



Challenge

Reliable and robust analysis of major, minor, and trace elements in black mass and cathode material.

Solution

High-Resolution ICP-OES with its Dual View PLUS option provides an extended linear dynamic range from sub-ppb level to %-range.

Intended audience

This AppNote is intended for the recycling sector of the battery industry.

Analysis of Black Mass and Cathode Material of Lithium-Ion Batteries using HR-ICP-OES

Introduction

Over the past few years, the battery industry has witnessed significant growth, particularly on the field of lithium-ion battery production. Due to their high energy capacity and extended lifecycle compared to other battery types, lithium-ion batteries are increasingly being recognized as essential components in various fields, including the automobile industry and portable devices like mobile phones or laptops, for example. Lithium-ion batteries can be categorized into different types based on their composition, such as lithium ferrous phosphate (LFP) or a combination of lithium, nickel, cobalt, and manganese (NCM). A major aspect in the value chain of the battery industry is environmental friendliness and sustainability. The recycling of battery materials is a crucial topic, driven by the goal of waste reduction. Currently, the European Union mandates a recycling efficiency of 50% by average weight of lithium-ion batteries ^[1]. However, there are plans to raise this rate to at least 65% by 2025 ^[2]. Following the decomposition of old batteries, the subsequent shredding and treatment process results in a

granular or powdery mixture called 'black mass'. This mixture comprises graphite, along with various metals (e.g., lithium, cobalt, copper, nickel, manganese) and their compounds. Notably, the composition of black mass can vary significantly depending on the specific battery type. In addition to analyzing the major elements that can be repurposed as raw materials for new batteries, determining the presence of trace and minor elements is also of interest, as these elements have the potential to impact the quality of the recycling material and the functioning of the new batteries. Before conducting the analysis, an effective sample preparation procedure is necessary to provide appropriate test solutions. This step is crucial for obtaining accurate measurement results using well-established analysis techniques such as atomic absorption spectroscopy (AAS) or inductively coupled plasma optical emission spectroscopy (ICP-OES). So far, there is no official guideline for sample preparation of battery materials for this purpose. Therefore, various experimental approaches are still being carried out.

For the measurements presented in this application note, shredded lithium-ion battery material (black mass) and cathode material was extracted with different acids and acid mixtures. The subsequent analysis was performed for major,

minor, and trace elements, using the high-resolution ICP-OES PlasmaQuant 9100 Elite.

Materials and Methods

Samples and sample preparation

Sample set 1:

Pyrolyzed black mass (LFP) of different particle sizes, treated by open hot block extraction using HNO_3 , HCl and H_2O_2 :

- Sample A: LFP black mass, fine (particle size 0-0.25 mm), V1
- Sample B: LFP black mass, coarse (particle size 0.25-0.5 mm)
- Sample C: LFP black mass, filter fraction
- Sample D: LFP black mass, fine (particle size 0-0.25 mm), V3

For preparation of the test solutions, an acid extraction with 2 replicates per sample was carried out. For this, 0.2 g of each sample was weighed into a graduated 50 mL extraction tube and 6 mL conc. HNO_3 , 2 mL H_2O_2 and 1 mL conc. HCl were added. These mixtures were heated on a heating block (HotBlock®, Environmental Express) for 2 h at 110 °C. After cooling to room temperature, the solutions were filled up to 50 mL with deionized water. Subsequently, the resulting particle-containing solutions were filtered. For this purpose, a stamp filter system was applied (FilterMate SC0401 Digestion Tube Filter, PTFE, Environmental Express) and the supernatant was used to prepare the final test solutions. For analysis, the sample solutions were diluted by a factor of 20 using 2% (v/v) HNO_3 .

Reagents

- HNO_3 (65%, p.a., Carl Roth)
- HCl (32%, p.a., VWR)
- H_2O_2 ($\geq 30\%$ for ultra-trace analysis, Sigma Aldrich)
- Single and multi-element standard solutions for ICP (Merck, Sigma Aldrich)

Sample set 2:

Provided acid extractions of cathode material using different reagent mixtures:

- Sample E: NMC, H_2SO_4 4M
- Sample F: NMC, H_2SO_4 4M + 15% H_2O_2
- Sample G: NMC, HNO_3 + HCl (1+3), solution pre-diluted 1:3
- Sample H: NMC, HNO_3 + HCl (1+3), solution pre-diluted 1:5

The submitted samples have been already prepared using different acid mixtures (H_2SO_4 only, H_2SO_4 + H_2O_2 and with aqua regia). The thermal treatment was carried out in open vessels at 100 °C for 1 h on a hot plate using an initial sample weight of 4 g. The particle-containing solutions (100-200 mL) were subsequently filtered. By subtraction of the filter residue mass from the initial weight of this sample set it was found that approx. 0.4-2.4 g went into solution. The supernatant of each filtration was analyzed either undiluted or diluted according to the element concentration using 2% (v/v) HNO_3 .

100 μL of a 50 mg/L yttrium solution was added to each test solution and calibration standard per 10 mL volume as an internal standard.

Instrumentation and method parameters

The analysis was performed on the High-Resolution ICP-OES PlasmaQuant 9100 Elite, equipped with an autosampler and a standard sample introduction kit for sample set 2. Since significant fluorine contents (AlF_3) had to be expected in sample set 1, a hydrofluoric acid resistant sample introduction system was applied (HF kit). Individual settings and components are summarized in Table 1. Detailed information about the method parameters and settings are listed in Table 2.

Table 1: Common instrument configuration and settings

Parameter	Specification - Sample set 1	Specification - Sample set 2
Plasma power	1350 W	1200 W
Plasma gas flow	14 L/min	13 L/min
Auxiliary gas flow	0.5 L/min	0.5 L/min
Nebulizer gas flow	0.6 L/min	0.5 L/min
Nebulizer	parallel path, PFA, 1 mL/min	concentric, borosilicate glass, 1 mL/min
Spray chamber	cyclonic, 50 mL, PTFE	cyclonic, 50mL, borosilicate glass
Outer tube / inner tube	ceramic/ceramic (alumina)	quartz glass/quartz glass
Injector	alumina, 2 mm id	quartz glass, 2 mm id
Pump tubing	PVC (sample: black/black, waste: red/red)	PVC (sample: black/black, waste: red/red)
Pump rate	1.0 mL/min	1.0 mL/min
Fast pump	4.0 mL/min	4.0 mL/min
Measuring delay/rinse time	45 s/45 s	45 s/45 s
Torch position	0 mm	0 mm

Table 2: Method parameters

Element	Line [nm]	Plasma view	Integrations	Read time [s]	Evaluation			
					Pixel	Baseline fit	Poly. deg.	Correction
Al	396.152	atten. axial ¹	Peak	1	3	ABC	auto	-
		axial ²	Peak	3	3	ABC	auto	IS (Y)
Cu	327.396	atten. axial ¹	Peak	1	3	ABC	auto	-
		axial ²	Peak	3	3	ABC	auto	IS (Y)
Li	670.791	atten. radial ¹	Peak	1	3	ABC	auto	-
		radial ²	Peak	3	3	ABC	auto	IS (Y)
Co	238.892	radial ²	Peak	3	3	ABC	auto	IS (Y)
Cr	206.158	axial ²	Peak	3	3	ABC	auto	IS (Y)
Fe	259.939	axial ²	Peak	1	3	ABC	auto	IS (Y)
Ga	294.364	axial ²	Peak	10	3	ABC	auto	IS (Y)
Mg	285.212	axial ²	Peak	1	3	ABC	auto	IS (Y)
Mn	257.610	radial ²	Peak	3	3	ABC	auto	IS (Y)
Mo	202.030	axial ²	Peak	5	3	ABC	auto	IS (Y)
Ni	231.603	radial ²	Peak	3	3	ABC	auto	IS (Y)
Si	251.611	axial ²	Peak	3	3	ABC	auto	IS (Y)
Ti	334.941	axial ²	Peak	3	3	ABC	auto	IS (Y)
Zn	206.200	axial ²	Peak	1	3	ABC	auto	IS (Y)

¹: applied for sample set 1²: applied for sample set 2, ABC: Automatic Baseline Correction, atten.: attenuation mode, IS (Y): Correction by internal standard (yttrium)

Calibration

Multi-element stock solutions were prepared using single element and multielement standard solutions (Merck, Sigma-Aldrich). The working standards were prepared by serial volume/volume dilution in polypropylene tubes of the stock solutions using 2% (v/v) HNO₃.

Calibration levels for each element were chosen based on the expected concentration ranges. The concentrations of the calibration standards are listed in Table 3 and examples for resulting calibration functions used for quantification are shown in Figure 1.

Table 3: Concentrations of the calibration standards

Standard	Conc [mg/L] - Sample set 1		Concentration [mg/L] - Sample set 2				Correction
	Al, Li	Cu	Al, Cr, Cu, Fe, Ga, Mg, Zn	Co, Mn, Ni	Li	Mo, Si, Ti	
Cal. std. 0	0	0	0	0	0	0	-
Cal. std. 1	1	1	0.025	0.5	0.25	0.01	IS (Y)
Cal. std. 2	5	5	0.25	5	2.5	0.1	-
Cal. std. 3	10	10	2.5	50	25	1	IS (Y)
Cal. std. 4	50	50	-	-	-	-	-
Cal. std. 5	-	100	-	-	-	-	IS (Y)

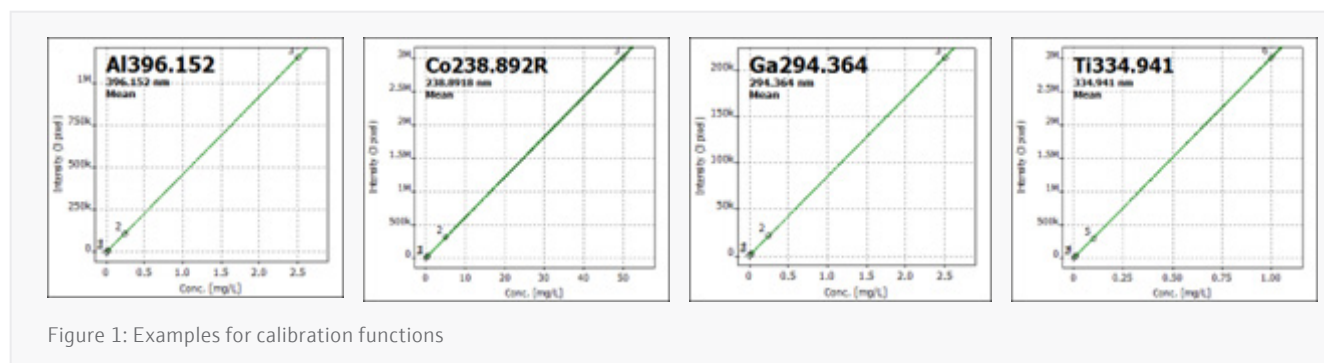


Figure 1: Examples for calibration functions

Results and Discussion

The following Tables 4 and 5 show the results for the elements of interest in the analyzed sample sets. To verify the accuracy of the method for the main components, the sample solutions were spiked with defined analyte concentrations (sample set 1: 10 mg/L Al/Li and 40 mg/L Cu; sample set 2: 10 mg/L Co/Mn/Ni, 5 mg/L Li, and 0.5 mg/L Cu). The results in g/kg are calculated for the initial sample weight (0.2 g and 4 g, respectively, see chapter "Samples and sample preparation").

Table 4: Measuring results – Sample set 1

Standard	Element	DF	Replicate #1		Replicate #2		QC stock recovery [%]
			Measured value [g/kg]	RSD _(n=3) [%]	Measured value [g/kg]	RSD _(n=3) [%]	
Sample A	Al	20	12.2	1.4	14.1	1.7	95.7
	Cu	20	44.4	1.7	44.4	1.3	93.3
	Li	20	26.7	0.8	30.4	0.4	92.6
Sample B	Al	20	27.2	1.0	25.9	1.4	97.2
	Cu	20	75.9	0.5	70.1	1.0	98.6
	Li	20	35.1	1.7	33.3	0.7	109
Sample C	Al	20	10.5	0.4	8.5	0.7	99.4
	Cu	20	22.4	0.6	21.0	0.6	95.6
	Li	20	11.3	0.9	10.8	1.9	105
Sample D	Al	20	45.0	1.4	48.9	0.4	93.7
	Cu	20	170	0.5	182	0.5	99.1
	Li	20	22.5	0.3	22.8	1.6	102

RSD: Relative standard deviation of three measurement replicates, DF: manual pre-dilution factor, QC stock: sample spiked with 10 mg/L Al/Li and 40 mg/L Cu

Table 5: Measuring results – Sample set 2

Element	DF	Sample E			Sample F		
		Measured value [g/kg]	RSD _(n=3) [%]	QC stock recovery [%]	Measured value [g/kg]	RSD _(n=3) [%]	QC stock recovery [%]
Al	10	1.22	1.5	-	1.24	1.8	-
Co	100	80.4	1.5	108	196	1.3	102
Cr	10	0.02	0.6	-	0.01	0.9	-
Cu	100	5.45	0.9	105	5.65	0.5	109
Fe	10	0.091	1.7	-	0.061	1.5	-
Ga	1	< LOD	-	-	< LOD	-	-
Li	100	63.7	0.7	107	74.5	0.7	106
Mg	10	0.085	1.0	-	0.105	1.3	-
Mn	100	73.7	0.8	106	183	1.1	101
Mo	1	0.0004	2.6	-	0.0003	1.8	-
Ni	100	82.9	1.5	103	199	1.5	103
Si	10	0.075	10.3	-	0.71	1.6	-
Ti	1	0.007	0.9	-	0.001	0.6	-
Zn	10	0.016	2.6	-	0.016	2.1	-

RSD: Relative standard deviation of 3 measurement replicates, DF: manual pre-dilution factor, LOD: Limit of Detection; QC stock: sample spiked with 10 mg/L Co/Mn/Ni, 5 mg/L Li, and 0.5 mg/L Cu

Continuation table 5: Measuring results – Sample set 2

Element	DF	Sample G			Sample H		
		Measured value [g/kg]	RSD _(n=3) [%]	QC stock recovery [%]	Measured value [g/kg]	RSD _(n=3) [%]	QC stock recovery [%]
Al	10	0.20	0.1	-	0.19	0.4	-
Co	100	112	0.6	102	113	1.5	102
Cr	10	0.018	0.5	-	0.018	0.7	-
Cu	100	2.87	1.2	98	2.89	0.6	99
Fe	10	0.091	1.6	-	0.096	0.8	-
Ga	1	< LOD	-	-	< LOD	-	-
Li	100	43.1	1.4	102	42.9	0.2	101
Mg	10	0.69	0.9	-	1.31	0.4	-
Mn	100	107	1.8	104	108	1.1	105
Mo	1	< LOQ	-	-	< LOQ	-	-
Ni	100	113	0.5	104	115	0.6	103
Si	10	2.71	1.1	-	3.63	1.4	-
Ti	1	0.003	0.5	-	0.003	1.1	-
Zn	10	0.39	1.7	-	0.67	2.1	-

RSD: Relative standard deviation of 3 measurement replicates, DF: manual pre-dilution factor, LOD: Limit of Detection; QC stock: sample spiked with 10 mg/L Co/Mn/Ni, 5 mg/L Li, and 0.5 mg/L Cu

The instrumental and method specific limits of detection (LOD) and limits of quantification (LOQ) of the analysis are given in Table 6. These values were determined by using the reagent blank method (3 or 9 times the standard deviation of 11 repeated measurements of the reagent blank). The calculation of the method specific LOD/LOQ comprises the dilution factor by sample preparation and additional manual dilution.

Table 6: Instrumental and method specific limits of detection (LOD) and limits of quantification (LOQ)

Element	LOD _{inst} [µg/L]	LOQ _{inst} [µg/L]	LOD _{meth} [mg/kg]	LOQ _{meth} [mg/kg]
Al ¹	1.3	3.9	6.5	19.5
Al ²	0.4	1.2	0.2	0.6
Co ²	1.0	3.0	5	15
Cr ²	0.5	1.5	0.25	0.75
Cu ¹	1.8	5.4	9.0	27.0
Cu ²	0.3	0.9	1.5	4.5
Fe ²	0.15	0.5	0.075	0.25
Ga ²	0.9	2.7	0.045	0.135
Li ¹	1.9	5.7	9.5	28.5
Li ²	0.1	0.3	0.5	1.5

Continuation table 6: Instrumental and method specific limits of detection (LOD) and limits of quantification (LOQ)

Element	LOD _{inst} [$\mu\text{g/L}$]	LOQ _{inst} [$\mu\text{g/L}$]	LOD _{meth} [mg/kg]	LOQ _{meth} [mg/kg]
Mg ²	0.1	0.3	0.05	0.15
Mn ²	0.1	0.3	0.5	1.5
Mo ²	0.3	0.9	0.015	0.045
Ni ²	1.0	3.0	5	15
Si ²	0.4	1.2	0.2	0.6
Ti ²	0.04	0.12	0.002	0.006
Zn ²	0.14	0.4	0.07	0.2

¹: method for sample set 1 (0.2 g sample, 50 mL volume, add. dilution 1:20)

²: method for sample set 2 (4 g sample, 200 mL volume, add. dilution see table 5)

LOD: Limit of Detection (3 times standard deviation of 11 blank measurements), LOQ: Limit of Quantification (9 times standard deviation of 11 blank measurements), inst.: instrumental, meth.: method specific

Summary

The high matrix tolerance as well as the high resolution and measurement sensitivity of the PlasmaQuant 9100 Elite enable an interference-free and robust analysis of the prepared sample solutions. The possibility to combine axial and radial plasma observation with additional attenuation mode for different elements in one method (Dual View PLUS) allows for an adaption of the measurement sensitivity and an increase of the linear working range. Thus, providing flexibility for individual analysis of analytes, which are present in varying concentration ranges. Software tools such as automatic baseline attachment (ABC) facilitate spectra evaluation and provide reliable measurement results. The extraction process using the open heating block (sample set 1) was conducted in duplicates. The measurement results of the individual replicates show a good comparability, affirming the reproducibility of the sample preparation procedure.

Using the spiking method, recoveries in the range of 92-110 % were determined for the analyzed elements, which indicates an interference-free analysis.

Upon using sulphuric acid for sample preparation (sample set 2) a signal suppressing matrix effect was observed, including the yttrium signal in the reagent blanks.

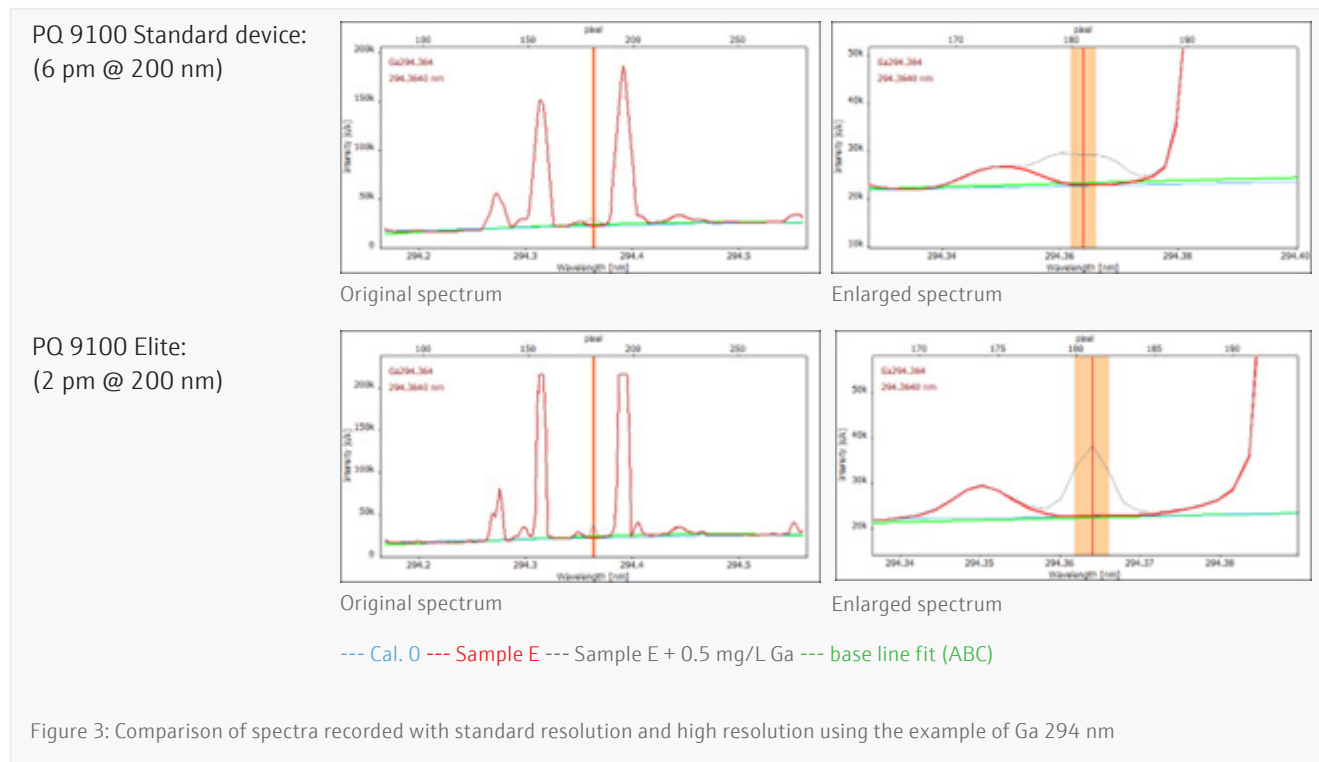
Consequently, a correction by the internal standard is recommended to improve the recovery of trace elements.

Sensitive analytical lines, which are commonly preferred for trace element evaluation, may be accompanied by discernible



Figure 2: PlasmaQuant 9100

emission bands originating from the sample matrix. Such bands can lead to partial overlap and potentially result in erroneously elevated measured values, particularly in the lower microgram-per-liter ($\mu\text{g/L}$) range. In this case the high-resolution spectrometer of the PlasmaQuant 9100 Elite (2 pm @ 200 nm) can be advantageous for a reliable and precise trace element analysis. Figure 2 shows an example for a low-resolution (6 pm @ 200 nm) spectrum of gallium at 294 nm compared to a high-resolution (2 pm @ 200 nm) spectrum in the observed sample matrix.



Recommended device configuration

Table 7: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9100 Elite	818-09101-2	High resolution ICP-OES
HF KIT for PlasmaQuant 9000 and PlasmaQuant 9100 series	810-88007-0	HF Kit
Teledyne Cetac ASX 560	810-88015-0	Autosampler with integrated rinse function

References

- [1] Official Journal of the European Union; DIRECTIVE 2006/66/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 6 September 2006 on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC, 2006, ANNEX III Part B, page 14
- [2] European Commission; Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL concerning batteries and waste batteries, repealing Directive 2006/66/EC and amending Regulation (EU) No 2019/1020, 2020, page 9

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