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Energy

Single quadrupole-inductively coupled plasma mass spectrometry (ICP-MS) as a tool for process control in lithium battery recycling

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Goal
To demonstrate the analysis of critical impurities in anode materials from recycled lithium-ion batteries with high sensitivity, accuracy, and robustness using single quadrupole ICP-MS.

Introduction
The transition to electric vehicles (EVs) is one of the key developments of the green energy revolution. As a result, the demand for fully electric vehicles has seen an acceleration in manufacturing capacity for both the vehicles themselves and the associated lithium-ion batteries as one of the core components. However, lithium-ion batteries are also used as important power storage materials in other areas, such as electricity storage from renewable energy sources, due to their power density and life cycle performance. In many cases, batteries that have reached their end of life in one application (i.e., vehicles) can still be efficiently and safely used for power storage in buildings. Nonetheless, the unprecedented ramp up in production also means that strategies and technology for complete and efficient recycling of used battery cells will have to be developed to fulfill the promise of a more sustainable future. Ultimately, the batteries used today should be considered under the principles of zero waste production and zero additional carbon footprint.

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A typical lithium-ion battery consists of four main parts—a cathode, separator, anode, and electrolyte (Figure 1). The main components that can be easily recovered for recycling purposes are the cathode and anode materials. However, due to the high purity requirements in the production of new battery cells, any recycling process must be able to deliver new raw materials with sufficient purity to meet the required material quality. This is particularly true for impurities, like trace elements. For the anode, which is produced from graphite powder, the purity level determines the product performance characteristics of thermal conductivity, strength, stability, and resistance.[1]

Lithium-ion battery charge
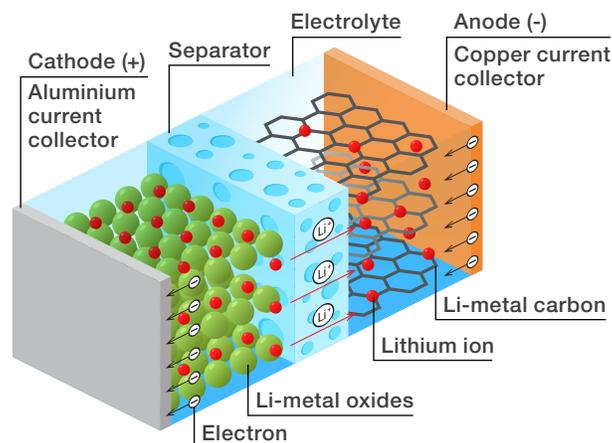
Figure 1. Lithium-ion battery diagram

In general, inductively coupled plasma mass spectrometry (ICP-MS) is the preferred analytical technique for the analysis of metals and related contaminants at low levels. However, the analysis of samples containing higher levels of total dissolved solids (TDS, typically above 0.5% w/v) or high acid concentration are a known challenge in ICP-MS. The complexity of the sample matrix can significantly affect the sensitivity of the instrument or cause problematic polyatomic interferences.

This application note describes an optimized analytical method for the analysis of recycled lithium battery anodes. The anode material (typically graphite powder) needs to be separated from the battery structure and any remaining binder materials. Finally, the recycled material needs to be dissolved to be accessible to ICP-MS based analysis. In this case, this is accomplished by microwave assisted digestion, providing a solution containing a high concentration of aqua regia. To overcome the analytical challenges described above, a Thermo Scientific™ iCAP™ RQplus ICP-MS equipped with the novel PLUS torch[2] was applied for the analysis, with superior interference removal achieved using kinetic energy discrimination (KED) with pure helium as the collision gas. The instrument was operated using Argon Gas Dilution (AGD)[3] to facilitate the direct analysis of a highly concentrated digestion solution.

Experimental
Instrumentation

An iCAP RQplus ICP-MS, fitted with the AGD option and operated using a low dilution level, was used for all analyses. In addition to the standard set up for AGD, the sample introduction system consisted of a Peltier cooled (at 2.7 °C) baffled cyclonic spray chamber, borosilicate microflow nebulizer, PLUS torch with a 2.5 mm i.d. removable quartz injector, and the EasyClick™ peristaltic pump (Figure 2). The EasyClick peristaltic pump features a self-tensioning tubing clip assembly that eliminates the need to manually adjust tubing tension and achieves stable sample uptake automatically. The instrument was operated using a single helium (He) kinetic energy discrimination (KED) mode for the interference-free analysis of all analytes over the full mass range. To automate the sampling process, a Thermo Scientific™ iSC-65 Autosampler with Step Ahead feature was used to increase sample throughput.[4] Table 1 summarizes the instrument configuration and analytical parameters.

Figure 2. The peristaltic pump (EasyClick) of the iCAP RQplus ICP-MS

Table 1. Instrument configuration and operating parameters

Parameter	Value
Nebulizer	MicroMist™ nebulizer 400 µL·min⁻¹
Peristaltic pump tubing	PVC orange-green tubing, 0.38 mm i.d. for both internal standard and sample
Peristaltic pump speed	25 rpm
Spray chamber	Quartz cyclonic, cooled at 2.7 °C
Torch	PLUS torch
Injector	2.5 mm i.d., Quartz
Interface	Nickel sampler and skimmer cone with high matrix insert
AGD setting	Low
Nebulizer flow (L·min⁻¹)	0.38
Additional gas, argon (% of range)	55
Plasma power	1,550 W
Nebulizer gas	0.23 L·min⁻¹
Additional gas flow (Ar)	0.80 L·min⁻¹
QCell setting	He KED
QCell gas flow	100% He 4.2 mL·min⁻¹
CR bias	-21 V
Q3 bias	-18 V
Scan setting	0.1 s dwell time, 5 sweeps, 3 main runs
Analysis time per sample	Total 2 min 38 s: including uptake and wash out
Autosampler	iSC-65 Autosampler

Software

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used for instrument auto tuning, using the readily available AGD tune sets, as well as for setting up measurement sequences and data acquisition. In addition, Qtegra ISDS Software is available with the iSC-65 Autosampler plug-in to provide additional, more powerful full automation analysis. In this study, two hardware key features were used for the analytical testing applications.

Step Ahead: Sends the probe to the rinse station during data acquisition, using the sample volume in the probe and transfer tubing to complete the analysis. Less sample volume is required, decreasing waste and instrument wear, decreasing rinse time, reducing rinse solution usage, and accelerating sample throughput.

Flexible sampling depths: Vial-specific probe depths in Qtegra ISDS Software enable correct sampling to avoid suspended graphite particles in specific sample locations that could otherwise lead to blockages. This minimizes maintenance and potential exchange of sample introduction components.[4]
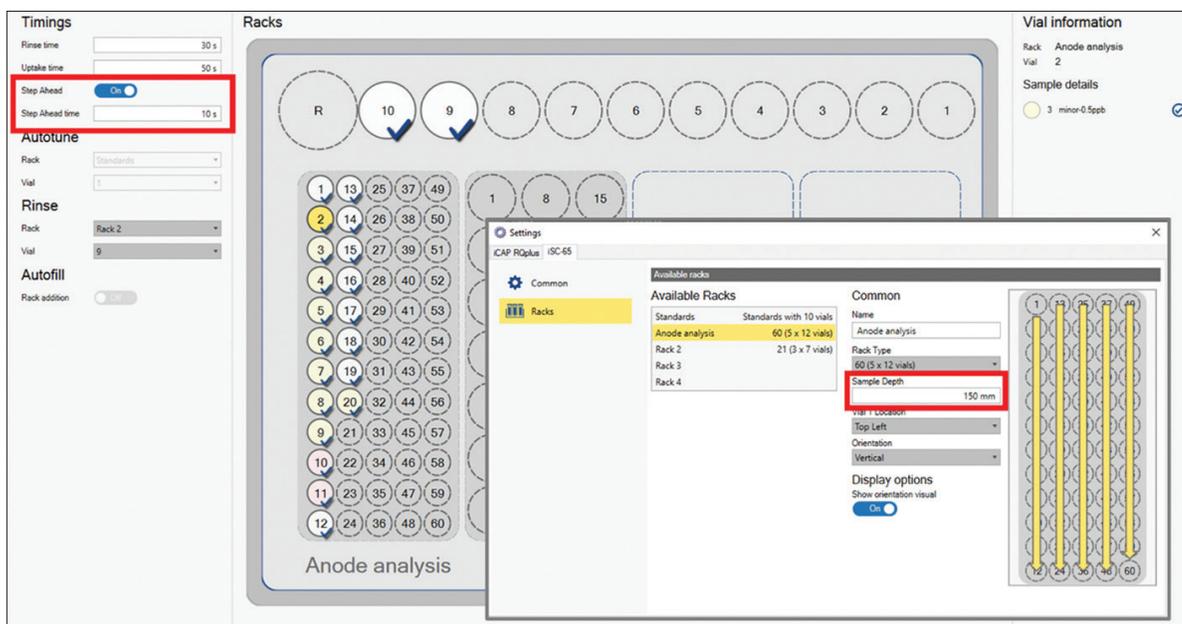
Figure 3. Qtegra ISDS Software screenshot of the settings view for the iSC-65 Autosampler plug in

Sample preparation

Polypropylene bottles were used for the preparation of all blanks, standards, and samples.

Two Li-battery anode recycling samples with different recycling processes were prepared to evaluate the iCAP RQplus ICP-MS system for this analysis. Both samples were digested before analysis. An aliquot of approximately 0.5 g of each sample was accurately weighed and acid digested using 8 mL aqua regia using a microwave system (Milestone ETHOS™ One, microwave heating program: ramp up temperature to 230 ˚C within 20 minutes and then hold at 230 ˚C for 25 minutes). After cooling, the samples were made up to a final volume of 50 mL using 0.1 m/v % HNO_3, so that the amount of total dissolved solids was around 1.0% (m/v), with an approximate 16% (m/m) of aqua regia* in the measured sample solution.

The acids employed for digestion were generally of the highest purity available and included HNO_3 (68% (m/v) Optima™ grade, Fisher Chemical™) and HCl (35% (m/v) Optima™ grade, Fisher Chemical™). The digestion protocol applied here does not allow a complete digestion of graphite, a highly chemically stable material. To achieve complete digestion, other acid mixtures and significantly higher digestion temperatures would need to be employed. Nonetheless, the outlined procedure is able to extract a high amount of typical metal contaminants from the sample, so that an assessment of the material quality after the separation of the anode is feasible. High acid concentrations can potentially cause corrosion in the plasma chamber and the interface region. As such, automated sample dilution using high purity argon delivered directly from the instrument was employed.

As can be seen in Figure 4, both samples showed particles remaining at the bottom of the vessel, which were separated from the supernatant using a Thermo Scientific™ Sorvall™ ST8 centrifuge at 4,500 rpm for 10 minutes at room temperature.

(A)   (B)
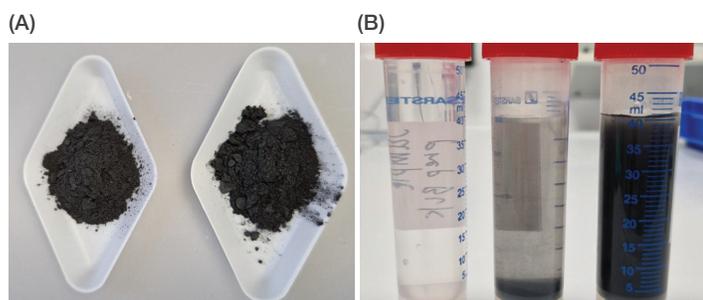
Figure 4. (A) Two graphite materials from recycled battery anodes as received as solids, (B) sample solution after microwave digestion (left: sample preparation blank, middle: 10 min after the microwave digestion, and right: directly after microwave digestion)

All blanks, calibration standards, spike recovery, and quality control (QC) solutions were prepared using a mixed acid diluent (2% v/v HNO_3 and 0.5% v/v HCl (Optima™ grade, Fisher Chemical™)) to allow for chemical stability of all elements in solution, and multi-element standards (SPEX™ CertiPrep™, Metuchen, NJ, USA). The calibration standards used in this study covered the concentration ranges listed in Table 2.

Table 2. Summary of the concentration details of the standard calibration, CCV (continuing calibration verification) and matrix spike recovery test

Element	Concentration range (µg·L⁻¹)	QC CCV (µg·L⁻¹)	Spike value in sample B (µg·L⁻¹)
Li	50–10,000	50	50
Cu	50–100,000	50	50
Ti, V, Co, Zn, Ga, Ge As, Rb, Zr, Nb, Mo, Ru, Pd, Ag, Cd, Sn, Sb, Te, Cs, Hf, Ta, W, Au, Hg, Pb, Bi, U	0.5–10	0.5	0.5
Be, B, Se	1–10	1	1
Al, Si, P, K, Na, Cr, Ni, Mn, Ca, Mg, Fe, Ba	50–1,000	50	50

To test the performance of the method for the analysis of such sample types over longer periods, and therefore to demonstrate analytical robustness for a high-throughput orientated laboratory, one of the prepared sample solutions was analyzed continuously over 9 hours. An internal standard solution, containing 20 µg·L⁻¹ Y, Rh, In, Lu and Tl in 2% v/v HNO_3 was added on-line to all samples via a T-piece (mixing rate between internal standard and samples 1:1) before entering the nebulizer. The details of internal standards used for each element are shown in Table 3.

Results and discussion

In general, inductively coupled plasma mass spectrometry (ICP-MS) is the preferred analytical technique for multi-elemental work, as it allows a wide range of contaminants, including platinum group metals and rare earth elements, to be analyzed with high sensitivity. In this study, data for 44 individual elements were collected, but this could be easily expanded to more than 60 elements. However, the analysis of samples containing high amounts of acids, in particular hydrochloric acid, can create challenges in ICP-MS. The presence of HCl can lead to the formation of polyatomic interferences, creating overlaps on key analytes, such as vanadium, chromium, germanium, and arsenic. These interferences can be overcome using collision/reaction cell technology, as described in the Experimental section. Whereas the nominal amount of TDS (approximately 1%) is not critical here (a significant portion of the sample was extracted rather than dissolved), the acid matrix of up to 16% (m/m) aqua regia requires dilution of the sample prior to analysis. This can be accomplished using liquid dilution or, alternatively, dilution of the sample aerosol with an inert gas such as argon.

Dilution with argon gas is a particularly attractive option, as samples can be placed directly on the autosampler without the need of a manual, time-consuming dilution step prior to analysis.

Sensitivity and linearity

Table 3 summarizes the instrument detection limits (IDLs) obtained, together with the coefficient of determination (R^2) for all 44 elements analyzed for ultra-trace analysis in this study. The IDLs were calculated as three times the standard deviation of ten replicate measurements of the calibration blank. The IDLs were well below 0.1 $\mu g \cdot L^{-1}$, even for often challenging analytes such as vanadium, chromium, germarium, and arsenic, especially when analyzed in solutions containing elevated amounts of chlorine, in this case originating from the aqua regia used for digestion. These detection limits therefore demonstrate the superior performance of the QCell collision/reaction cell (CRC) used in the iCAP RQplus ICP-MS, allowing suppression of even abundant polyatomic interferences in the toughest sample matrices.

Table 3. Summary of calibration results, LODs, and applied internal standard for all target analytes

	R^2	LOD ($\mu g \cdot L^{-1}$)	Internal standard		R^2	LOD ($\mu g \cdot L^{-1}$)	Internal standard
^{7}Li	0.9996	0.54	^{89}Y	^{78}Se	0.9934	0.8	^{89}Y
^{9}Be	0.9839	0.26	^{89}Y	^{85}Rb	0.9989	0.004	^{89}Y
^{11}B	0.9997	5.63	^{89}Y	^{90}Zr	0.9968	0.02	^{103}Rh
^{23}Na	0.9998	5.21	^{89}Y	^{93}Nb	0.9977	0.05	^{103}Rh
^{24}Mg	0.9901	0.19	^{89}Y	^{95}Mo	0.9973	0.08	^{103}Rh
^{27}Al	0.9999	0.45	^{89}Y	^{101}Ru	0.9984	0.003	^{103}Rh
^{28}Si	0.9997	5.55	^{89}Y	^{105}Pd	0.9982	0.01	^{103}Rh
^{31}P	0.9996	8.30	^{89}Y	^{107}Ag	0.9986	0.06	^{103}Rh
^{39}K	0.9998	3.84	^{89}Y	^{111}Cd	0.9988	0.005	^{115}In
^{44}Ca	0.9973	5.07	^{89}Y	^{118}Sn	0.9986	0.05	^{115}In
^{48}Ti	0.9952	0.10	^{89}Y	^{121}Sb	0.9986	0.01	^{115}In
^{51}V	0.9970	0.01	^{89}Y	^{125}Te	0.9985	0.08	^{115}In
^{52}Cr	0.9998	0.05	^{89}Y	^{133}Cs	0.9986	0.005	^{115}In
^{55}Mn	0.9997	0.02	^{89}Y	^{138}Ba	0.9985	0.03	^{115}In
^{56}Fe	0.9998	0.58	^{89}Y	^{178}Hf	0.9972	0.004	^{175}Lu
^{59}Co	0.9975	0.07	^{89}Y	^{181}Ta	0.9976	0.001	^{175}Lu
^{60}Ni	0.9999	0.67	^{89}Y	^{182}W	0.9975	0.03	^{175}Lu
^{63}Cu	0.9999	0.25	^{89}Y	^{197}Au	0.9974	0.06	^{175}Lu
^{66}Zn	0.9970	0.13	^{89}Y	^{202}Hg	0.9974	0.04	^{175}Lu
^{71}Ga	0.9974	0.003	^{89}Y	^{208}Pb	0.9984	0.006	^{205}Tl
^{72}Ge	0.9978	0.01	^{89}Y	^{209}Bi	0.9985	0.010	^{205}Tl
^{75}As	0.9974	0.03	^{89}Y	^{238}U	0.9984	0.001	^{205}Tl

Accuracy

The results obtained for two samples investigated in this study along with method detection limits (MDLs) are summarized in Table 4. MDLs are based on the IDLs summarized in Table 3 and employing the dilution factor of 100 incurred during the digestion process. The two results obtained for both samples were also corrected for the dilution factor, such that the results displayed here refer to the concentration in the undigested solid material received originally. Individual replicates of each sample showed excellent precision with RSD (%) within ±5% (n=20) across different concentration ranges. Individual samples contained varying concentrations of various elements such as lithium, magnesium, phosphorus, calcium, manganese, iron, nickel, and copper. Samples showed a particularly wide range of copper concentrations. This is likely a result of the collection of the graphite from the recycled anode material, with accidental scratching of the copper substrate of the anode during graphite recovery.

Sample A was collected without any recycling process, but sample B was from the early stage of the purification process. Therefore, the obtained analysis results are in agreement with the quality of the anode recycling process.

To test the accuracy of the method, a spike recovery test was performed using sample B. The results obtained demonstrate excellent recovery result within 84% to 104% and within 4.4% RSD for all analytes, including elements such as vanadium, chromium, germanium, and arsenic, which, as previously mentioned, are particularly affected by polyatomic interferences involving chlorine. Using He KED analysis mode provides the advantage of eliminating the interference from the high concentration of HCl and minimizing the analysis time for optimum accuracy and productivity.

Table 4. Quantification results for the anode samples and spike recovery results

	MDL (µg·kg⁻¹)	Sample A (n=20)		Sample B (n=20)		Spike recovery (n=10)	
		µg·kg⁻¹	RSD (%)	µg·kg⁻¹	RSD (%)	Recovery (%)	RSD (%)
^{7}Li	53.5	936,714	0.9	56,330	2.0	95.5	1.8
^{9}Be	26.3	<MDL	-	<MDL	-	104.6	3.2
^{11}B	563.3	3,729	3.8	11,939	2.9	105.0	3.2
^{23}Na	521.5	18,038	1.5	16,650	2.7	98.9	1.9
^{24}Mg	18.5	14,469	2.2	1,678	2.1	88.8	2.4
^{27}Al	45.4	20,073	1.2	24,701	1.5	84.4	1.8
^{28}Si	555	44,194	1.8	40,427	1.5	85.1	2.7
^{31}P	830	94,460	3.0	9,352	3.1	85.4	4.3
^{39}K	384	3,771	1.7	5,684	2.1	91.8	2.8
^{44}Ca	507	75,245	2.0	6,645	2.4	88.5	2.8
^{48}Ti	10.3	3,040	2.4	1,008	1.6	97.7	1.7
^{51}V	0.9	196	2.1	106	2.2	88.7	1.8
^{52}Cr	4.9	8,378	1.5	2,930	1.4	84.8	1.8
^{55}Mn	2.0	96,674	1.4	839	1.3	88.3	1.4
^{56}Fe	58.2	31,645	1.4	11,352	1.6	86.6	1.6
^{59}Co	6.6	613	1.4	96	0.9	85.1	1.1
^{60}Ni	67	6,849	0.9	1,940	0.9	89.5	1.3
^{63}Cu	25	5,855,996	1.0	75,445	1.0	96.6	1.3
^{66}Zn	13.2	1,595	2.9	270	1.7	89.9	2.0
^{71}Ga	0.3	19	3.0	17	2.1	92.9	2.5
^{72}Ge	1.0	98	3.8	256	3.9	103.8	3.7
^{75}As	3.0	216	2.5	73	3.6	88.3	3.0
^{78}Se	78.8	274	3.8	245	3.1	95.5	4.4

Table 4 continued. Quantification results for anode samples and spike recovery results

	MDL (µg·kg⁻¹)	Sample A (n=20)		Sample B (n=20)		Spike recovery (n=10)	
		µg·kg⁻¹	RSD (%)	µg·kg⁻¹	RSD (%)	Recovery (%)	RSD (%)
^{85}Rb	0.4	31	1.9	62	1.8	91.9	2.7
^{90}Zr	2.3	446	1.7	173	1.5	91.5	1.6
^{93}Nb	4.9	38	4.3	11	6.3	93.6	1.6
^{95}Mo	8.3	594	1.6	474	1.5	89.0	2.1
^{101}Ru	0.3	<MDL	-	<MDL	-	105.7	2.2
^{105}Pd	1.3	6	4.9	5	3.9	113.3	1.7
^{107}Ag	5.6	39	1.0	79	1.3	102.1	1.3
^{111}Cd	0.5	108	3.8	5	3.8	105.5	2.8
^{118}Sn	5.1	167	2.0	67	1.6	91.4	1.0
^{121}Sb	0.9	24	5.8	18	2.2	99.6	1.2
^{125}Te	8.0	<MDL	-	<MDL	-	101.4	4.2
^{133}Cs	0.5	13	2.6	15	1.7	100.1	1.1
^{138}Ba	2.6	13,011	1.8	47,953	1.8	95.7	1.5
^{178}Hf	0.4	11	3.1	4	2.3	94.6	1.6
^{181}Ta	0.1	2	3.5	1	2.3	97.8	1.6
^{182}W	2.7	32	3.2	16	2.4	100.9	0.8
^{197}Au	6.3	<MDL	-	<MDL	-	104.0	2.8
^{202}Hg	38.3	198	3.9	<MDL	-	102.0	5.2
^{208}Pb	0.6	914	1.5	534	1.3	91.1	1.2
^{209}Bi	1.0	12	1.9	7	0.8	109.2	0.8
^{238}U	0.1	27	1.8	9	1.1	114.6	1.2

Evaluation of long-term robustness

To simulate high-throughput analysis, a larger batch of samples containing the aforementioned matrix composition was scheduled for analysis. After generating the calibration curves and initially verifying their validity, the batch contained several blocks containing unknown samples together with applicable QC checks. The total number of solutions analyzed was 189 (including 160 unknown samples and 29 calibration standards and QC checks), requiring a total analysis time of approximately 9 hours.

The relative standard deviation of all CCVs (n=9) for all 44 elements showed excellent recovery (within 88% to 109%) with a relative standard deviation of ±4.0% within the batch (Figure 5). This indicates that the iCAP RQplus ICP-MS allows for robust and reliable long-term analysis even for samples containing a highly varying composition of the sample matrix.
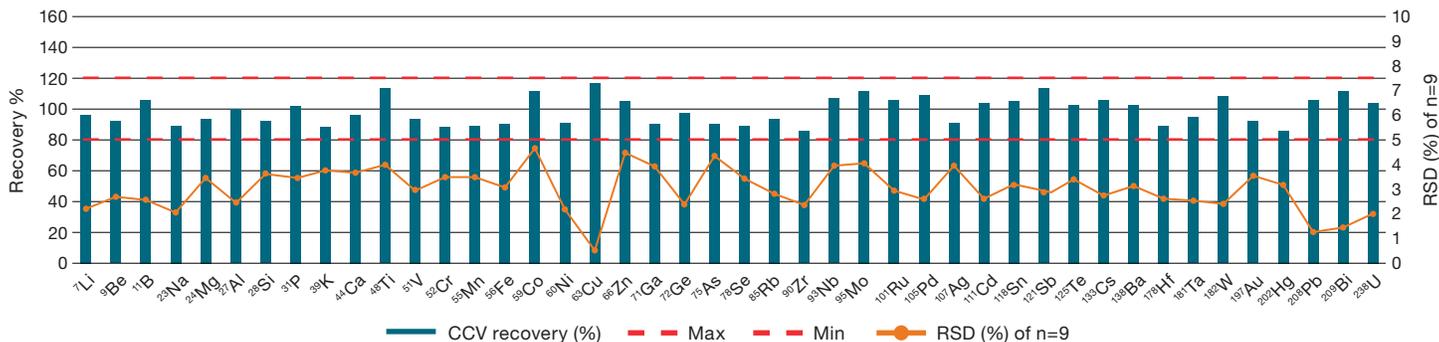
Figure 5. QC continuous calibration verification (CCV) results for all 44 elements measured
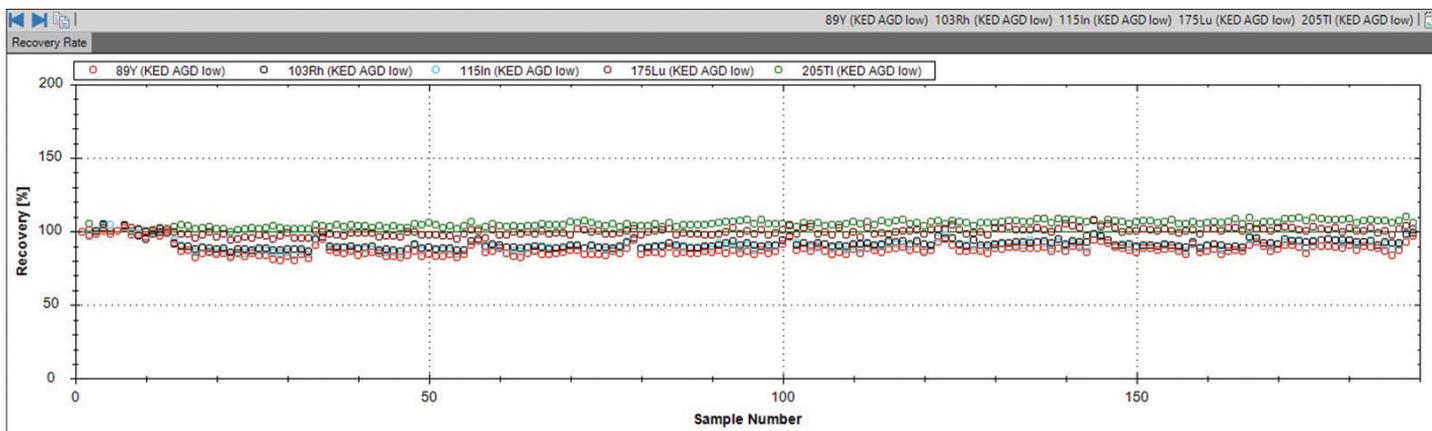
Figure 6. Response of the internal standards in a batch covering about ~9 hours of uninterrupted analysis of 189 samples

The response of the internal standards is shown in Figure 6. All internal standards showed reliable and predictable recovery (within approximately 84% to 108%) over the entire runtime of the batch, demonstrating robust analytical performance even in the presence of a high concentration of aqua regia as the primary acid matrix in the sample.

Conclusions

The iCAP RQplus ICP-MS, operated using AGD, enables analysts to perform accurate and reliable elemental analysis in challenging samples. This was demonstrated for the analysis of 44 elements in a large number of samples, covering a wide range of target concentrations. The analytical method was rigorously tested for performance, and the results obtained clearly demonstrated the following analytical advantages for anode solution analysis:

- AGD-low mode with excellent sensitivity allowed the aspiration of anode recycling with 16% (m/m) aqua regia samples and allowed excellent MDLs to be obtained, eliminating the need for labor-intensive further manual sample dilution, and accelerating sample throughput using a Step Ahead feature for minimizing total analysis time.

- High performance He KED mode provided the advanced performance required for the accurate determination of elements typically suffering from polyatomic interferences in the presence of higher amounts of hydrochloric acid.

- Excellent CCV recovery and spike recovery results, as well as stable and consistent internal standards response, were obtained across a batch containing 189 samples of a 1% w/w TDS anode solution, demonstrating the reliability of the method.

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