



Challenge

Automated fast and reliable analysis of major elements in black mass

Solution

High-resolution continuum-source (HR-CS) AAS contrAA 800 for fast sequential analysis in combination with the autosampler AS-FD with intelligent dilution function

Intended audience

Recycling sector of the battery industry

Analysis of Black Mass of Lithium-ion Batteries using HR-CS AAS

Introduction

Over the past few years, the battery industry has witnessed significant growth, particularly in 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 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 the 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 spectrometry (AAS) or inductively coupled plasma optical emission spectrometry (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, black mass was extracted with an acid mixture (HNO_3 , HCl , H_2O_2). The subsequent analysis was performed using the HR-CS flame AAS contrAA 800 F.

Materials and Methods

Samples and Sample Preparation

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 two replicates per sample was carried out. For this, 0.2 g of each sample were 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 with 1% (v/v) HNO_3 and 0.1% (m/v) Cs/La buffer according to the applied calibration range.

Table 2: Method and evaluation parameters

Element	Wavelength [nm]	Flame type	Fuel gas flow [L/h]	Burner height [mm]	Burner rotation [°]	No. of eval. pixels	Meas. time [s]	Background correction
Al	396.1520	$\text{N}_2\text{O}/\text{C}_2\text{H}_2$	230	5	0	3	3	IBC
Cu	324.7540	air/ C_2H_2	40	6	0	3	3	IBC
Li	670.7845	air/ C_2H_2	40	5	0	3	3	IBC

IBC: Iterative Baseline Correction

Calibration

The standards for external calibration were prepared automatically by the autosampler AS-FD from manually prepared stock solutions containing 1% (v/v) HNO_3 and 0.1% (m/v) Cs/La buffer. The concentrations of the calibration solutions are listed in table 3. The resulting calibration functions are presented in figure 1.

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 element standard solutions for AAS (1000 mg/L each, Merck)
- CsCl/LaCl₃ buffer solution (100 g/L each, Honeywell)

Instrumentation and Method Parameters

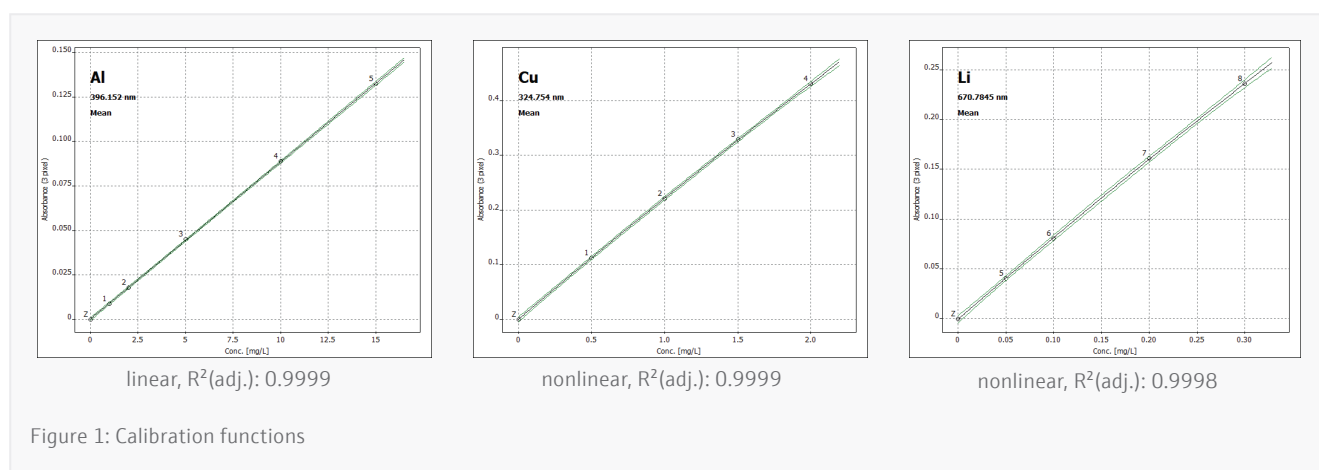
The analysis was performed with the high-resolution continuum-source flame AAS contrAA 800 F. Detailed information on the instrument configuration and method parameters are given in the following tables 1 and 2.

Table 1: General instrument configuration

Parameter	Specification
Instrument	contrAA 800 F
Autosampler	AS-FD
Burner head	50 mm
Other accessories	Scraper (for N_2O flame) Switching valve SFS 6.0

Table 3: Concentration of the calibration solutions

Standard	Concentration [mg/L]		
	Al	Cu	Li
Stock solution	50	10	1.0
Cal. 0	0	0	0
Cal. std. 1	1	0.5	0.05
Cal. std. 2	2	1.0	0.1
Cal. std. 3	5	1.5	0.2
Cal. std. 4	10	2.0	0.3
Cal. std. 5	15	-	-



Results and Discussion

The measurement results of both replicates for the individual samples are listed in table 4. To check for non-spectral interferences, the measuring solutions were spiked with a known analyte concentration and their recovery rate was determined („QC-spike“).

Table 4: Measurement results and recovery of the QC-spike

Sample	Element	DF	Replicate #1		Replicate #2		
			Measured analyte value [g/kg]	RSD _(n=3) [%]	Measured analyte value [g/kg]	RSD _(n=3) [%]	Recovery QC-spike* [%]
Sample A	Al	20	11.5	0.7	13.6	0.7	100
	Cu	1000	40.1	1.6	38.8	1.0	99.0
	Li	1000	22.4	0.5	23.9	0.4	101

Sample	Element	DF	Replicate #1		Replicate #2		
			Measured analyte value [g/kg]	RSD _(n=3) [%]	Measured analyte value [g/kg]	RSD _(n=3) [%]	Recovery QC-spike* [%]
Sample B	Al	20	25.3	0.8	25.5	0.8	95.5
	Cu	1000	62.9	0.8	62.7	0.3	97.1
	Li	1000	27.3	0.5	27.6	0.2	93.5
Sample C	Al	20	9.5	0.5	7.5	0.3	104
	Cu	100	22.8	1.6	21.2	0.6	99.3
	Li	1000	10.4	0.3	10.6	0.4	92.0
Sample D	Al	20	42.0	0.9	42.4	1.0	91.2
	Cu	1000	160	1.1	163	0.2	96.3
	Li	1000	19.1	0.7	18.9	0.6	96.0

DF: Manual dilution factor, RSD: relative standard deviation (3 measurement replicates)

*QC-spike: 5 mg/L Al, 1 mg/L Cu, 0.1 mg/L Li

The instrumental (LOD) and methodic limits of detection (MLD) as well as limits of quantification (LOQ/MLQ) are listed below (table 5). These values were determined by using the reagent blank method (3- or 9-fold standard deviation of 11 measurement repetitions of the reagent blank). The method-specific limits for the solid samples (mg/kg) consider a sample weight of 0.2 g per 50 mL filling volume.

Table 5: Limits of detection and quantification

Element	Line [nm]	LOD [$\mu\text{g/L}$]	LOQ [$\mu\text{g/L}$]	MLD [mg/kg]	MLQ [mg/kg]
Al	396.1520	12	36	3.0	9.0
Cu	324.7540	0.5	1.5	0.13	0.38
Li	670.7845	0.2	0.6	0.05	0.15

LOD/LOQ: Limit of detection/quantification

MLD/MLQ: Method-specific limit of detection/quantification

Summary

The contrAA 800 F offers the possibility of a fast-sequential analysis. Therefore, the test sample is aspirated once and during this time all the measuring wavelengths defined in the method are measured consecutively. Methods that require different flame gases (acetylene/air, acetylene/ N_2O) can be set and processed one after the other in the same sequence. The automatic burner head cleaner "Scraper" regularly clears the burner slit of carbon deposits during measurements using nitrous oxide flame so that clogging is avoided. The calibration standards can be mixed automatically by the AS-FD autosampler. In addition, automatic sample dilution is possible if the calibration range is exceeded. This fully automates the analysis process for routine use.

All wavelengths between 185-900 nm are available for analysis by using a Xenon short-arc lamp as a continuous radiation source. Due to this, no element-specific lamp change is necessary compared to classical AAS systems. In addition, the burn-in time of the radiation source can be omitted. The high resolution of the spectrometer (2 pm @ 200 nm) also provides additional information on the spectral vicinity of the analyte peak (Figure 3), whereby possible spectral interferences can be identified and corrected if necessary.

After an acid extraction, the submitted black mass samples could be analyzed without any interferences using the

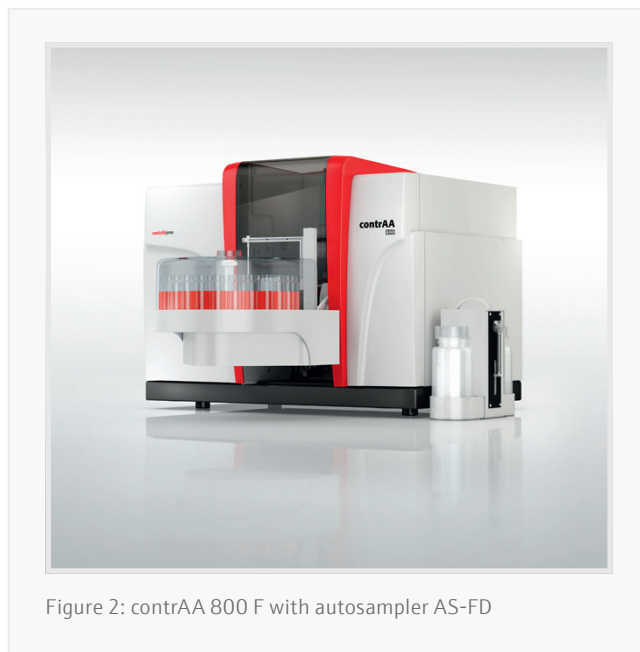
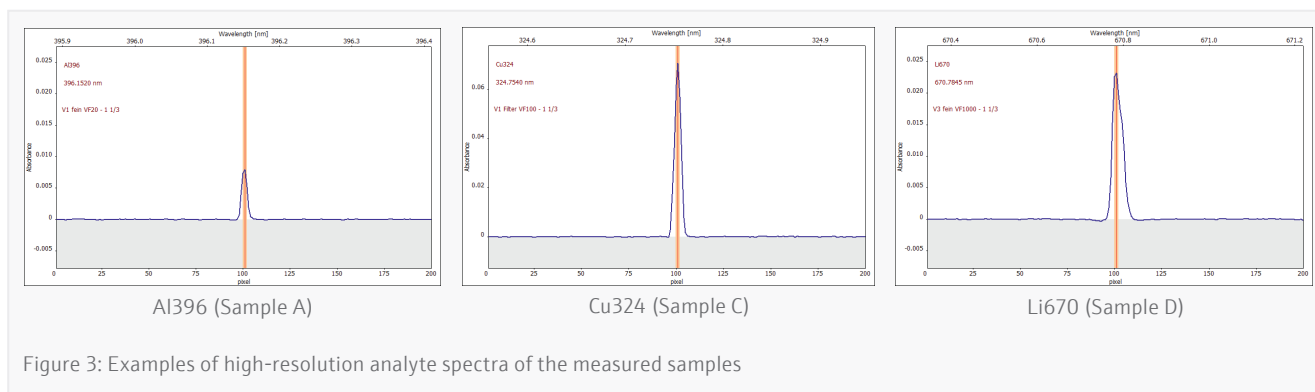


Figure 2: contrAA 800 F with autosampler AS-FD

high-resolution continuum-source flame AAS contrAA 800 F. Each sample was prepared and measured in duplicate. The measurement results of the individual replicates are well comparable, indicating a reproducible sample preparation procedure. Using the spiking method, recovery rates in the range of 91.2-101% were determined for the analyzed elements. This indicates an analysis unaffected by matrix effects.



Recommended device configuration

Table 6: Overview of devices, accessories, and consumables

Article	Item number	Description
contrAA 800 F	815-08000-2	High-Resolution Continuum-Source Flame-AAS (HR-CS AAS)
AS-FD Autosampler	810-60501-0	Autosampler with automatic dilution function
Sample rack 139 positions	810-60503-0	Sample rack 139 positions for AS-F and AS-FD, 129 position for 15 mL vials and 10 positions for 50 mL vial
Sample rack 54 positions	810-60502-0	Sample rack 54 positions for AS-F and AS-FD, 54 positions for 50 mL
Burner head NO/AC (50 mm)	810-60057-0	Burner head with 50 mm slit for acetylene/air and acetylene/nitrous oxide flame operation
Scraper	810-60127-0	Automatic burner head cleaner for nitrous oxide flame operation
Segmented Flow Star SFS 6.0	810-60129-0	Switching valve
Consumable set F for Flame technique	810-60258-0	Consumable set for flame technique for approximately 1000 analysis or 1 year

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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