Application Note

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Determination of Metals in Recycled Li-ion Battery Samples by ICP-OES

Quantifying 18 metals in “black mass” battery materials using the Agilent 5800 ICP-OES

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Introduction

Lithium-ion batteries (LIBs) have been the power source of choice in consumer electronics for many years due to their high energy storage capacities, fast charging capabilities, and durability (*1*). LIBs are also increasingly used in electric vehicles (EVs) and storage solutions for energy generated from renewable sources. With LIBs being such an integral part of many modern-day technologies, attention is being given to dealing with the rising amounts of electronic (e)-waste generated from used (spent) LIBs. Many countries are investing in recycling e-waste, as an alternative to disposal in landfill or incineration (*2*).

LIBs contain elements such as Li, Mn, Co, and Ni, which are increasingly scarce, so spent LIBs represent a substantial secondary source of these critical elements. Recovering valuable metals from e-waste can slow the depletion of finite resources and reduce over-reliance on traditional mining to maintain supply chains for the production of batteries (*2*). Also, recycling LIBs reduces the potential impact of metals leaching into the environment during waste disposal (*3*).

Special battery recycling plants dismantle, shred, and process used LIBs into a "black mass" powder. Metals used in the main components of the battery are contained in the black mass material (*4*). Black mass can be refined into commodity grade graphite, cobalt hydroxide, and lithium carbonate for reuse. Reliable quality control (QC) analytical methods are needed to test the purity of any recovered materials.

Currently, no industry standard methods exist for the determination of elements in black mass samples. However, inductively coupled plasma optical emission spectroscopy (ICP-OES) is specified in a number of standard methods that relate to contaminant element control of chemicals used to make LIBs. In China, for example, standard methods that use ICP-OES include YS/T 928.4, GB/T 24533-2019, GB/T 26300-202, and GB/T 26008-2020. Robust and stable instruments, such as the Agilent 5800 Vertical Dual View (VDV) ICP-OES, are therefore widely used by LIB raw material suppliers and battery manufacturers to determine elements in LIB raw materials and components (*5 to 9*). The performance characteristics of the 5800 ICP-OES are equally applicable to the analysis of complex e-waste samples including LIB black mass material.

In this study, the 5800 VDV ICP-OES was used to measure 18 elements in e-waste recycling materials generated from spent LIBs. The Agilent IntelliQuant Screening smart tool within the Agilent ICP Expert Pro software was used to simplify method development and minimize sample remeasurements (*10*). Intelligent Rinse was used to maximize sample throughput of the complex, high matrix samples by automatically optimizing the rinse time between samples.

Instrumentation

The 5800 VDV ICP-OES was fitted with a SeaSpray nebulizer, double-pass glass cyclonic spray chamber, and demountable 1.8 mm i.d injector torch. An Agilent SPS 4 autosampler was used for sample introduction. Instrument operating parameters are given in Table 1.

Table 1. Agilent 5800 VDV ICP-OES instrument operating conditions.

Parameter	Radial	Axial
Read Time (s)	5	10
Replicates	3	
Sample Uptake Delay (s)	15	
Stabilization Time (s)	5	10
Rinse Time (s)	60*	
Pump Speed (rpm)	12	
RF Power (kW)	1.4	
Aux Flow (L/min)	1.0	
Plasma Flow (L/min)	12	
Nebulizer Flow (L/min)	0.65	
Viewing Height (mm)	8	NA
Sample Pump Tubing	White-white	
Waste Pump Tubing	Blue-blue	
Background Correction	FBC and FACT	

*FBC: Fitted Background Correction; FACT: Fast Automated Curve-fitting Technique. *Maximum rinse time defined for Intelligent Rinse.*

Method development

IntelliQuant Screening allows analysts to learn more about the elemental content of unknown samples by running a quick, full spectrum scan that takes a few seconds to complete (*10*). The data generated by IntelliQuant Screening provides automated spectral interference identification, which provides a selection of interference-free wavelengths. IntelliQuant Screening also identifies and estimates the concentration of elements in the samples, helping to determine a suitable calibration concentration range for elements included in the quantitative method. The concentration data can be presented as a periodic table 'heat map' view, as shown in Figure 1 for a black mass sample. The heat map showed that cobalt (Co) was the most abundant element in the sample.

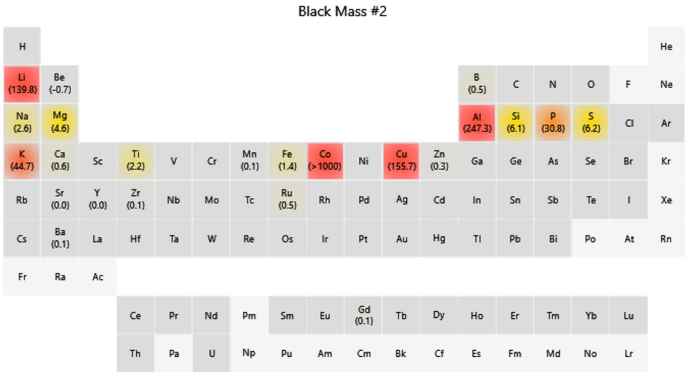


Figure 1. IntelliQuant Screening elemental 'heat map', showing which elements are present in one of the black mass e-waste LIB samples and the semiquantitative concentration (ppm).

Standard and sample preparation

LIB black mass samples were provided as finely ground powders by a battery recycling plant in Singapore. Approximately 0.20 g of the black mass samples were digested in 20 mL aqua regia on a hot plate at 250 to 300 °C for three hours. The solutions were filtered through a 0.45 µm syringe filter to remove any undigested carbon and made up to 50 mL with de-ionized water (DIW). Each sample was prepared in duplicate. A digest blank was also prepared in duplicate. The digested samples were further diluted five times for the analysis of high concentration elements (Al, Co, Cu, Li, S, P, Mg, Si, Ni, Na, Ti, and Fe). The external calibration standards and quality control (QC) samples were prepared in the same acid matrix as the samples.

The calibration concentration ranges for the elements are listed in Table 2. Calibration standards and spiked samples were prepared from Agilent multi-element calibration standards 2A and standard 4, Agilent single element 1000 ppm stock standards for Co and P, and Merck ICP multi-element standard.

Table 2. Calibration range for all elements included in the quantitative method.

Elements	Calibration Concentration Range (ppm)
Co	0 to 500
Al, Cu, Li	0 to 50
P, Si	0 to 10
Mg, Na, S	0 to 5
Other elements	0 to 2

Intelligent Rinse

The Intelligent Rinse function within ICP Expert software monitors the intensities of nominated element wavelengths during the rinse period and controls the SPS 4 autosampler rinse times (*11*). The software automatically ends the rinse when element intensities reach a user-specified threshold. There are three defined washout thresholds within Intelligent Rinse: quick, moderate, and thorough. Monitoring signal intensities means that rinse periods vary, depending on the time taken to wash out each sample. In this study, rinse times varied from 3 s for blanks, 21 to 43 s for calibration standards and 17 to 60 s for samples, based on the concentration (threshold setting) of Al, Co, Li, and Mg. Intelligent Rinse is a simple way to optimize both sample throughput and argon usage.

Background correction

The ICP Expert software includes easy-to-use background correction techniques: Fitted Background Correction (FBC) and Fast Automated Curve-fitting Technique (FACT). Both techniques were applied in this study.

FBC uses a sophisticated mathematical algorithm to model the background signal under the analyte peak, eliminating the need to manually determine off-peak background correction points. FBC was selected for most elements where there were no direct spectral overlaps. Figure 2 shows an example of automatic background fitting using FBC for Zr 339.198 nm. FBC provided accurate correction of the background structure arising from the argon emission line, enabling accurate detection of Zr in the black mass samples.

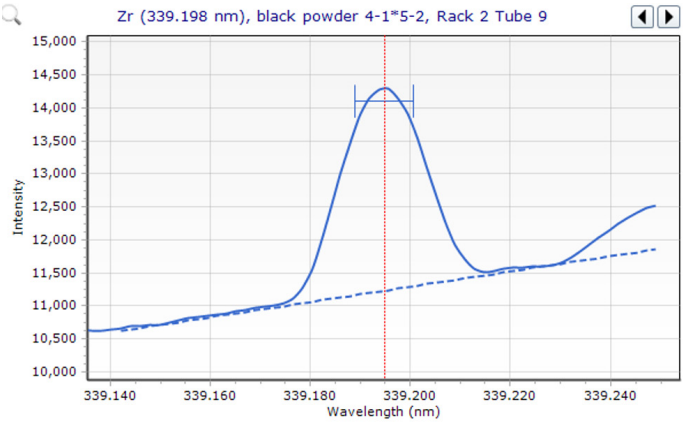


Figure 2. Automatic background fitting for Zr 339.198 nm using FBC.

For elements that were affected by more complex background signals, FACT was used. Figure 3 shows a FACT model for Na 589.592 nm with correction for Ba 589.612 nm. FACT modeled the Ba interfering peak (red dashed line) and resolved the analyte signal (green line) from the combined peak (blue line), providing accurate results for Na.

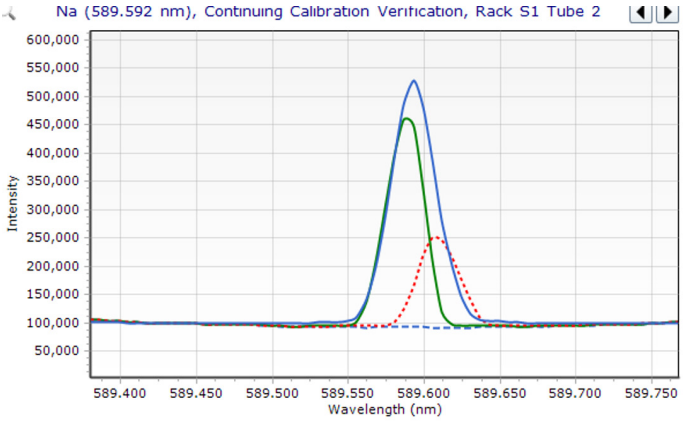
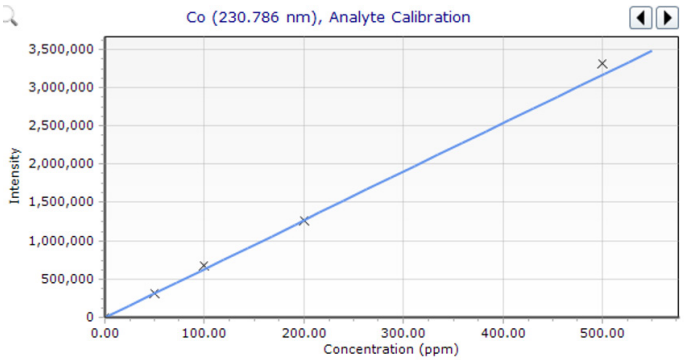
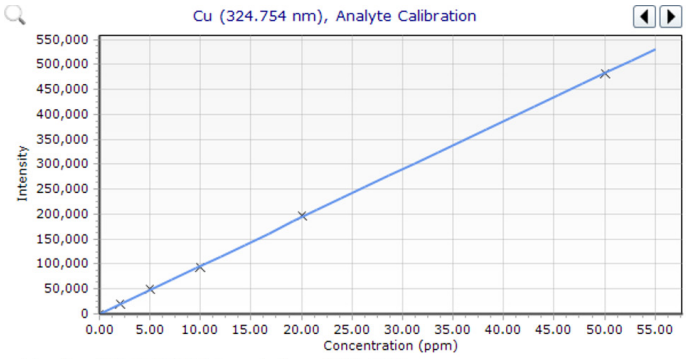


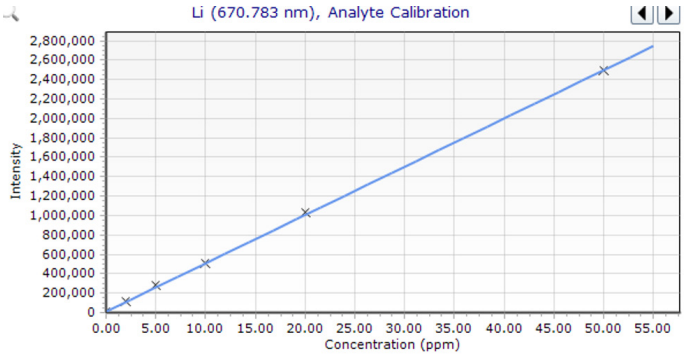
Figure 3. FACT model for correction of a Ba interference on Na (shown in blue). The Ba 589.612 nm (red dashed) interference line is overlapping the Na 589.592 nm (green) line. The light blue dashed line represents the blank.

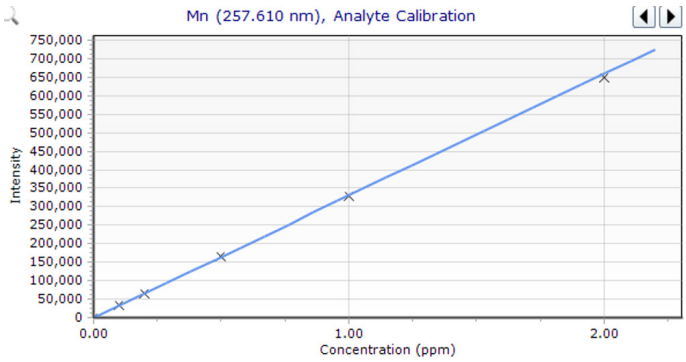
Results and discussion

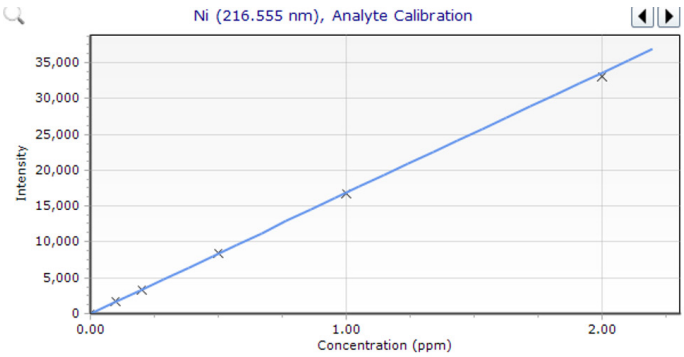
Representative calibration curves for Co, Cu, Li, Mn, Ni, and P are presented in Figure 4.











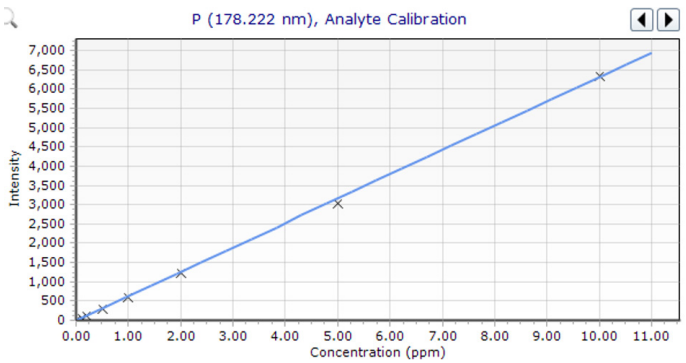


Figure 4. Representative calibration curves for Co, Cu, Li, Mn, Ni, and P.

Detection (LOD) and quantification limits (LOQ) are shown in Table 3. The LODs and LOQs were based on the measurement of 11 method blanks and calculated as 3 x standard deviation (SD) and 10 x SD, respectively. The method detection limits (MDL) were calculated as three SD of the concentration determined for each element, multiplied by the dilution factor (DF) of 250 or 1250 times. The linear regression (R) values for the calibration plots are also shown in Table 3. The MDLs show the suitability of the 5800 VDV ICP-OES for the determination of a wide range of elements in black mass samples. Also, the response of the 5800 was linear over the calibration range for all elements, as indicated by R values above 0.999.

Table 3. Agilent 5800 VDV ICP-OES calibration coefficients (R) and detection limits (*DF 1250, **DF 250).

Element, Wavelength (nm)	Correlation Coefficient	Plasma View Mode	Background Correction	LOD (µg/L)	LOQ (µg/L)	MDL, (mg/kg)
Al 396.152	0.99994	Radial	Fitted	11.3	37.7	14.0*
Ba 493.408	0.99999	Axial	Fitted	0.51	1.69	0.13**
Ca 396.847	0.99998	Axial	Fitted	0.49	1.63	0.12**
Co 230.786	0.99978	Radial	Fitted	4.09	13.6	5.10*
Cr 267.716	1.00000	Axial	Fitted	0.54	1.79	0.14**
Cu 324.754	0.99992	Radial	Fitted	4.96	16.5	6.20*
Fe 259.940	0.99999	Axial	Fitted	0.69	2.29	0.90*
Li 670.783	0.99992	Radial	Fitted	8.35	27.8	10.0*
Mg 279.553	0.99995	Radial	Fitted	0.28	0.94	0.35*
Mn 257.610	0.99998	Radial	Fitted	0.47	1.56	0.12**
Na 589.592	0.99905	Axial	FACT	0.39	1.30	0.49*
Ni 216.555	0.99997	Axial	Fitted	1.02	3.39	1.30*
P 178.222	0.99978	Radial	Fitted	9.46	31.5	12.0*
S 180.669	0.99984	Axial	Fitted	4.05	13.5	5.10*
Si 251.611	0.99953	Axial	Fitted	3.49	11.6	4.40*
Ti 334.941	0.99999	Axial	Fitted	0.14	0.47	0.20*
Zn 209.200	0.99997	Axial	Fitted	0.49	1.64	0.12**
Zr 339.198	1.00000	Axial	Fitted	0.23	0.75	0.058**

Sample results

Concentrations of the 18 target elements in the four black mass samples were quantified against the calibration curves. The quantitative results shown in Table 4 have been corrected for the dilution factor, so are reported in mg/kg (or %) in the original solid black mass samples.

Al, Co, Cu, and Li were measured above the 1% level in all four samples, while the concentration of other elements varied from <1% to the ppm level. The results show the suitability of the 5800 VDV ICP-OES for the analysis of both high and low concentration elements in the same run.

Table 4. Quantitative results for four separate black mass samples determined using the Agilent 5800 VDV ICP-OES. The data has been corrected for sample mass and final mass. Units: mg/kg unless specified as %.

Element, Wavelength (nm)	Black Mass Sample #1	Black Mass Sample #2	Black Mass Sample #3	Black Mass Sample #4
Al 396.152	3.23%	3.70%	2.52%	3.10%
Ba 493.408	32.3	25.4	51.1	65.4
Ca 396.847	71.6	91.8	77.9	98.7
Co 230.786	32.0%	30.0%	27.6%	28.6%
Cr 267.716	7.49	6.98	10.5	7.57
Cu 324.754	1.35%	1.43%	1.84%	2.86%
Fe 259.940	268	231	220	364
Li 670.783	3.94%	3.70%	3.49%	3.63%
Mg 279.553	0.12%	0.12%	0.12%	811
Mn 257.610	16.1	12.6	35.1	195
Na 589.592	437	449	519	504
Ni 216.555	61.9	64.2	115	288
P 178.222	0.31%	0.42%	0.35%	0.37%
S 180.669	0.11%	0.12%	0.11%	0.11%
Si 251.611	247	0.11%	0.11%	0.11%
Ti 334.941	468	438	510	440
Zn 209.200	24.6	21.2	37.6	22.2
Zr 339.198	24.4	26	18.9	28.1

Long-term stability

To determine the stability of the 5800 VDV ICP-OES, 198 solutions were analyzed over seven hours. The solutions consisted of the four black mass samples and the CCV solution. The recoveries of the elements in the CCV solution were plotted against time, as shown in Figure 5. All recoveries were within ±10% of expected values, with ≤2.1% RSD for all elements, demonstrating the excellent robustness and precision of the method over the extended run (Table 5).

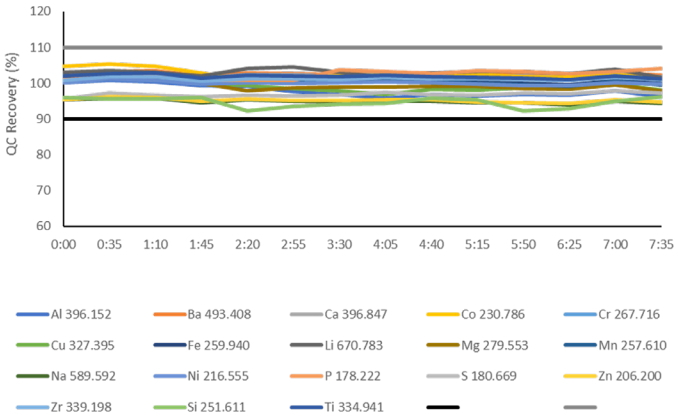


Figure 5. Stability of the Agilent 5800 VDV ICP-OES during the analysis of 198 solutions run over seven hours, with no recalibration and no internal standard correction. The CCV QC sample was analyzed every 10 samples.

Table 5. Concentration of elements in the CCV QC solution and %RSD of measurements taken over seven hours.

Element	Concentration (ppm)	RSD (%)	Element	Concentration (ppm)	RSD (%)
Al	20	1.84	Mn	1	0.69
Ba	1	0.46	Na	1	0.60
Ca	1	0.49	Ni	1	0.59
Co	200	1.45	P	1	1.23
Cr	1	0.6	S	1	0.58
Cu	20	1.88	Si	1	2.06
Fe	1	0.64	Ti	1	0.52
Li	20	0.87	Zn	1	0.62
Mg	1	1.49	Zr	1	0.37

Spike recoveries

The four black mass samples were spiked with a low level of the target elements. All recoveries were within ±15% of the expected values (Table 6), demonstrating the accuracy of the method for the determination of low concentrations of the target elements in the LIB e-waste samples.

Table 6. Spike recovery results for four black mass samples measured using the Agilent 5800 VDV ICP-OES. Units: mg/L

Element, Wavelength (nm)	Black Mass Sample #1				Black Mass Sample #2			
	Spike Level	Measured Conc	Spiked Measured Sample	Spike Recovery (%)	Spike Level	Measured Conc	Spiked Measured Sample	Spike Recovery (%)
Al 396.152	18	28.3	44.4	90	20	35.3	54.07	94
Ba 493.408	0.2	0.153	0.3304	89	0.2	0.114	0.295	91
Ca 396.847	0.2	0.266	0.436	85	0.2	0.363	0.535	86
Co 230.786	200	280.4	470.9	95	200	277	459	91
Cr 267.716	0.2	0.0322	0.214	91	0.2	0.0314	0.216	92
Cu 324.754	18	11.5	30.08	104	20	14.4	33.9	97
Fe 259.940	1	0.242	1.30	106	1	0.217	1.15	93
Li 670.783	18	33.8	49.7	88	20	33.6	52.6	95
Mg 279.553	1	1.009	2.044	104	1	1.062	1.94	88
Mn 257.610	0.2	0.0687	0.246	89	0.2	0.0604	0.241	90
Na 589.592	1	0.4047	1.55	114	1	0.4047	1.505	110
Ni 216.555	1	0.0566	1.12	106	1	0.0468	0.984	94
P 178.222	1	2.61	3.69	108	4	3.807	7.75	99
S 180.669	1	0.928	1.88	95	1	1.12	2.06	94
Si 251.611	1	0.310	1.25	94	1	0.914	1.84	92
Ti 334.941	1	0.4074	1.36	95	1	0.396	1.35	96
Zn 209.200	0.2	0.117	0.289	86	0.2	0.0858	0.262	88
Zr 339.198	0.2	0.1089	0.289	90	0.2	0.117	0.299	91
Element, Wavelength (nm)	Black Mass Sample #3				Black Mass Sample #4			
	Spike Level	Measured Conc	Spiked Measured Sample	Spike Recovery (%)	Spike Level	Measured Conc	Spiked Measured Sample	Spike Recovery (%)
Al 396.152	20	21.7	40.89	96	20	27.03	46.4	97
Ba 493.408	0.2	0.233	0.4095	88	0.2	0.2004	0.381	90
Ca 396.847	0.2	0.269	0.443	87	0.2	0.383	0.554	86
Co 230.786	200	234	423	95	200	228	419	95
Cr 267.716	0.2	0.0425	0.225	91	0.2	0.0346	0.218	92
Cu 324.754	20	15.4	34.9	98	20	27.4	46.9	98
Fe 259.940	1	0.196	1.15	95	1	0.387	1.47	109
Li 670.783	20	29.0	48.5	98	20	28.4	48.2	99
Mg 279.553	1	1.049	1.96	91	1	0.646	1.75	110
Mn 257.610	0.2	0.1502	0.327	88	1	0.1508	1.26	111
Na 589.592	1	0.4082	1.490	108	1	0.422	1.57	115
Ni 216.555	1	0.0994	1.048	95	1	0.2201	1.31	109
P 178.222	4	2.87	6.93	101	4	2.88	6.76	97
S 180.669	1	0.9081	1.88	97	1	0.846	1.82	98
Si 251.611	1	0.863	1.87	101	1	0.831	1.79	96
Ti 334.941	1	0.43	1.40	97	1	0.342	1.31	97
Zn 209.200	0.2	0.152	0.325	87	0.2	0.0965	0.272	88
Zr 339.198	0.2	0.076	0.264	94	0.2	0.1088	0.294	93

Conclusion

The Agilent 5800 VDV ICP-OES was used for the measurement of metals in Li-ion recycling samples—known as black mass samples—following hot plate digestion in aqua regia.

Method set up was simplified using smart software tools within the ICP Expert software.

- The samples were quickly scanned using IntelliQuant Screening to identify and estimate the concentration of elements. The semiquantitative results were then used to establish the calibration range and selection of interference-free wavelengths for each target analyte.
- FBC and FACT background correction routines within the software successfully corrected for highly complex background structures and spectral interferences.
- Sample throughput was maximized using Intelligent Rinse to optimize the rinse time between samples.

In the absence of suitable reference materials for black mass samples, the accuracy of the 5800 ICP-OES method was confirmed by spike recovery data in the samples of ±15%. The method was stable over seven hours, as shown by recoveries of the CCV standard within ±10% of expected values and RSD <2.1% for all elements. The quantitative results for the four black mass samples reported Al, Co, Cu, and Li above 1% and other elements at the low percentage level to the ppm level.

The performance data demonstrates the suitability of the 5800 VDV ICP-OES method for the routine, accurate measurement of high and low concentration elements in black mass samples in the same run. The method can determine economically valuable elements such as Co, Mn, Ni, and Li, as well as contaminant elements such as Fe, Cu, and Zn.

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