MICAP-OES 1000

Analysis of metals in recycled lithium-ion battery components with a N_2 plasma ICP-OES system

Introduction

Lithium-ion batteries (LiBs) are widely used in consumer electronics, electric vehicles (EVs) and many renewable energy systems. With LiBs being used for so many applications in modern products and their use increasing very rapidly, efficient recycling is crucial for sustainability [1,2]. Supply constraints in their raw materials and the rising costs for dealing with the waste generated from spent LiBs clearly underscore the need to develop efficient recycling processes. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is commonly utilized to monitor the recovery of the critical metals in this electronic waste.

This note describes the use of the simultaneous MICAP™ OES-1000 N_2 ICP-OES system for routine analysis of shredded LiBs (known as black mass) processed with an acidic leach step. Elemental results from the MICAP on a black mass sample are presented to demonstrate accurate analysis for this complex sample.

RADOM™
INSTRUMENTS

Instrumentation

Used LiBs are typically shredded into a material commonly called “black mass”, which predominately consists of lithium, cobalt, nickel, manganese, and graphite. While there are several methods used to extract the desired metals from this solid mixture, in this work an acidic leach solution was utilized. The Radom Instruments MICAP-OES 1000 was configured with a standard aqueous sample introduction system. A single-pass cyclonic spray chamber and high-solids slurry nebulizer were connected to the standard torch for introduction of samples into the N_2 plasma.

Microwave energy in the MICAP is coupled into the Cerawave™ ring in a highly efficient process that creates the magnetic fields required to inductively couple energy into the robust N_2 plasma source. The 4 MP sCMOS camera simultaneously collects the resulting emission lines from the high-resolution spectrometer.

Experimental Conditions

The analysis was performed on the simultaneous MICAP ICP-OES (Figure 1) utilizing the conditions shown listed in Table 1. Samples were introduced with an autosampler, with each sample analysis taking approximately 3 minutes to complete.

Figure 1. MICAP-OES 1000 N_2 ICP-OES

Table 2 provides specifics on the analyte and Yttrium (Y) internal standard (I/S) wavelengths used for this analysis, as well as the detection limits obtained from 3x standard deviation of 10 blank measurements. Two mixed element stock standards were utilized to cover the analytes of interest, indicated by calibration groups A and B.

Table 1. Operational conditions for oil analysis

Parameter	Value
Torch	Quartz 1-piece, 1.5mm injector
Spray Chamber	Single pass glass cyclonic
Nebulizer	Glass Expansion Slurry
Sample Tubing	Wht/Wht PVC (1.02 mm ID)
Drain Tubing	Blu/Yel PVC (1.52 mm ID)
Rinse	3 % HCl + 1% HNO3 (v/v)
Stabilization Time	15 sec
Power	1000 W
Coolant Gas Flow	14 L/min N_2
Auxiliary Gas Flow	0.4 L/min N_2
Nebulizer Gas Flow	0.7 L/min N_2
Peristaltic Pump	60 rpm
Plasma Viewing	Axial
Camera Exposure	10 sec (1000 ms @ 10 exps)
# of Repeats	3

Table 2. Analyte wavelengths utilized and corresponding 3σ detection limits

Analyte Wavelength (nm)	Calibration Group	Detection Limit (ppm)
Al 396.152	A	0.002
B 249.772	A	0.004
Ba 493.408	A	0.0001
Ca 396.847	A	0.0002
Cd 228.802	A	0.013
Co 345.350	A	0.010
Cr 283.563	A	0.007
Cu 324.754	A	0.0011
Fe 240.489	A	0.043
Li 610.364	A	0.008
Mg 280.270	A	0.0006
Mn 257.610	A	0.002
Na 588.995	A	0.0008
Ni 361.939	A	0.009
Pb 283.305	A	0.072
Zn 213.857	A	0.015
P 214.915	B	0.54
Si 25.432	B	0.038
Ti 323.451	B	0.002
W 429.461	B	0.030
Zr 339.198	B	0.007
Y 371.029 (I/S)	A,B	-

Standard and Sample Preparation

The calibration standards, blanks, and samples were prepared from two aqueous multielement standards (Inorganic Ventures, Christiansburg, VA, USA) and (Spex CertiPrep, Buffalo, NY, USA) . A Yttrium (Y) internal standard was added at a final concentration of 5 ppm to all solutions. Calibration Group A standards were prepared with 0.1, 0.25, 2,5, and 10 ppm levels, while Group B standards were prepared with 0.5, 2.5, and 10 ppm levels. The blank and calibration standards were prepared in 18 MΩ DI water containing 3% HCl and 1% HNO_3 (v/v).

A black mass sample was obtained from a local battery recycling facility. A 0.2 g sample was digested in triplicate with 20 mL of aqua regia in a digestion block set to 120 ° C for two hours. After cooling, the samples were brought up to 50 mL with the addition of Type I water. Prior to final dilution of 2x and 100x, each of the samples were filtered through 5 micron syringe filters to remove undissolved material.

Results

The MICAP was calibrated as described above and all wavelengths were viewed in the Radom Intuitive Software (RIS) Profiles View to verify no spectral interferences existed and to set peak integration points. The emission lines utilized for quantitation were selected from numerous line options available. For the high concentration elements, the highest sensitivity line available was often not utilized. The simultaneous, full wavelength range data collection provided the ability during method development to confirm accurate measurements across multiple emission lines for each element.

Figure 2 provides emission peaks observed in the black mass sample for the analytes of Li, Ni, and Co. The baseline resolution observed for these selected peaks demonstrate the high resolving power of the MICAP spectrometer. This capability helps ensure the analyte results are not impacted by spectral interferences from potential components.

Internal standard recoveries for Y were monitored throughout the analysis. The excellent stability of the MICAP is clearly evidenced as the % recoveries for Y stayed well within +/- 5% during the session.

The three black mass sample aliquots demonstrated some variation in the elemental concentrations observed, which was expected from the different sizes of ground particles present solid sample. Table 3 on the next page presents the concentrations measured in these samples with the MICAP. Due to the wide variation in elemental concentrations, both a 2x and a 100x dilution of the sample digestate was analyzed. With this wide range of concentrations, it is important to take note of the % and ppm levels reported for the various recycled battery components.

The black mass sample #1 was also spiked with known analyte levels to monitor the accuracy within this matrix (Table 3). Each analyte was measured using the same dilution as used to report the sample concentrations, and addition levels were 0.5 ppm for Group A elements & 2 ppm for Group B elements.

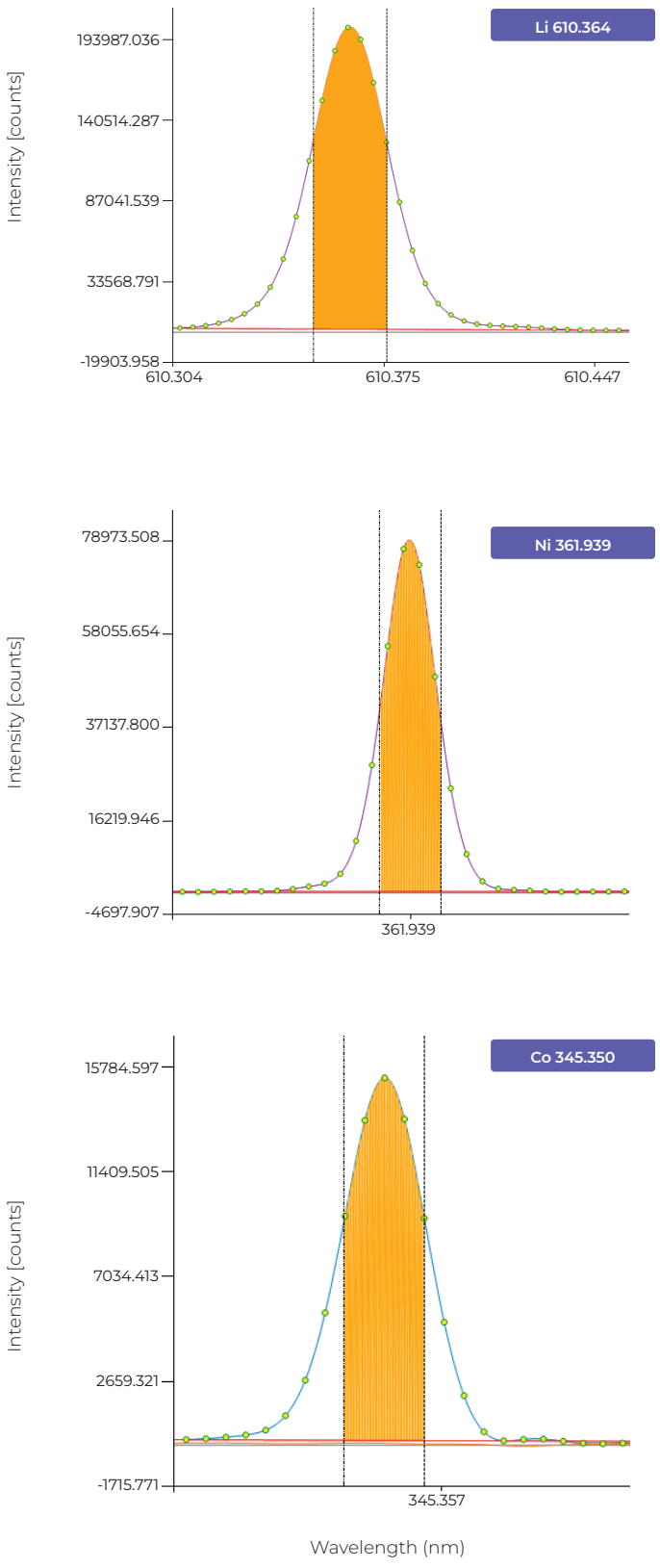

Figure 2. Profiles view of Li, Ni & Co emission lines measured in black mass sample. The integrated peak areas selected for quantitation are indicated in gold.

Table 3. Analysis results for shredded LiB black mass sample aliquots, units expressed in % or ppm. Dilution factor analyzed is from digested sample matrix.

Analyte	Units Reported	Dilution Measured	Black Mass Sample Results			Matrix Spike % Rec
			1	2	3	
Al	%	100x	3.85	3.65	2.95	108
B	ppm	2x	39.6	29.9	31.4	100
Ba	ppm	2x	111	64.5	107	110
Ca	ppm	2x	521	473	416	102
Cd	ppm	2x	<20	<20	<20	107
Co	%	100x	24.1	23.0	23.4	107
Cr	ppm	2x	27.6	25.9	21.1	101
Cu	%	100x	5.28	5.22	4.61	108
Fe	%	2x	0.21	0.38	0.22	100
Li	%	100x	3.62	3.40	3.53	107
Mg	ppm	2x	768	701	713	107
Mn	%	100x	3.02	2.99	3.02	105
Na	ppm	2x	474	532	467	110
Ni	%	100x	4.59	4.45	4.46	102
P	%	2x	0.37	0.40	0.41	108
Pb	ppm	2x	98.3	113	274	100
Si	ppm	2x	375	352	351	106
Ti	ppm	2x	100	98.7	97.8	99
W	ppm	2x	<100	<100	<100	104
Zn	ppm	2x	158	162	156	103
Zr	ppm	2x	59.0	46.4	54.6	99

Conclusions

The MICAP-OES 1000 N_2 ICP-OES demonstrated its capability to quickly and easily determine the elemental composition of this shredded LiB black mass sample. Small variations observed between each sample aliquot demonstrated the expected non-homogeneous nature of this sample matrix. Confirmation of individual elemental results were verified with simultaneous monitoring of multiple emission lines for each element. Analytical spike recoveries also helped confirm the accuracy of the results obtained with the MICAP.

References

1. Directive (EU) 2023/1542 of the European Parliament and of the Council of 12 July 2023 concerning batteries and waste batteries, amending Directive 2008/98/EC and Regulation (EU) 2019/1029 and repealing Directive 2006/66/EC, http://data.europa.eu/eli/reg/2023/1542/2025-07-31

2. Global Regulations for Sustainable Battery Recycling: Challenges and Opportunities, Argonne National Laboratory, 29 March 2025, https://doi.org/10.3390/su17073045

Scan the code to access our website for additional information and our resources