

Elemental Analysis of Intermediate Feedstock Chemicals for Li-Ion Batteries (LIBs) by ICP-OES

Quality control of unrefined cathode-metal solutions from recycled LIBs by Agilent 5800 VDV ICP-OES



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Introduction

Rechargeable battery technology is integral to overcoming the world's reliance on fossil fuels for transport and power generation. The switch to cleaner sources of energy is needed to reduce emissions of carbon dioxide into the atmosphere and to lower levels of airborne pollutants, including nitrogen oxides (NO_x) and particulate matter (PM). Lithium-ion batteries (LIBs) are already widely used to power various consumer electronics, electric vehicles (EVs), and in grid-scale energy storage systems designed to store electricity generated from renewable sources. However, since LIB technology is still in the development phase, research is continuing apace to further improve battery capacity, efficiency, range, and to lower the cost of production (1, 2).

Designers and manufacturers of LIBs need to balance performance characteristics, useful lifespan, safety, and cost through selection of materials used for the cathode, separator, electrolyte, and anode. There is also an increasing focus on sourcing the critical raw materials—such as lithium (Li), graphite, nickel (Ni), manganese (Mn), and cobalt (Co)—that are needed in the production of LIBs. Investment is increasing in recycling facilities for end-of-life (used) battery cells, as a cost-effective and cleaner alternative source of metals to mining natural ores. By “de-manufacturing” LIBs, battery grade metal feedstocks, such as Li, Ni, Mn, and Co compounds can be recovered and re-used in the manufacture of new LIBs in a closed-loop process.

The cathode of a LIB typically consists of Li combined with a metal oxide compound. The higher the Li content, the larger the battery capacity. Examples of metal oxide compounds include Co oxide (LCO), Ni Mn Co oxide (NMC or NCM), Ni Co Al oxide (NCA), or Ni Mn Co Al oxide (NMCA). Co-free cathode materials have also been developed, including Li Fe phosphate (LFP) and Li Mn oxide (LMO) (3). Irrespective of the composition of the cathode, its performance can be affected by the presence of elemental impurities in metal feedstocks, such as Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, and Zn. The determination of elements in chemicals and materials used during the manufacturing of LIBs is therefore vital for quality assurance/control (QA/QC) of the final products. Samples include process chemicals used to prepare commodity metal feedstocks, battery grade feedstocks, and midstream battery components i.e., anode, cathode, and electrolyte materials. All these sample-types are tested for impurities before LIB manufacture.

In this study, intermediate-grades of Li, Ni, Mn, and Co recovered from a LIB recycling process as LiOH, CoSO₄, NiSO₄, and MnSO₄, respectively, were provided for analysis by ICP-OES.

Intermediate-grade chemicals would be further refined before being used as battery-grade feedstocks of Li, Ni, Mn, and Co for use in the manufacture of NMC cathode materials. Robust instrumentation is needed for impurity analysis of reclaimed LIB chemicals since the high total dissolved solids (TDS) content of LIB process materials can be challenging for ICP-OES. Any undissociated matrix in high TDS samples may deposit on the sample introduction system or quench the plasma, impacting the long-term stability and the accuracy of measurements.

To handle high salt matrices over long runs, the Agilent 5800 Vertical Dual View (VDV) ICP-OES uses a vertical plasma, a solid-state radio frequency (SSRF) generator operating at 27 MHz, and Cooled Cone Interface (CCI). The CCI helps to maximize the analytical linear range of the instrument by deflecting the cooler tail of the plasma and avoiding interferences that form in the region.

When reading the vertical plasma in axial view mode, elements at trace concentration levels can be measured, while major elements can be viewed in radial mode.

To help with method development and sample-knowledge, the samples were first analyzed using the IntelliQuant Screening function of Agilent ICP Expert Pro software. The semiquantitative screening data provides valuable information on the identity and concentration of elements in a sample. The data can be used to establish a suitable calibration concentration range for the elements included in the quantitative method. IntelliQuant Screening data also identifies spectral interferences and recommends the best, interference-free wavelengths to use in the quantitative method, ensuring the accuracy of the final results.

The 5800 VDV ICP-OES was operated in axial and radial view mode to quantify trace impurities and major elements, respectively, in each sample solution. To ensure that sufficient rinse times were used during the analysis of high matrix samples, Intelligent Rinse was selected in the ICP Expert Pro software. The Intelligent Rinse routine automatically optimizes the rinse time between samples depending on user-selected threshold settings.

Experimental

Standard and sample preparation

The Ni, Mn, and Co samples were received as ~1% salt solutions and the Li sample as ~0.1% from the American Battery Technology Company. The LIB recycling chemicals had been digested in nitric acid (HNO₃) on a hot plate, and refined to separate and purify Li, Ni, Mn, and Co products into separate aqueous solutions at ~10,000 ppm each. Each sample solution was further diluted 10-fold, using 5% nitric acid (HNO₃) before analysis by ICP-OES.

Agilent standards were used to prepare the calibration standards and sample spikes. The standards included Multi-element Calibration Standard QC27, Calibration Mix Majors (Ca, Fe, K, Mg, and Na), and single element standards for Sn, Hg, Mn, Li, Co, and Ni.

For QC purposes, a 200 µg/L standard solution (prepared separately from the calibration standard) was used as a continuing calibration verification (CCV) solution. Internal standard (IS) solutions were prepared from Agilent single element standard solutions of Y and Rb at 5 and 100 mg/L, respectively. Rb 780.026 nm was only used with K 766.491 nm in axial mode.

All standards, spikes, and QC solutions were prepared by matching the 5% HNO₃ acid concentration used for sample preparation.

Instrumentation

The 5800 VDV ICP-OES was fitted with a SeaSpray nebulizer, double-pass glass cyclonic spray chamber, a one-piece 1.8 mm i.d injector Easy-fit torch, and an argon humidifier. The argon humidifier reduces desolvation at the nebulizer caused by samples with a high TDS content and greatly improves the stability of the instrument over long runs. An Agilent SPS 4 autosampler was used for sample introduction.

The Intelligent Rinse function within ICP Expert Pro software was used to monitor the intensities of nominated element wavelengths during the rinse period and to control the SPS 4 autosampler rinse times. 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, 22 to 60 s for calibration standards, and 32 to 60 s for the salt samples, based on the concentration (threshold setting) for Li, Ni, Mn, Co, Hg, and Si. Intelligent Rinse is a simple way to achieve effective and accurate washout, while optimizing sample throughput and argon usage. Instrument operating parameters are given in Table 1.

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

Parameter	Axial	Radial
Read Time (s)	15	8
Replicates	3	
Sample Uptake Delay (s)	24	
Stabilization Time (s)	15	1
Rinse Time (s)	60*	
Pump Speed (rpm)	12	
RF Power (kW)	1.2	
Aux Flow (L/min)	1.0	
Plasma Flow (L/min)	12	
Nebulizer Flow (L/min)	0.70	
Viewing Height (mm)	NA	8
Sample Pump Tubing	White-white	
Internal Standard Pump Tubing	Orange-green	
Waste Pump Tubing	Blue-blue	
Background Correction	Fitted, FACT, Off-peak	

*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 only takes a few seconds to complete. The concentration data can be presented as a periodic table 'heat map' view, as shown in Figure 1 for the 10-fold diluted Li salt solution. The heat map showed that Li was the most abundant element in the sample.

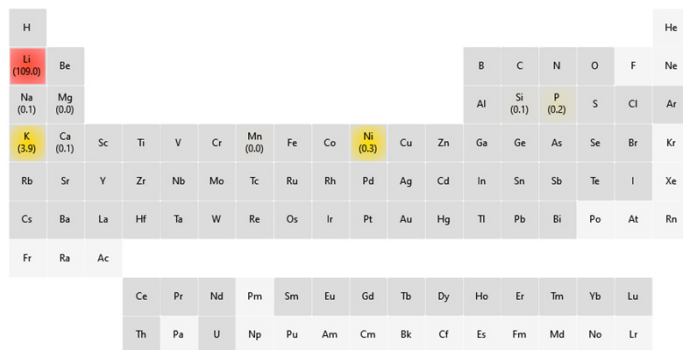


Figure 1. IntelliQuant heat map of the 10 times diluted Li salt solution showing which elements are present in the sample and the semiquantitative concentration (mg/L).

Background correction

The ICP Expert software includes smart background correction techniques including Fitted Background Correction (FBC) and Fast Automated Curve-fitting Technique (FACT). An example of a FACT model for the correction of the Mn interference on Cr 267.716 nm is shown in Figure 2. FACT subtracts the contribution to the analyte signal from the interference and the blank, providing an accurate result for Cr (green line).

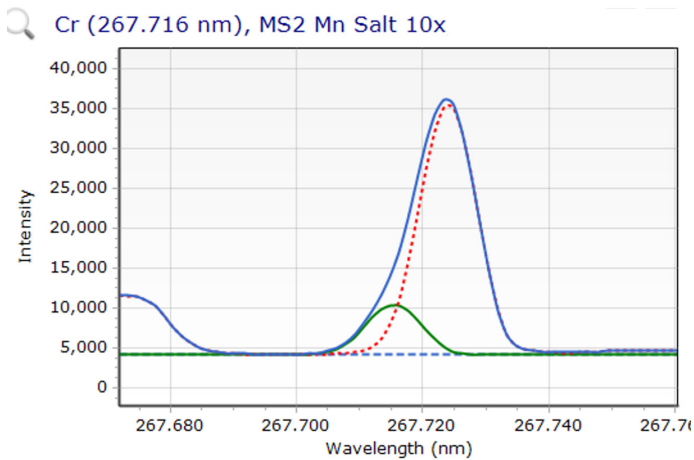


Figure 2. FACT model for correction of a Mn interference on Cr (total signal shown by the solid blue line). The Mn 267.725 nm (red dashed) interference line is overlapping the Cr 267.716 nm (solid green) analyte line. The signal from the blank is shown by the light blue dashed line.

Results and discussion

Representative calibration curves for As, Cd, and Hg in axial view (0.05 to 0.5 mg/L), and Co in radial view (Co-R: 0.05 to 500 mg/L) are shown in Figure 3. Calibration curves for all elements were linear with a correlation coefficient greater than 0.999 and less than 10% calibration error on each calibration point.

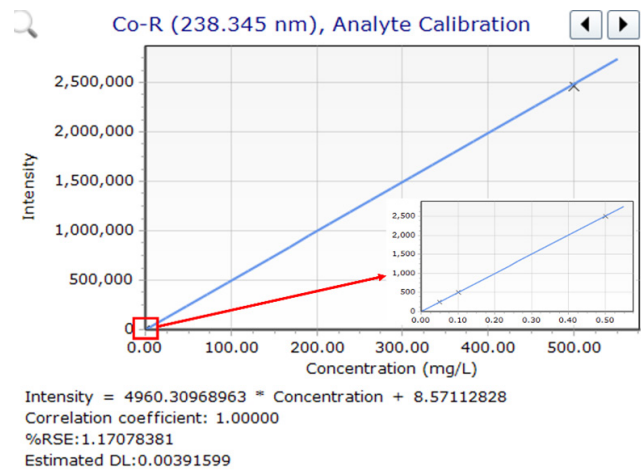
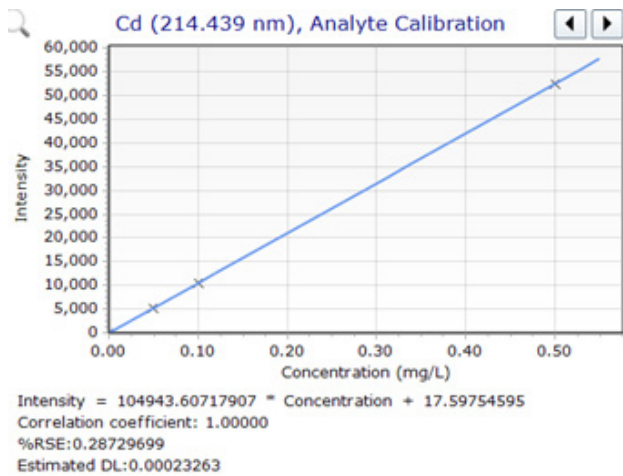
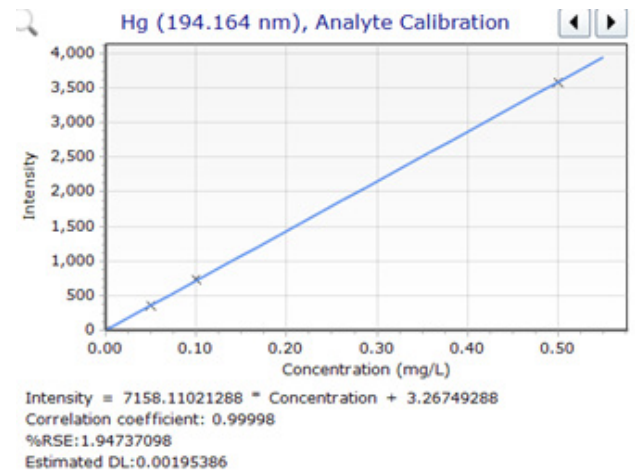
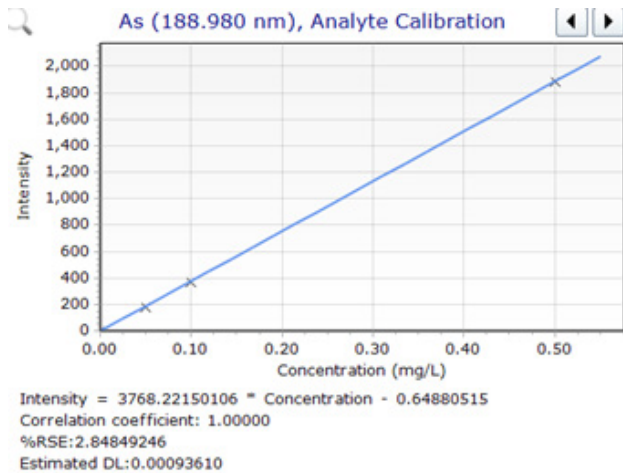


Figure 3. Calibration curves for As, Cd, and Hg in axial mode and Co in radial mode.

Method detection limits (MDLs)

To ensure the detection of low concentrations of trace elements in the presence of high concentrations of Li, Mn, Ni, and Co, four metal salt blank solutions were prepared at 500 ppm. The 500 ppm Li, Mn, Ni, and Co salt solutions were spiked at 5 µg/L with a multi-element standard. The MDLs were based on 3.14 x standard deviation (SD) of seven measurements of the trace elements in each metal salt blank solution. To avoid spectral interference on Fe 259.940 nm from the Mn salt matrix and to improve the MDL, a secondary Fe wavelength, Fe 238.204 nm, was used, as indicated by the gamma (γ) symbol in Table 2.

The MDLs for the primary salt elements (Li, Ni, Mn, and Co) were calculated using the 5% HNO₃ acid solution spiked at 5 µg/L. The wavelengths used to analyze the high concentration of the salt elements are indicated by the section (§) symbol in Table 2.

Table 2. Method detection limits for impurity elements in salt solutions and for Li, Mn, Ni, and Co in 5% HNO₃. All elements were spiked at 5 µg/L.

Element	Background Correction Method	Element Wavelength (nm)	MDL	MDL in 500 ppm Salt Solutions			
				5% HNO ₃ (µg/L)	Li (µg/L)	Ni (µg/L)	Mn (µg/L)
Al	FACT	Al 396.152	0.68	0.83	0.69	0.75	0.71
As	FBC	As 188.980	2.00	1.54	1.84	2.15	1.13
Ba	FBC	Ba 455.403	0.17	0.69	0.05	0.06	0.26
Ca	FBC	Ca 396.847	0.16	0.52	0.08	0.05	0.29
Cd	FBC	Cd 214.439	0.17	0.25	0.15	0.08	0.33
*Co	FBC	Co 238.892	0.17	0.55	0.34	0.31	NA
	FBC	§Co-R 238.345	3.63	NA	NA	NA	NA
Cr	FACT	Cr 267.716	0.29	0.28	0.17	1.02	0.28
Cu	FBC	Cu 324.754	0.41	0.48	0.49	0.48	1.05
*Fe	FBC	γFe 238.204	0.22	NA	NA	0.35	NA
	FBC	Fe 259.940	0.24	0.54	0.72	NA	0.68
Hg	Off-Peak Left	Hg 194.164	0.82	1.18	0.57	1.52	1.79
K	Off-Peak Right	K 766.491	1.31	2.34	1.42	1.39	1.3
*Li	FBC	Li-R 670.783	6.78	NA	13.49	5.07	6.48
	FBC	§Li-R 610.365	2.68	NA	NA	NA	NA
Mg	FBC	Mg 279.553	0.14	0.27	0.05	0.86	0.27
*Mn	FBC	Mn 257.610	0.16	0.25	0.04	NA	0.23
	FBC	§Mn-R 293.305	2.09	NA	NA	NA	NA
Mo	FBC	Mo 202.032	0.47	0.69	0.41	0.45	0.4
Na	FACT	Na-R 589.592	5.63	10.9	5.84	3.62	3.78
*Ni	FBC	Ni 230.299	0.53	0.77	NA	1.06	1.20
	FBC	§Ni-R 231.604	1.79	NA	NA	NA	NA
Pb	FBC	Pb 220.353	1.82	1.35	1.86	1.14	1.09
Si	FBC	Si 251.611	1.01	1.07	1.11	1.41	1.09
Sn	FACT	Sn 189.925	0.67	0.71	1.3	1.2	0.73
Zn	FBC	Zn 206.200	0.26	0.59	0.31	0.39	0.52

*Combination of wavelengths were used for these elements. γSecondary wavelength used to avoid spectral interferences on trace element. §Wavelengths used to analyze the high concentration of primary salt elements. NA = not applicable.

Quantitative data and spike recoveries

Most elements were present in the four salt samples at low concentration (<100 µg/L) levels (Table 3). A high concentration of Co (1735 µg/L) was determined in the Mn salt solution, while Na was found in the Mn and Co salts at 635 and 1527 µg/L, respectively. To avoid further sample dilution of the respective metal salt solutions, Li, Ni, Mn, and Co were analyzed in radial view using additional suitable wavelengths, Li 610.365 nm, Ni 231.604 nm, Mn 293.305 nm, and Co 238.345 nm. The 5800 VDV ICP-OES includes freeform optics to enhance spectral resolution and an advanced Vista Chip III detector that provides the flexibility to measure additional wavelengths without a time penalty (4).

In the absence of suitable certified reference materials for the application, spike recovery tests were used to check the accuracy of the method. The Li, Mn, Ni, and Co salt samples were diluted 10x in 5% HNO₃ acid and analyzed using the 5800 VDV ICP-OES. The four salt samples were then spiked with the target elements at 50 µg/L. The spike recoveries were within 100 ± 15% for all analytes (Table 3), showing that all elements were unaffected by any matrix effects arising from the Li, Mn, Ni, or Co sample matrices. The excellent spike recovery data confirms the suitability of the 5800 VDV ICP-OES for the accurate analysis of trace impurities in LIB raw materials.

Table 3. Quantitative results for four separate solutions of Li, Mn, Ni, and Co salts at 10x dilution using the Agilent 5800 VDV ICP-OES and spike recovery data.

Element, Wavelength (nm)	Metal Salt Solution (µg/L)				Spiked with 50 µg/L Standard (µg/L)				Spike Recovery %			
	Li Salt	Ni Salt	Mn Salt	Co Salt	Li Salt	Ni Salt	Mn Salt	Co Salt	Li Salt	Ni Salt	Mn Salt	Co Salt
Al 396.152	2.6	0.7	<MDL	<MDL	55.4	56	53.6	51.2	106	111	113	107
As 188.980	2.5	3.1	2.1	5.9	54.4	52.8	54.5	54.6	104	99	105	97
Ba 455.403	1.8	<MDL	<MDL	<MDL	49.9	48.6	49.3	49	96	97	99	98
Ca 396.847	90.9	6.7	57.2	8.3	143	53.3	106	55.3	105	93	98	94
Cd 214.439	<MDL	<MDL	0.4	0.4	50.5	48.7	48.7	49.2	101	97	97	98
*Co 238.892	<MDL	3	1735	930000	49.1	51.8	1786	-	98	98	102	-
Cr 267.716	<MDL	<MDL	3	0.9	49.4	48.5	50.9	50	99	98	96	98
Cu 324.754	1	<MDL	5.5	7.6	51.9	50.6	58.5	58.7	102	103	106	102
*Fe 259.940	1.5	<MDL	1.8	7	50.5	51.5	50.2	56.2	98	103	97	98
Hg 194.164	2.9	3.3	5	9.5	49	49.4	52.1	54.8	92	92	94	91
K 766.491	4.9	2.1	1.8	12.6	57.5	55.5	48.5	59.1	105	107	93	93
*Li-R 670.783	74000	<MDL	<MDL	<MDL	-	53.6	54	52.6	-	93	106	100
Mg 279.553	3.7	1.7	2.6	7.6	52.2	50.5	49	56.5	97	98	93	98
*Mn 257.610	<MDL	0.2	923000	28.3	48.8	49.1	-	77.2	97	98	-	98
Mo 202.032	<MDL	<MDL	<MDL	<MDL	51.4	48.1	49.2	48.8	103	97	98	98
Na-R 589.592	<MDL	49	635	1527	63.5	91.8	677	1576	109	86	85	98
*Ni 230.299	106	1168000	17.9	19.5	155	-	68.4	67.9	98	-	101	97
Pb 220.353	<MDL	<MDL	104	<MDL	48.5	48.2	152	45.4	99	99	94	95
Si 251.611	21.6	<MDL	45.1	4.5	74.7	47.6	91.4	52.9	106	93	93	97
Sn 189.925	<MDL	<MDL	<MDL	<MDL	49.7	44.7	46.4	49.6	99	91	93	99
Zn 206.200	0.7	1.6	1.2	0.6	52.3	50.1	50	50	103	97	98	99

*Combination of wavelengths were used for these elements (see Table 2 for information on lines).

Stability test

To check the stability of the instrument and long-term validity of the calibration, 17 measurements of the CCV were completed over eight-hours without recalibration. The CCV standard (200 µg/L) was measured after every 10 samples. The concentrations of the 17 CCV measurements were plotted against time, as shown in Figure 4. Accurate measurements within ±10% of the expected value (indicated by the blue dashed lines) were obtained.

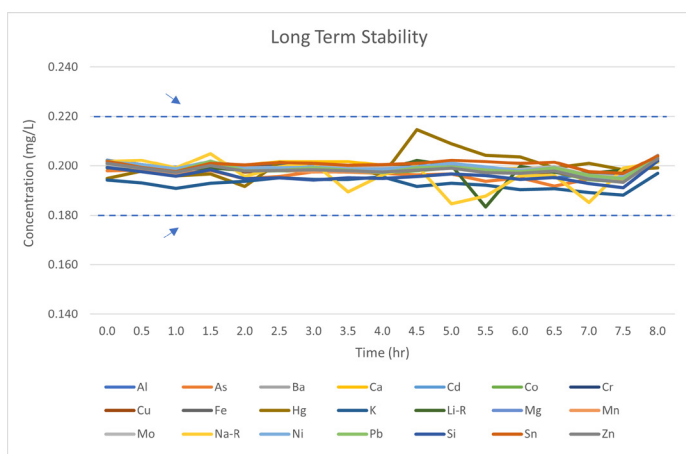


Figure 4. Long-term stability showing recoveries of the 200 µg/L CCV solution measured over 8 h.

Conclusion

The Agilent 5800 VDV ICP-OES was used to analyze 21 elements in unrefined (intermediate) battery metal feedstocks of Li, Ni, Mn, and Co recovered from a LIB recycling process. The study provided a valuable demonstration of the 5800's ability to check LIB process chemicals for impurities, informing the recycling process development and final QC of battery grade metal feedstocks.

During method development, IntelliQuant Screening helped determine the calibration range and identify interference-free wavelengths for the analytes. Excellent calibration linearity was obtained for major and minor elements over a wide concentration range and the method detection limits for all elements in 500 ppm salt solutions were well below 1 mg/kg.

Recoveries of all 21 elements spiked at 50 µg/L in the four salt samples were within 100 ± 15%. The results confirm the accuracy, matrix tolerance, and the robustness of the method for the analysis of trace elements in high TDS samples. The instrument was stable during an eight-hour analytical run, as shown by recoveries within ±10% of all elements in the 17 measurements of the 200 µg/L CCV solution.

The study demonstrated the suitability of the 5800 VDV ICP-OES method for the accurate measurement of multiple elements in Li, Ni, Mn, and Co salts reclaimed from spent LIBs. The method quantified the economically valuable major elements in the salt samples, as well as contaminants by minimizing carryover and optimizing sample analysis time via Intelligent Rinse.

References

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3. Wang, Y. *et al*, High-Voltage “Single-Crystal” Cathode Materials for Lithium-Ion Batteries, *Energy Fuels*, **2021**, 35, 1918–1932
4. Innovative Freeform Optical Design Improves ICP-OES Speed and Analytical Performance, Agilent publication, [5994-5891EN](#)

Agilent part numbers

G8020-68005	Easy-fit fully demountable torch with 1.8 mm quartz injector for Agilent 5000 series ICP-OES
G8010-60256	Double-pass spray chamber, glass cyclonic design with ball joint socket and UniFit drain outlet, for Agilent 5000 series ICP-OES
G8010-60255	SeaSpray concentric glass nebulizer for Agilent 5000 series ICP-OES
G8010-60346	Nebulizer gas humidifier for 5000 Series ICP-OES
3710034400	Peristaltic pump tubing, PVC, white/white, 12/pk
3710068300	Peristaltic pump tubing, PVC, orange/green, 12/pk
3710034600	Peristaltic pump tubing, PVC, blue/blue, 12/pk
1610132400	Y-piece connector for online addition of internal standard/ionization buffer
5190-9418	Quality Control Standard 27, multi-element calibration standard solution for 27 elements at 100 ppm
6610030700	Agilent multi-element calibration majors mix stock solution at 500 ppm
5190-8485	Agilent 1000 ppm single element stock solution for Hg
5190-8543	Agilent 1000 ppm single element stock solution for Sn
5190-8409	Agilent 10,000 ppm single element stock solution for Li
5190-8423	Agilent 10,000 ppm single element stock solution for Ni
5190-8415	Agilent 10,000 ppm single element stock solution for Mn
5190-8377	Agilent 10,000 ppm single element stock solution for Co
5190-8232	Agilent 10,000 ppm single element stock solution for Y
5190-8441	Agilent 10,000 ppm single element stock solution for Rb

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