Application Note

Energy and Chemicals

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Sustainable Lithium-Ion Battery Recycling: Recovery of Metals in Green Solvents by ICP-OES

Fast analysis of deep eutectic solvents using Agilent 5800 VDV ICP-OES with switching valve

Author

Leo Huang,
Agilent Technologies, Inc.

Introduction

The global rechargeable battery market has grown rapidly over recent years, driven by the use of lithium-ion batteries (LIBs) in electric vehicles (EVs), portable electronics, and energy storage systems.[1] This trend is expected to continue as countries transition from fossil fuels to cleaner energy solutions to reduce carbon emissions.[1] However, the LIB industry's reliance on critical elements—particularly lithium (Li), cobalt (Co), and nickel (Ni) that are used in key battery components like the anode and cathode—poses some challenges for the sector. Issues with supply or cost can impact the availability of these key metals, potentially limiting LIB production and causing prices to fluctuate.[2] Given these challenges, recovering metals from end-of-life (or spent) LIBs is gaining attention. Recovering and re-using materials can help meet the demand for critical elements, stabilize prices, and support a more sustainable circular economy in LIB manufacturing.[3]

Currently, two primary industrial processes are used for recycling spent LIBs: pyrometallurgy and hydrometallurgy. Pyrometallurgy involves the high-temperature extraction of metals, which is energy demanding and yields relatively poor-quality output.[3] Hydrometallurgy requires the use of numerous extractants and a longer process but achieves better metal recoveries than pyrometallurgy.[3] However, the hydrometallurgical process produces large quantities of acidic and alkaline wastewater, which can threaten the environment if not properly managed.[3]

Deep eutectic solvents (DESs) are an emerging class of green solvents that offer a novel solution for LIB recycling. Made from mixtures of biodegradable components, DESs are easy to prepare, inexpensive, nontoxic, and reusable.[4] Scientists are actively investigating how the unique properties of DESs can be used to efficiently leach critical metals from spent LIBs.[4]

To verify the effectiveness of DESs in terms of metal-recovery rates, researchers often use a multi-element analytical technique such as inductively coupled plasma optical emission spectroscopy (ICP-OES). However, analyzing leached metals in DESs by ICP-OES is not without its challenges. The high Total Dissolved Solids (TDS) matrix samples can cause wear on the sample introductory system, potentially introducing errors in the results. There is also a need for a wide Linear Dynamic Range (LDR), as the elemental profile of end-of-life LIBs can vary greatly.

The Agilent 5800 Vertical Dual View (VDV) ICP-OES is widely used to determine metals and other elements in LIB battery materials.[5] Designed for robustness and stability, the 5800 enables the fast, simultaneous measurement of over 70 elements in many sample types. The wide LDR of the instrument's Vista Chip III detector enables a range of elements to be analyzed in the same sample, avoiding the need to perform multiple dilutions.[6] This field-proven instrument uses advanced tools and accessories to support the development of new methods, making it ideal for LIB recycling initiatives, such as facilitating the recovery of valuable metals using DESs.

The Agilent Advanced Valve System 7-port switching valve (AVS 7)[7] and Agilent SPS 4 autosampler accessories were used with the 5800 to automate the analysis, improve sample throughput, and reduce wear on the instrument's sample introduction system. Sample introduction was controlled by the Agilent ICP Expert Pro instrument-control software. In this study, analysis times per sample were reduced from ~90 to 41 s using the AVS due to its efficient rinse mechanisms. The faster read times minimize wear on components and can reduce argon consumption by 50% or more.

The software also includes the IntelliQuant Screening smart feature, a useful tool that is used to identify the elemental content of the samples and to assist with method development.[8] The semiquantitative data generated by IntelliQuant Screening provides analysts with confidence when setting the calibration range for the analytes, selecting the best wavelengths, and identifying any unexpected spectral interferences arising from the sample matrix.

In this application, the 5800 VDV ICP-OES was used to determine eight representative elements of spent LIBs spiked in a choline chloride and urea (ChCl:Urea) DES solution. The analytes aluminum (Al), Co, copper (Cu), iron (Fe), Li, manganese (Mn), Ni, and phosphorus (P) were selected based on their presence in various types of cathode active materials (CAMs).

Experimentation

Instrumentation

The Agilent 5800 VDV ICP-OES was equipped with the integrated AVS 7-port switching valve and SPS 4 autosampler. Compared to the AVS 6, the 7-port system enables the internal standard to be directly plumbed to the valve.

The 5800 ICP-OES was fitted with a SeaSpray nebulizer, double-pass glass cyclonic spray chamber, and an Agilent Easy-fit 1.8 mm id injector one piece torch. All instrumentation was controlled by ICP Expert Pro software.

The instrument operating conditions for a simple automated workflow are provided in Tables 1 and 2.

Table 1. Agilent 5800 VDV ICP-OES instrument and method parameters.

Parameter	Setting
Viewing Mode	Radial
Viewing Height (mm)	8
RF Power (kW)	1.35
Nebulizer Flow (L/min)	0.7
Plasma Flow (L/min)	12
Aux Flow (L/min)	1
Replicates	3
Rinse Time (s)	3
Read Time (s)	5
Stabilization Time (s)	7
Sample Pump Tubing	White/white
Internal Standard Pump Tubing	Orange/white
Waste Pump Tubing	Blue/blue

Table 2. Agilent AVS 7 operating parameters.

Parameter	Setting
Sample Loop Size (mL)	1
Pump Rate – Uptake (mL/min)	35.1
Pump Rate – Inject (mL/min)	9
Valve Uptake Delay (s)	8.2
Bubble Injection Time (s)	2.0
Pre-emptive Rinse Time (s)	1.5

Method development

IntelliQuant Screening software

As part of the ICP Expert Pro software, IntelliQuant Screening collects full-spectrum data within a few seconds with little input needed by the analyst.[8] The IntelliQuant algorithm then processes the full-spectrum data against premeasured calibrations, generating a semiquantitative reading for every element present in the sample.[9] As shown in Figure 1, the data can be presented in a table and as a periodic table heat map, and the analyst can also review the spectrum in detail. The easy-to-interpret star rating system indicates which analyte wavelengths are likely subject to spectral interferences, background shifts, or poor sensitivity. Figure 2 shows how IntelliQuant Screening can be used to select the most sensitive line for Al before any samples are analyzed using the quantitative method.

By enabling analysts to select the best wavelength for the quantitative analysis and identifying the calibration range of each element, IntelliQuant is an easy-to-implement, time-saving method development tool. It is especially useful when developing a new method to analyze unknown samples, such as leached metals in DES solvents.

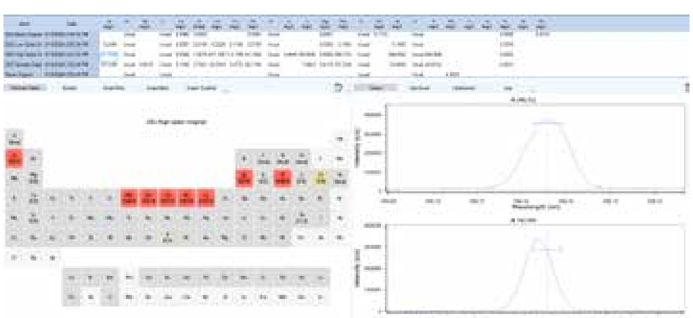


Figure 1. The IntelliQuant algorithm generates semiquantitative results for each sample analyzed during the IntelliQuant Screening full-spectrum scan.

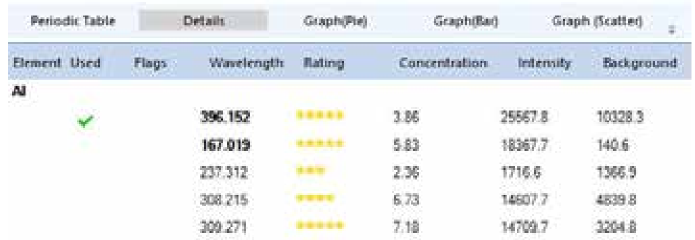


Figure 2. Using aluminum as an example, IntelliQuant identifies the best wavelength to use for each analyte. The software automatically applies a star rating to the various analyte wavelengths and assigns a green tick symbol to the recommended line.

Standard and sample preparation

Calibration standards

The diluent was prepared by diluting HNO_3 (Emsure, Merck) with 18.2 MΩ de-ionized water (Merck Millipore) to form a final matrix of 2% HNO_3. Both the calibration blank and standards were then prepared in the 2% HNO_3 matrix. As shown in Table 3, the calibration standards were prepared at 1, 10, and 100 mg/L for all eight elements with additional standards prepared at 200 and 500 mg/L for five elements. The standards were prepared by diluting Agilent 1000 and 10,000 mg/L single element calibration standard solutions with the diluent. The concentrations of the calibration solutions (Table 3) provided a wide linear range for each element, while maintaining excellent detection limits.

Table 3. Calibration points for all elements.

Analytes	Concentration of Calibration Standards (mg/L)
Co, Fe, Mn, Ni, P	0, 1, 10, 100, 200, 500
Al, Cu, Li	0, 1, 10, 100

DES preparation

The DES was prepared gravimetrically by combining ChCl (≥98% Sigma-Aldrich) and urea (Sigma-Aldrich) in a 1:2 molar ratio. With continuous stirring throughout, the viscous ChCl:Urea liquid mixture was heated to 80 °C and maintained at that temperature for several hours. The DES was allowed to cool to room temperature before being weighed gravimetrically (5 g into a 50 mL vial) and diluted 1:10 with 2% HNO_3. Before analysis, aliquots of the diluted DESs were vortexed for 30 s to ensure a consistent mixture. The detection limits were calculated using these DES samples, termed "sample blanks" in the detection limit section.

DES spiked solutions

To represent leached metals in DESs, two sets of DES spiked solutions were prepared in triplicate using Agilent single element stock solutions of each analyte. The spike concentrations were chosen to represent typical and extreme levels encountered in real-world applications. Spikes of Al, Cu, and Li were prepared at 0.2 and 90 mg/L to test both the detection limits and mid-range quantification accuracy for the analytes. Spikes for Co, Fe, Mn, Ni, and P were prepared at 0.2 and 400 mg/L to evaluate the system's performance over a wider dynamic range.

For the long-term stability test, the remainder of the DES spiked solutions were combined and unspiked DES solution was added to create enough volume for the seven-hour test.

Quality control solutions

For quality control (QC) purposes, a blank solution of 2% HNO_3 was used as the continuing calibration blank (CCB). Two solutions containing 1 and 100 mg/L respectively of all elements were used as continuing calibration verification (CCV) solutions. The CCV solutions were prepared from Agilent 1000 and 10,000 single element stock standard solutions.

Internal standard solution

An internal standard (IS) solution containing 5 mg/L yttrium (Y), 20 mg/L indium (In), and 50 mg/L tellurium (Te) was prepared in 2% HNO_3 from Agilent 1000 mg/L single element stock standard solutions. The IS solution was used to correct for any matrix effects or ionization interferences arising from the DES matrix.

Background correction

The Fitted Background Correction (FBC) and Fast Automated Curve-fitting Technique (FACT) interference correction techniques in the ICP Expert software were used in this study. FBC mathematically models the background spectrum under the analyte peak, providing fast, automatic, and accurate background correction of both simple and complex background structures.[10] FBC, which requires no input from the user, was applied to all analytes in this study, apart from Li 670.783 nm. FACT was used to enhance accuracy by eliminating interferences from the argon background signal at 670.803 nm and providing definitive correction against the matrix-related interferences arising from the DES.[11]

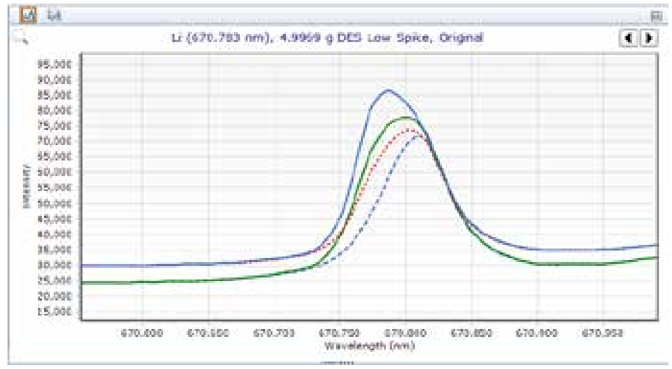
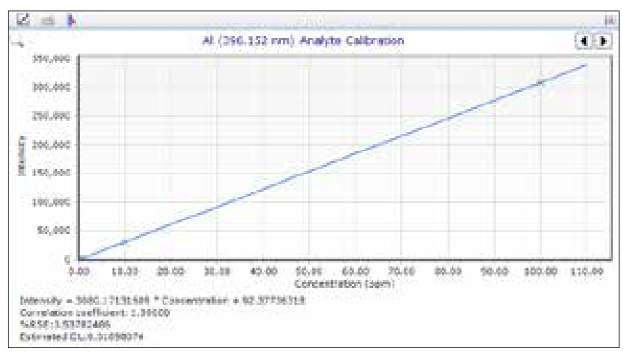


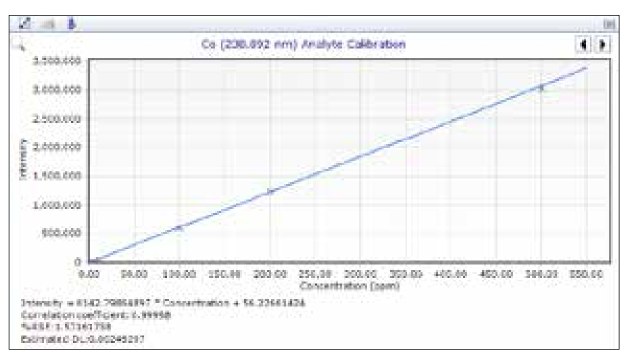
Figure 3. FACT model used to correct argon- and matrix-based interferences on Li (the corrected signal is represented by the solid blue line). The signal from the Ar 670.803 and DES-based interferences (red dashed line) overlaps the analyte Li 670.783 (green line). The blank is represented by the light blue dashed line.

Results and discussion

Calibration

The instrument was calibrated to ensure precise detection of analytes across a wide concentration range in the DES. Al, Co, Cu, Fe, Li, Mn, Ni, and P were calibrated between 1 and 100 mg/L or 1 and 500 mg/L, as detailed in Table 3. Linear calibration curves were obtained for all elements, with correlation coefficients >0.9999, as shown in Figure 4.





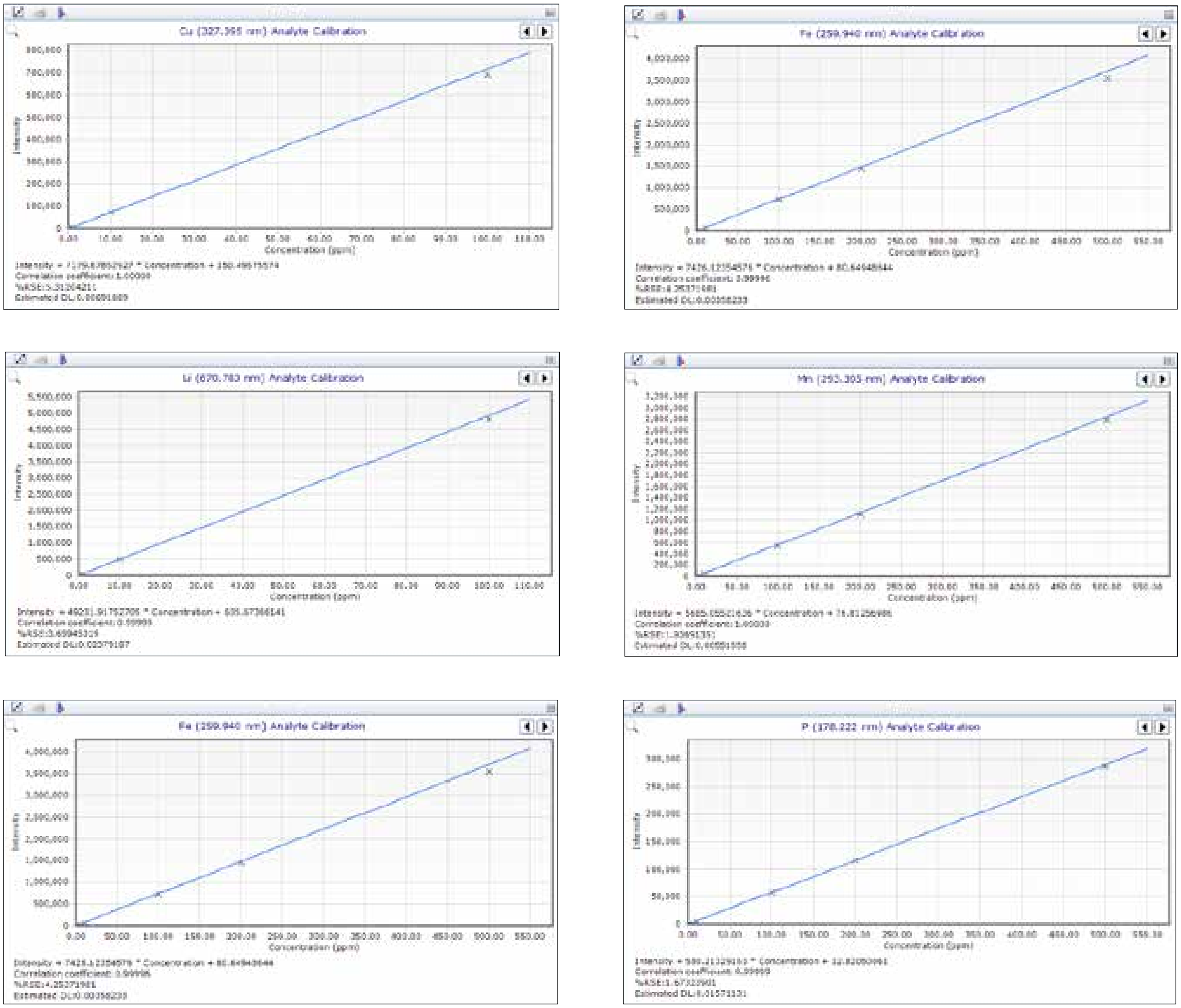


Figure 4. Calibration curves for Al, Co, Cu, Fe, Li, Mn, Ni, and P. The curves show the excellent linearity of the Agilent 5800 ICP-OES, as indicated by the correlation coefficient (R) values above 0.9999 for all analytes.

Detection Limits

The limits of quantification (LOQs) and method detection limits (MDLs) were calculated based on the analysis of 10 solutions over three non-consecutive days on one instrument. The LOQs were calculated by multiplying the standard deviation of 10 sample blank replicates by 10, while the MDLs were determined by multiplying the standard deviation of the sample blank replicates by three. The MDLs reported as 'in solution' do not take account of the dilution factor, whereas the dilution factor of 10 has been applied to the 'in sample' results (Table 4).

Spike recoveries

In the absence of suitable certified reference materials (CRMs) for the application, spike recovery tests were used to check the accuracy of the method.

The DES samples were spiked with both low and high levels of the analyte elements, as detailed in Table 5. The spiked samples were prepared in triplicate and analyzed over three non-consecutive days. All recoveries were within 100 ±10% for all analytes, as shown in Table 5.

The excellent spike recovery data confirms the suitability of the 5800 VDV ICP-OES method for the accurate analysis of both low and high concentrations of Al, Co, Cu, Fe, Li, Mn, Ni, and P in complex ChCl:Urea DES solutions.

Table 4. Analyte, background correction, calibration information, internal standard (IS), LOQs, and MDLs in the sample blank. The "in sample" MDLs have been corrected for the dilution factor.

Element and Wavelength (nm)	Background Correction	Correlation Coefficient	IS and Wavelength (nm)	LOQ (mg/L)	MDL in Solution (mg/L)	MDL in Sample (mg/kg)
Al 396.152	Fitted	1.00000	Y 371.029	0.042	0.013	0.13
Co 238.892	Fitted	0.99998	In 410.176	0.007	0.002	0.02
Cu 327.395	Fitted	1.00000	Y 371.029	0.017	0.005	0.05
Fe 259.940	Fitted	0.99996	In 410.176	0.010	0.003	0.03
Li 670.783	FACT	0.99999	Y 371.029	0.043	0.013	0.13
Mn 293.305	Fitted	1.00000	In 410.176	0.011	0.004	0.04
Ni 230.299	Fitted	0.99996	In 410.176	0.023	0.007	0.07
P 178.222	Fitted	0.99999	Te 214.282	0.049	0.015	0.15

Table 5. Spike recovery results of DES samples spiked with low and high concentrations of the eight analytes, measured using the Agilent 5800 VDV ICP-OES.

Element and Wavelength (nm)	DES Measured (mg/L)	Spike Level (mg/L)	DES Spike Measured (mg/L)	Spike Recovery (%)	Spike Level (mg/L)	DES Spike Measured (mg/L)	Spike Recovery (%)
Al 196.152	0.018	0.2	0.225	104	90	89.8	100
Co 238.892	<MDL	0.2	0.197	99	400	401	100
Cu 327.395	<MDL	0.2	0.205	103	90	91.5	102
Fe 259.940	0.018	0.2	0.224	103	400	396	99
Li 670.783	<MDL	0.2	0.189	94	90	91.5	102
Mn 293.305	<MDL	0.2	0.198	99	400	403	101
Ni 230.299	<MDL	0.2	0.197	99	400	400	100
P 178.222	0.030	0.2	0.224	97	400	387	97

Note: Al, Fe, and P were detected in the unspiked DES samples, likely due to trace impurities in the chemicals such as 98% purity ChCl used to prepare them.

Long-term stability

To determine the stability of the 5800 VDV ICP-OES, 645 solutions were analyzed over seven hours (41 s per sample). The solutions consisted of the QC solutions and a combination of the remaining spiked DES solutions plus unspiked DES solution. The recoveries of the elements in the CCV solution remained within 100 ±10% over the run, as shown in Figure 5. Recoveries of the spiked analytes in the DES sample were also within 100 ±10% of their expected values throughout the run, with ≤2.2% RSD for all elements, as shown in Table 6.

Both sets of stability data demonstrate the 5800 ICP-OES method's excellent robustness and precision throughout the analysis of complex DES-matrix samples.

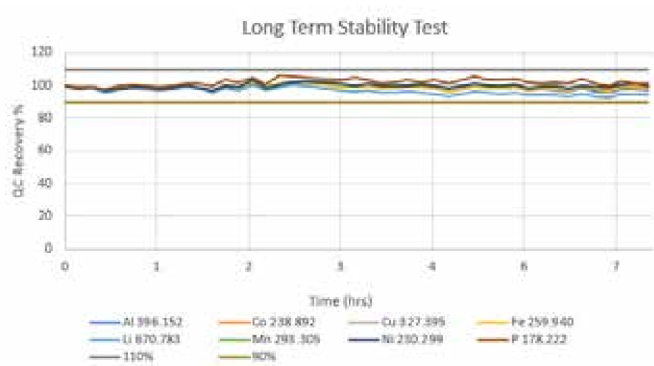


Figure 5. Long-term stability test showing recovery of the CCV solution analyzed over seven hours. The solid lines show the ±10% control limits.

Table 6. %RSD of measurements taken over seven hours (41 s per sample), and average % recovery data. n = 425.

Element	RSD (%)	Average Recovery (%)
Al	1.79	98
Co	1.72	99
Cu	1.67	99
Fe	1.66	98
Li	2.20	96
Mn	1.80	99
Ni	1.71	99
P	2.10	101

Conclusion

The Agilent 5800 VDV ICP-OES with the integrated AVS 7 switching valve effectively determined valuable LIB-related elements in DES. Leaching metals from end-of-life LIBs using DESs offers a more sustainable alternative to traditional metallurgical processes for battery recycling. Under the control of Agilent ICP Expert Pro software, the 5800 enabled the fast, robust, and accurate analysis of eight representative elements of LIBs in a spiked ChCl:Urea DES solution. The following hardware and software tools were used to ensure the quality of the quantitative data:

- IntelliQuant Screening streamlined method development by recommending optimal calibration ranges and interference-free wavelengths for all analytes, ensuring accurate analysis of analytes in DESs.
- The AVS 7 improved sample throughput requiring only 41 s per sample compared to 90 s without the AVS. It also minimized costs by lowering argon consumption to 9.8 L per sample and less frequent cleaning of consumables such as the torch and nebulizer.
- FBC automatically corrected the background structures for Al, Co, Cu, Fe, Mn, Ni, and P and FACT deconvoluted the Li peak from more complex background spectra.

The accuracy of the 5800 ICP-OES method was confirmed by recoveries of all analytes spiked at high and low levels in DES, with results within 100 ±10%. Excellent long-term stability was demonstrated when 645 solutions were analyzed over seven hours. Recoveries of the QCs and spiked DES samples were within ±10% of the expected values. Good precision was achieved for the spiked DES sample measurements, with RSDs ≤2.2% for all elements.

The performance of the 5800 VDV ICP-OES with AVS 7 demonstrates its suitability for the fast, quantitative analysis of critical LIB-related elements such as Co, Mn, and Li in complex matrices like ChCl:Urea DES.

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9. Agilent IntelliQuant Software: For greater sample insight and simplified method development, Agilent publication, 5994-1516EN
10. Fitted Background Correction (FBC)—fast, accurate and fully-automated background correction 5991-4836EN
11. Real-time Spectral Correction of Complex Samples using FACT Spectral Deconvolution Software, 5991-4837EN

Agilent part numbers

Description	Part Number
Easy-fit one piece torch, 1.8 mm id quartz injector, for 5000 Series VDV/SVDV ICP-OES	G8010-60228
Double-pass spray chamber, glass cyclonic design with ball joint socket and UniFit drain outlet, for Agilent 5000 series ICP-OES	G8010-60256
Nebulizer, concentric SeaSpray glass nebulizer for Agilent 5000 series ICP-OES	G8010-60255
Sample loop, for ADS/AVS, 1.00 mL, 1.00 mm id, 1/pk	5005-0423
Peristaltic pump tubing, white/white, 12/pk	3710034400
PVC peristaltic pump tubing, orange/white, 12/pk	3710046900
Peristaltic pump tubing, blue/blue, 12/pk	3710034600
Waste container kit, 10 L with Stay Safe cap and filter	5005-0437
Agilent 1000 ppm single element stock solution for Al, 500 mL	5190-8243
Agilent 10,000 ppm single element stock solution for Co, 500 mL	5190-8377
Agilent 1000 ppm single element stock solution for Co, 500 mL	5190-8347
Agilent 1000 ppm single element stock solution for Cu, 500 mL	5190-8349
Agilent 1000 ppm single element stock solution for Fe, 500 mL	5190-8472
Agilent 10,000 ppm single element stock solution for Fe, 500 mL	5190-8403
Agilent 1000 ppm single element stock solution for In, 500 mL	5190-8468
Agilent 1000 ppm single element stock solution for Li, 500 mL	5190-8478
Agilent 1000 ppm single element stock solution for Mn, 500 mL	5190-8484
Agilent 10,000 ppm single element stock solution for Mn, 500 mL	5190-8415
Agilent 1000 ppm single element stock solution for Ni, 500 mL	5190-8492
Agilent 10,000 ppm single element stock solution for Ni, 500 mL	5190-8423
Agilent 1000 ppm single element stock solution for P, 500 mL	5190-8500
Agilent 10,000 ppm single element stock solution for P, 500 mL	5190-8429
Agilent 1000 ppm single element stock solution for Te, 500 mL	5190-8534
Agilent 1000 ppm single element stock solution for Y, 500 mL	5190-8556

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