Li_2CO_3.

Table 5: Analysis of sample and spike recovery study

Element	**Line [nm]**	**Li_2CO_3 Sample**			
		Spiked amount [mg/L]	**Found amount [mg/L]**	**RSD [%]**	**Spike recovery [%]**
Al	396,152	0.1	0.099	1.0	99
Ca	315,887	0.1	0.097	0.5	97
Cu	327,396	0.1	0.100	1.1	100
Fe	259,940	0.1	0.099	0.2	99
K	766,481	0.1	0.099	0.1	99
Mg	280,271	0.1	0.100	0.5	100
Mn	259,372	0.1	0.099	0.4	99
Na	589,592	0.1	0.097	1.0	97
Ni	221,648	0.1	0.099	0.2	99
Pb	220,353	0.1	0.098	1.3	98
S	180,672	0.1	0.100	1.1	100
Si	251,611	0.1	0.099	1.0	99
Zn	206,200	0.1	0.099	0.2	99

RSD ... Relative standard deviation (determined by 3 replicate measurements)

Long-term stability

Instrument robustness is critical for laboratories analyzing high salt containing matrices such as Li_2CO_3 solutions. The high-frequency generator of the PlasmaQuant 9100 Elite provides a plasma with superior durability to deliver a strong and constant signal intensity, even for samples with high salt contents. To demonstrate the robustness of the instrument the quality control (QC) sample was continuously aspirated for 4.5 hours. This monitoring resulted in analyte recoveries in the range of 93-105% (see Figure 3). Relative standard deviations below 2.2% indicate a highly stable performance of the instrumentation throughout the long-term measurement.

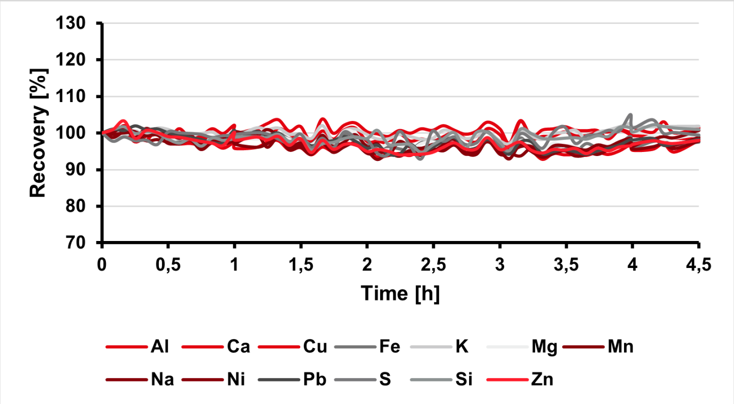


Figure 3: Percentage recoveries of spiked analytes (0.1 mg/L) in a 5% (w/v) Li_2CO_3 solution throughout a 4.5-hour sequence. RSD values were below 2.2% for all elements

Summary

The presented method describes the use of a HR ICP-OES in a high salt configuration for the analysis of lithium carbonate samples. It could be demonstrated that the requirements in terms of sensitivity, stability, and accuracy to perform the analysis of battery grade Li_2CO_3 samples can be easily met. The intelligent torch design of PlasmaQuant 9100 Elite prevents the formation of salt deposits on crucial glassware parts and ensures easy torch handling during maintenance. The high sensitivity of the PlasmaQuant 9100 Elite offers the option of further diluting high salt containing matrices which overall reduces the instrument downtime without compromising the investigated product's specification requirements. The methodology can be easily extended to other battery materials such as LiOH with the same advantages that a HR ICP-OES would provide.

Figure 4: PlasmaQuant 9100 Elite

References

[1] Chinese Standard: GB/T 11064.16-2013, Methods for chemical analysis of lithium carbonate, lithium hydroxide monohydrate and lithium chloride - Part 16: Determination of calcium, magnesium, copper, lead, zinc, nickel, manganese, cadmium and aluminum content - Inductively coupled plasma atomic emission

[2] IEC 62321:2013, Determination of certain substances in electrotechnical products - Part 4: Mercury in polymers, metals and electronics by CV-AAS, CV-AFS, ICP-OES and ICP-MS

[3] http://lithium-chemical.com/ and https://www.targray.com/, accessed January 2022

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