Challenge
Quantitative control for impurities in matrix-rich nickel and cobalt sulfate

Solution
The PlasmaQuant 9100 Elite high-resolution ICP-OES achieves excellent sensitivity, interference selection, and matrix tolerance with its industry-leading high-resolution optical system

Intended audience
Industries of anode and cathode materials for lithium-ion battery applications

Impurities in Nickel and Cobalt Sulphate by HR-ICP-OES

Introduction

The rapid development of lithium-ion battery technology has triggered a revolution in the electronics and automotive industry and emphasized the need for reliable energy storage. Lithium-ion batteries consist of several components, with the anode material playing a central role in energy storage and release. The anode material constitutes approximately 5% to 15% of the total material, and the quality and purity of the anode material is crucial for battery performance and safety. Contaminants in the anode materials can significantly affect electrochemical performance and must, therefore, be carefully controlled. Contaminants in electrode materials consist of components other than the main element and elements introduced through encapsulation and doping. These contaminants are typically introduced through raw materials or during the production process and can seriously impair battery electrochemical performance. Therefore, it is of paramount importance to control these contaminants at the source. Some metallic contaminants, for example, can not only reduce the proportion of active material in the electrode but also catalyze undesired side reactions between the electrode material and the electrolyte. In extreme cases, these contaminants can even breach the separator, posing a substantial safety risk. Thus, it is indispensable to accurately determine the content of these contaminants to ensure high-quality batteries with optimal performance and safety. The content of impurities in nickel and cobalt sulfate, the primary raw materials for ternary materials, directly impacts the price and quality of these materials and is typically measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The HR ICP-OES PlasmaQuant 9100 Elite provides high optical resolution and enables precise analysis of impurities, even at very low concentrations in the ppb range in the sample. Since even minimal impurities in ternary materials during production significantly reduce battery lifespan, high detection capability is a superior advantage in production optimization. Special attention must be paid to potential spectral interferences in ICP-OES analysis that can be caused by the main element nickel and the line-rich element cobalt.

These interferences can compromise data accuracy and must, therefore, be carefully considered and corrected during analysis. To meet high-quality requirements, it is necessary to examine not only metallic elements but also non-metallic elements such as silicon, phoswphorus, and sulfur for quality control. These elements can also influence the performance of ternary materials and must be included in the analysis to enable a comprehensive assessment of material quality.

The precise determination of impurity content in primary raw materials and the accurate characterization of ternary materials are crucial to ensure competitive prices and high-quality battery products. ICP-OES analysis plays a crucial role in this and enables manufacturers to optimize material composition for the best performance characteristics and long-term reliability of lithium-ion batteries.

Materials and Methods

Samples and reagents

- Multi-element standard solution: 100 mg/L, National Non-Ferrous Metals GNM M295388 2013 for the determination of As, P, Zn, Cd, Pb, Co, Mn, Fe, Cr, Mg, Cu, Na, Li
- Multi-element standard solution: Inorganic IV-26: Si 50 mg/L, B 100 mg/L, K 1000 mg/L
- Single element standard solution: 1000 mg/L Li, National Non-Ferrous Metals

Four samples were examined in this study:

- $CoSO_4$ 211220 D (referred to as Co220)
- $CoSO_4$ 211217 D (referred to as Co217)
- $NiSO_4$ Q018A2201710 (referred to as Ni1710)
- $NiSO_4$ Q018A2201711 (referred to as Ni1711)

Sample preparation

Each sample was carefully weighed to exactly 1 g and then diluted with ultrapure water to a total volume of 50 mL to perform the analysis. The dilution was done to an accuracy of 0.1 mg to ensure the precision of the results.
The samples were then analyzed on the PlasmaQuant 9100 Elite to determine impurity levels and dopant recoveries. The accurate sample preparation and use of the PlasmaQuant 9100 Elite allowed the impurities and dopants in the samples to be precisely quantified.

Table 1: Unit settings

Parameter	Specification
Plasma power	1250 W
Plasma gas flow	15 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.5 L/min
Nebulizer	Concentric nebulizer for high salt content, borosilicate, 1.0 mL/min
Spray chamber	Cyclonic spray chamber with dip tube, 50 mL, borosilicate
Outer tube / inner tube	Syalon[1] / Quartz
Injector	Quartz, inner diameter 1 mm
Pump tubing	PVC (Sample: black/black, waste: red/red)
Pump rate	0.8 mL/min
Delay/purge time	20 s/25 s

[1] Ceramic outer tube extends plasma torch life in sodium-rich matrices

Table 2: Method parameters

Element	Line [nm]	Plasma-observable	Integration	Measuring time [s]	Evaluation			
					Pixel	Baseline	Polynomial	Correction
As	188.979 197.200	axial	Peak	2	3	ABC	auto	-
P	178.224	axial	Peak	2	3	ABC	auto	-
Zn	206.200	axial	Peak	2	3	ABC	auto	-
Cd	228.802	axial	Peak	2	3	ABC	auto	-
Ni	216.555	axial	Peak	2	3	ABC	auto	-
Pb	220.353 283.305	axial	Peak	2	3	ABC	auto	-
Co	237.863	axial		2	3	-	-	-
Mn	257.610	axial	Peak	2	3	ABC	auto	-
Fe	258.588 259.940	axial	Peak	2	3	ABC	auto	-
Cr	267.716	axial	Peak	2	3	ABC	auto	-
Mg	285.213	axial	Peak	2	3	ABC	auto	-
Cu	324.754	axial	Peak	2	3	ABC	auto	-
Al	167.022 396.152	axial	Peak	2	3	ABC	auto	-
Ca	396.847	radial	Peak	2	3	ABC	auto	-
Na	589.592	radial	Peak	2	3	ABC	auto	-
Li	670.791	radial	Peak	2	3	ABC	auto	-
Si	251.611	axial	Peak	2	3	ABC	auto	-
B	249.773 208.955	axial	Peak	2	3	ABC	auto	-
K	766.491	radial	Peak	2	3	ABC	auto	-

Calibration

The standards for external calibration were prepared from multi-element as well as single-element standard solutions. The concentrations of the prepared calibration solutions for each sample matrix are listed in Table 3. Examples of resulting calibration functions are shown in Figure 1.

Table 3: Concentrations (mg/L) of the calibration standards for external calibration

Standard	As, P, Zn, Cd, Ni, Pb, Co, Mn, Fe, Cr, Mg, Cu, Al, Ca, Na, Li	B	K	Si
Cal. 0	0	0	0	0
Std. 1	0.001	0.02	0.2	0.01
Std. 2	0.01	0.04	0.4	0.02
Std. 3	0.05	0.06	0.6	0.03
Std. 4	0.1	0.1	1	0.05
Std. 5	-	0.2	-	0.1

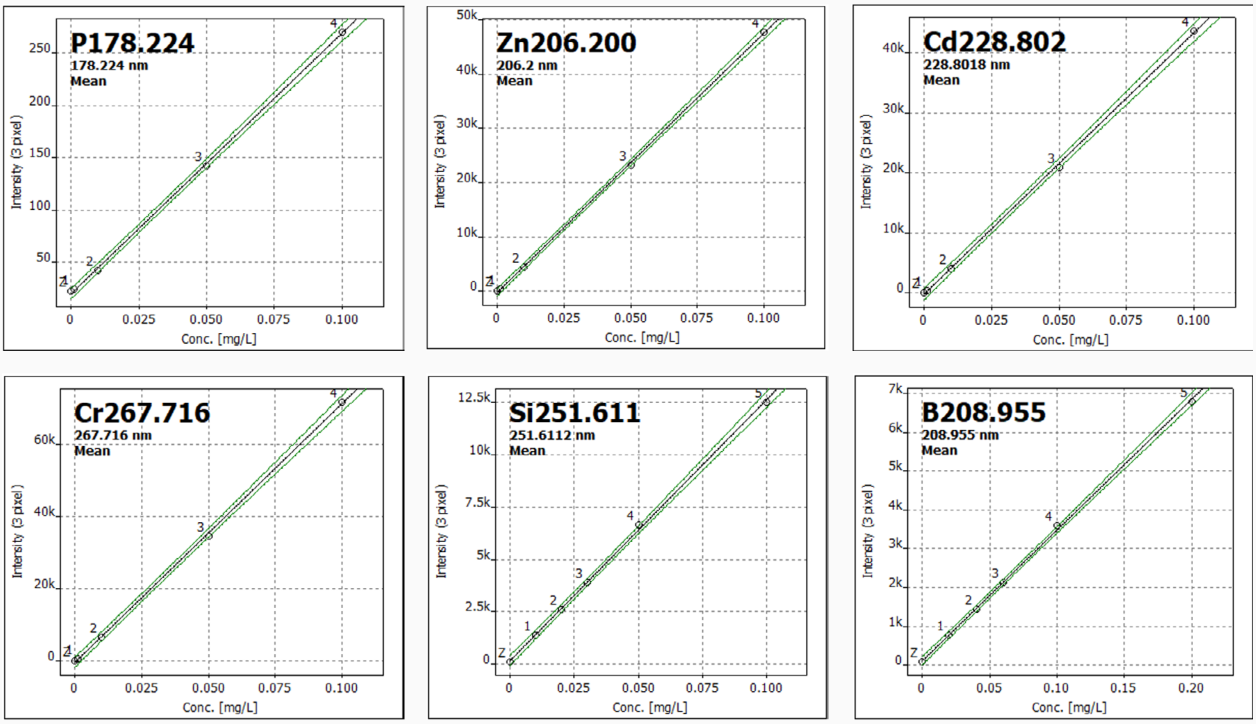

Figure 1: Examples of calibration functions

Results and Discussion

The following Tables 4 and 5 summarize the measurement results of the two nickel sulphate and cobalt sulphate samples. The samples Ni1710 and Co217 were additionally spiked with 0.1 ppm of each analyte (“QC spike“) and the recovery rate was determined.

Table 4: Measurement results and QC spike recovery in nickel sulphate

Element	Line [nm]	Measured Conc. Sample Ni1710 [mg/kg]	Measured Conc. Sample Ni1711 [mg/kg]	Recovery rate QC spike [%]
As	197.200	0.23	0.34	93
P	178.224	2.22	2.25	87
Zn	206.200	<0.1	<0.1	84
Cd	228.802	0.07	0.06	82
Pb	283.305	0.61	0.46	85
Co	237.863	<0.1	<0.1	92
Mn	257.610	0.03	0.03	88
Fe	259.940	0.19	0.21	89
Cr	267.716	0.03	0.04	85
Mg	285.213	9.30	8.68	89
Cu	324.754	0.19	0.16	90
Al	396.152	0.09	0.09	88
Ca	396.847	0.10	0.08	85
Na	589.592	8.69	8.10	86
Li	670.791	42.87	43.59	-
Si	251.611	1.94	1.90	83
B	208.955	1.87	2.07	90
K	766.491	0.62	0.35	95

Table 5: Measurement results and QC spike recovery in cobalt sulphate

Element	Line [nm]	Measured Conc. Sample Co217 [mg/kg]	Measured Conc. Sample Co220 [mg/kg]	Recovery rate QC spike [%]
As	188.979	<0.1	<0.1	91.1
P	178.224	3.12	3.34	94.6
Zn	206.200	0.26	0.26	81.5
Cd	228.802	0.80	0.83	84.0
Ni	216.555	24.54	19.43	85.6
Pb	220.353	2.92	2.20	89.8
Mn	257.610	0.75	1.27	87.5
Fe	258.588	2.089	1.926	82.1
Cr	267.716	0.061	0.052	82.8
Mg	285.213	5.23	2.75	86.7

Element	Line [nm]	Measured Conc. Sample Co217 [mg/kg]	Measured Conc. Sample Co220 [mg/kg]	Recovery rate QC spike [%]
Cu	324.754	0.70	0.69	93.8
Al	167.022	<0.1	<0.1	85
Ca	396.847	0.63	0.52	88.6
Na	589.592	9.97	9.37	93.4
Li	670.791	0.43	0.34	-
Si	251.611	1.15	1.14	86.6
B	249.773	<0.1	<0.1	110.6
K	766.491	0.69	0.96	100.1

Thanks to the remarkable spectral resolution of the PlasmaQuant 9100 Elite at 2 picometers (@ 200 nanometers), the comprehensive evaluation of analytes is facilitated without encountering spectral overlaps attributed to matrix-related effects. Figures 2 and 3 elucidate this phenomenon by employing silicon and boron as illustrative examples in diverse sample matrices.

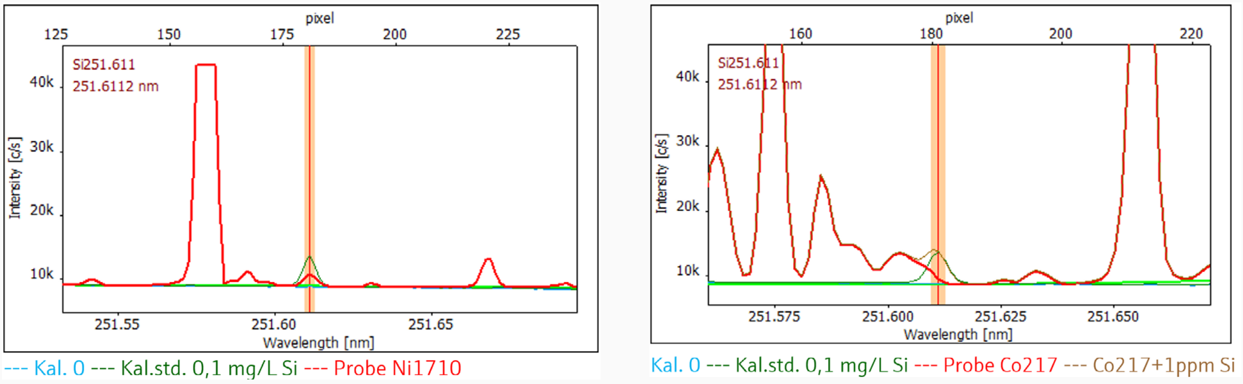

Figure 2: Enlarged spectra of Si in nickel sulphate (left) and Si in cobalt sulphate (right)

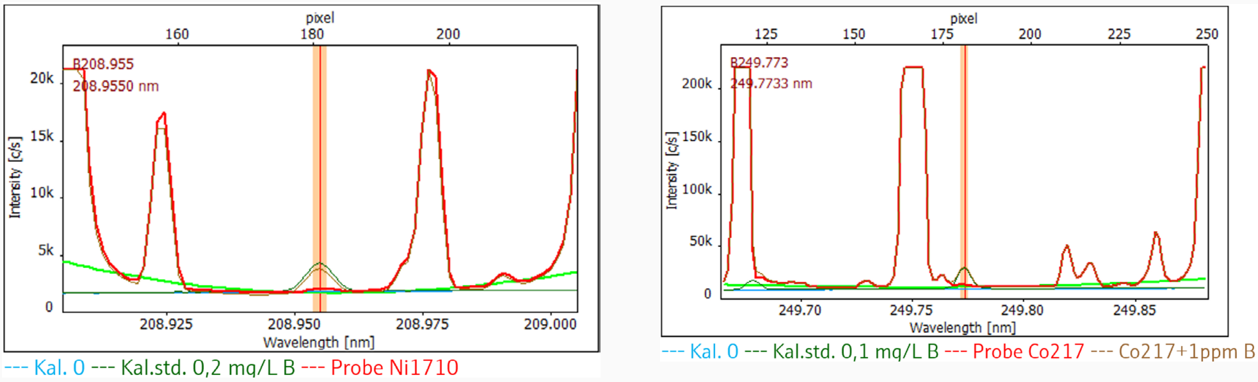

Figure 3: Enlarged spectra of B in nickel sulphate (left) and B in cobalt sulphate (right)

Summary

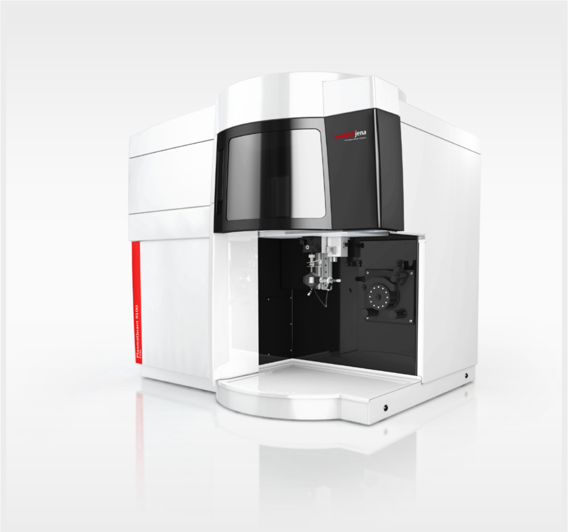

Figure 4: PlasmaQuant 9100 Elite

The PlasmaQuant 9100 Elite was used for the analysis of 18 elements in nickel and cobalt sulfate. The tested elements included aluminum (Al), arsenic (As), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), lead (Pb), zinc (Zn), silicon (Si), phosphorus (P), and nickel (Ni). The analysis results showed that these elements were present in a low concentration range of 0.001 to 0.1 ppm. The linearity of the results was good, with a linear regression coefficient ranging from 0.9991 to 0.99997. The accuracy of the results was confirmed through recovery tests falling within the range of 80% to 110%. This demonstrates the precision and reliability of the ICP-OES analysis on the PlasmaQuant 9100 Elite. The high optical resolution of the instrument allowed for an effective signal-to-noise ratio and thus low detection limits for the analyzed elements, enabling precise measurement of low concentrations and improving the accuracy of the analysis. Specifically, in the UV range, the PlasmaQuant 9100 Elite provided accurate and reliable results for the elements phosphorus (P) with a concentration range of 0.001 to 0.1 ppm, boron (B) with a concentration range of 0.02 to 0.2 ppm, and silicon (Si) with a concentration range of 0.01 to 0.1 ppm. Due to the high optical resolution of the instrument, there were no spectral interferences between the elements. Overall, the PlasmaQuant 9100 Elite delivers stable, accurate, and reliable results, making it an excellent tool for precisely measuring the content of impurity elements in nickel and cobalt sulfate. Using the PlasmaQuant 9100 Elite for analysis significantly contributes to quality control and research in battery manufacturing.

Recommended device configuration

Table 6: Overview of required devices and consumables

Article	Article Number	Description
PlasmaQuant 9100 Elite	818-09101-2	High resolution ICP-OES
Teledyne Cetac ASX 560	810-88015-0	The ASX-560 from Teledyne CETAC Technologies, a next-generation autosampler with integrated purge function, is slim and robust.
Salt-Kit	810-88009-0	Sample introduction system recommended for aqueous samples with high salt contents (e.g., brine, sea water applications)

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