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Application News

Inductively Coupled Plasma Atomic Emission Spectrometer ICPE-9820

Determination of Essential Metals and Trace Elements in Black Mass using ICPE-9820

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User Benefits

- Simultaneous analysis of essential metals (Li, Co, Ni, etc.) and trace elements in black mass can be analyzed, thus contributing to LiB recycling.
- ICPE-9820 can achieve accurate analysis with lower argon gas consumption and running cost using mini torch.

■ Introduction

There has been a surge in demand for lithium-ion batteries (LiBs) in recent years, driven primarily by the increasing global demand for consumer electronics demand and the shift towards electric vehicles in the automobile industry [1]. As a result, there is a substantial need for essential metals like cobalt (Co), lithium (Li), manganese (Mn), and nickel (Ni) to meet the growing production demands of LiBs. However, these valuable metals have limited global reserves, and the extraction process has adverse environmental effects.

To address these concerns, a sustainable approach such as LiBs recycling is necessary. Through the recycling process, essential metals can be reclaimed from spent batteries and repurposed as raw material for new batteries. This, in turn, minimizes waste generated from spent batteries. Currently, the European Union has set a minimum recycling efficiency of 50% by average weight of spent batteries [2].

One common method for recycling of LiBs and other electronic waste such as printed circuit boards, involves physical and thermo-mechanical processing to generate a granular powder mixture known as black mass. This mixture comprises varying concentrations of essential metals, graphite and electrolyte residues, and impurities such as trace elements. Analyzing black mass for both essential metals and trace elements is crucial for optimizing the separation techniques, thereby yielding recycled materials with desired characteristics for manufacturing of new batteries.

In this application news, Shimadzu ICPE-9820 (Figure 1), a simultaneous inductively coupled plasma (ICP) atomic emission spectrophotometer was used to conduct simultaneous analysis of elements in a black mass sample. With its dual plasma axial/radial axis viewing, analysis of elements present from trace to high level concentrations can be performed.

Fig. 1 ICPE-9820 simultaneous ICP atomic emission spectrometer

■ Sample and Standard Preparation

One black mass sample was provided as finely ground powder by a local battery recycling plant.

The component elements of black mass sample were pretreated using microwave digestion [3] and aqua regia, which is considered to be easy for dissolving metals, and applied to the component analysis of black mass sample. Approximately 100 mg of the black mass sample was added to a digestion vessel, followed by addition of 3.75 mL of concentrated hydrochloric acid (conc. HCl) and 1.25 mL of concentrated nitric acid (conc. HNO_3). After incubation for 15 minutes, the vessels were sealed, and microwave digestion was carried using the heating program in Table 1.

Table 1 Microwave digestion program

Step	Temperature (℃)	Power (W)	Duration (minutes)
1	240	1800	25 (ramp)
2	240	1800	40 (hold)

After microwave digestion, the digested samples were cooled to room temperature, followed by adding of deionized water to a volume of 50 mL. The residual graphite in the digested solution was allowed to settle, and the solutions were filtered through a 0.45 µm PTFE syringe filter. The digested samples were then further diluted 10 times before analysis. Two replicates of the sample were carried out. A sample blank solution was prepared in a similar procedure, without adding the sample to the digestion vessel during microwave digestion.

Calibration standards were prepared from commercially available single-element standard solutions and the calibration concentration ranges for the target elements are shown in Table 2. The calibration standards were acid matched to the digested samples using a mixed acid diluent. Yttrium (Y) was used as an internal standard and was added to all blanks, calibration standards and digested sample solutions prior to sample analysis.

Table 2 Calibration concentration range for target elements

Elements	Calibration Concentration Range (mg/L)
Co, Mn, Ni	0 – 50
Al, Cu, Fe, Li	0 – 10
B, Ca, Cr, Mg, Na, P, Si, Ti, Zn, Zr	0 - 2

Instrument and Measurement Conditions

Measurement was conducted using Shimadzu ICPE-9820 simultaneous ICP atomic emission spectrometer. The instrument and analytical conditions are shown in Table 3.

Table 3 Instrument and analytical conditions

Instrument	:	ICPE-9820
Radio frequency power	:	1.2 kW
Plasma gas flowrate	:	10.0 L/min
Auxiliary gas flowrate	:	0.60 L/min
Carrier gas flow rate	:	0.70 L/min
Nebulizer	:	Nebulizer 10
Spray Chamber	:	Cyclone Chamber
Plasma Torch	:	Mini Torch
Observation	:	Axial (AX) / Radial (RD)

Results and Discussion

Calibration Curve and Detection Limits

Figure 2 shows some example calibration curves for Al, Co, Li, Ni, Si and Zr.

The linear regression (R) of the calibration curves obtained are shown in Table 4. For most target elements, the R values obtained were higher than 0.9999, except for Na. This indicates good linearity was achieved for the selected wavelengths. Instrument Detection Limit (IDL) and Limit of Quantitation (LOQ) for the target elements are also shown in Table 4. The IDLs and LOQs are calculated from 3 and 10 times the standard deviation (σ) of 10 replicate measurements of a calibration blank respectively.

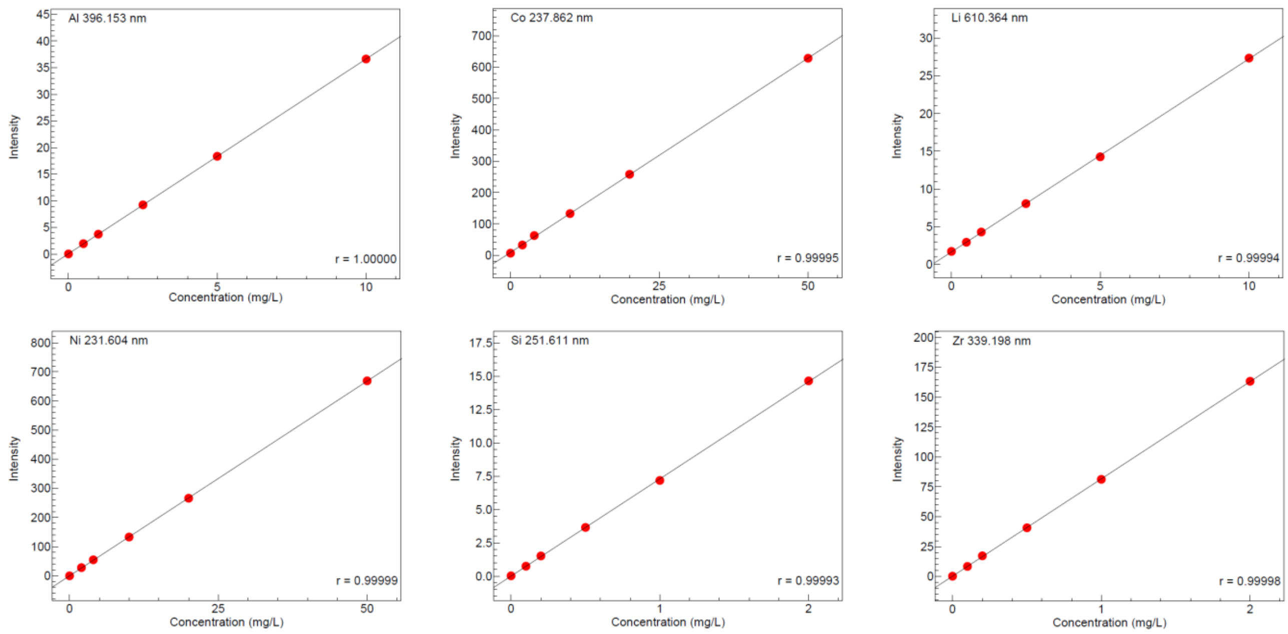

Fig. 2 Example calibration curve for Al, Co, Li, Ni, Si and Zr

Table 4 Linear regression, IDL and LOQ

Element	View Direction	Measured Wavelength (nm)	Linear Regression (R)	IDL (mg/L)	LOQ (mg/L)
Al	Radial	396.153	1.00000	0.04	0.1
B	Axial	208.959	0.99998	0.003	0.009
Ca	Radial	393.366	0.99995	0.0002	0.0006
Co	Radial	237.862	0.99995	0.01	0.04
Cr	Axial	267.716	0.99998	0.002	0.007
Cu	Axial	327.396	0.99997	0.005	0.02
Fe	Axial	259.940	0.99999	0.002	0.007
Li	Radial	610.364	0.99994	0.1	0.4
Mg	Axial	280.270	0.99998	0.0001	0.0003
Mn	Radial	257.610	0.99999	0.001	0.003
Na	Axial	589.592	0.99923	0.0008	0.003
Ni	Radial	231.604	0.99999	0.009	0.03
P	Axial	178.287	0.99995	0.04	0.1
Si	Axial	251.611	0.99993	0.001	0.004
Ti	Axial	337.280	0.99995	0.0003	0.001
Zn	Axial	202.548	0.99994	0.0007	0.002
Zr	Axial	339.198	0.99998	0.0007	0.002

IDL = 3 × σ × slope of calibration curve
LOQ = 10 × σ × slope of calibration curve

Quantitative Analysis of Black Mass and Spike Recovery

Table 5 shows the concentrations of 17 target elements in 2 replicates of the black mass sample, which were quantitatively measured using the calibration curve. The concentration results are reported in either wt% or mg/kg, calculated based on the dilution factor and initial sample weight. Elements such as Al Cu, Co, Li, Mn and Ni has concentration more than 1 wt%, while concentration for other elements were below 1 wt%. This demonstrates that both high and low concentration elements could be performed in a single analysis using ICPE-9820.

Table 5 Quantitative results for 2 replicates of black mass sample

Element	Black Mass Sample (Repetition 1)	Black Mass Sample (Repetition 2)
Unit : wt%		
Al	2.14	1.96
Co	10.4	9.49
Cu	1.33	1.65
Fe	0.37	0.40
Li	3.13	3.16
Mn	5.26	5.73
Ni	9.88	10.9
P	0.25	0.25
Unit: mg/kg		
B	28.3	21.2
Ca	387.3	229.2
Cr	46.2	52.9
Mg	194.6	185.3
Na	150.9	146.2
Si	705.1	721.3
Ti	143.0	222.8
Zn	157.9	154.2
Zr	320.3	337.5

A spike recovery test was performed to assess the effect of sample matrix interference on the analysis. The spike recovery results are presented in Table 6, showing recoveries ranging from 93 to 112% for all target elements. This indicates that the sample matrix effect has a minimal effect on the analysis.

Table 6 Spike recovery results for black mass sample

Element	Measured Value (mg/L)	Spike Level (mg/L)	Spiked Measured Value (mg/L)	Recovery (%)
Al	4.32	1.0	5.25	93
B	0.006	0.5	0.53	104
Ca	0.08	0.5	0.59	101
Co	21.0	5.0	26.6	112
Cr	0.01	0.5	0.52	101
Cu	2.67	1.0	3.69	102
Fe	0.74	1.0	1.76	102
Li	6.31	1.0	7.32	101
Mg	0.04	0.5	0.55	102
Mn	10.6	5.0	15.8	104
Na	0.06	0.5	0.55	98
Ni	19.9	5.0	25.5	112
P	0.52	0.5	1.02	100
Si	0.14	0.5	0.65	101
Ti	0.03	0.5	0.54	103
Zn	0.03	0.5	0.53	99
Zr	0.06	0.5	0.57	101

■ Conclusion

This application news demonstrated the use of ICPE-9820 for analysis of black mass samples. With its high sensitivity AX, and RD view observation for high concentration analysis, the ICPE-9820 enables simultaneous analysis across a wide concentration range, from low to high. Furthermore, the favorable spike recovery results indicate the high accuracy of the analysis.

■ Reference

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