

Energy

Managing the challenges of analyzing battery materials using triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS) equipped with Argon Gas Dilution

Authors

Tomoko Vincent¹, Daniel Kutscher¹,
Mikael D. Axelsson², Ibrija Musfique³

¹Thermo Fisher Scientific, Germany,

²Thermo Fisher Scientific, Sweden,

³Northvolt Revolt AB, Sweden

Keywords

Argon Gas Dilution, battery, cathode, high matrix, high resolution, ICP-MS, KED, lithium, recycling, triple quadrupole, TQ-O₂ mode

Goal

To demonstrate the analysis of critical elemental impurities in highly concentrated solutions (up to 5.3% w/w) of cathode materials used in lithium-ion batteries with high sensitivity, accuracy, and robustness using triple quadrupole ICP-MS.

Introduction

The transition to electric vehicles (EVs) is one of the key developments of the green energy revolution, and the resulting demand for these vehicles shows an unprecedented speed in ramping up manufacturing capacity for both the vehicles themselves and the lithium-ion batteries that power them. Lithium-ion batteries are one of the most important power storage materials for EVs due to their power density and life cycle performance. With the high, and increasing, demand for batteries, questions arise around their fate at the end of their lifetime. Key areas of concern are recycling, to recover valuable raw materials and maintain sustainability in the supply chain, and issues surrounding environmental contamination following inappropriate battery disposal.

A typical lithium-ion battery consists of four main parts, namely the cathode, separator, anode, and electrolyte (Figure 1). To meet the required performance criteria (i.e., long battery lifetime and maximum achievable charge capacity), it is important to monitor not only the concentration ratio of the main components (typically nickel, manganese, cobalt, and lithium in nickel manganese cobalt (NMC) batteries, or iron, phosphorus, and lithium in lithium iron phosphate (LiFePO₄) batteries and lithium ferrophosphate (LFP) batteries), but also trace impurities in both the precursor materials and the finished products.¹

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 (below $1 \mu\text{g}\cdot\text{L}^{-1}$). However, the analysis of samples containing higher levels of total dissolved solids (TDS, typically above 0.5% w/v) is a known challenge in ICP-MS. The complexity of the sample matrix can significantly affect the sensitivity of the instrument, cause intensity fluctuation of the internal standard (suppression and drift), and lead to increased system maintenance with unwanted downtime due to clogging of the interface cone orifices, torch injector, or nebulizer. To analyze complex samples, dilution must be performed, either 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 off-line manual dilution step prior to analysis.

A further challenge for the analysis of battery materials such as cathodes, when using conventional, single quadrupole ICP-MS, are polyatomic interferences generated by the principal components of the samples. For example, in addition to the well-known argon-based interferences, all major selenium isotopes can be affected by nickel oxide-based interferences, such as $[\text{}^{60}\text{Ni}^{16}\text{O}]^+$ (on ^{78}Se) and $[\text{}^{64}\text{Ni}^{16}\text{O}]^+$ (on ^{80}Se), rendering low level analysis of this critical contaminant with a single quadrupole ICP-MS system impossible.²

Lithium-ion battery charge

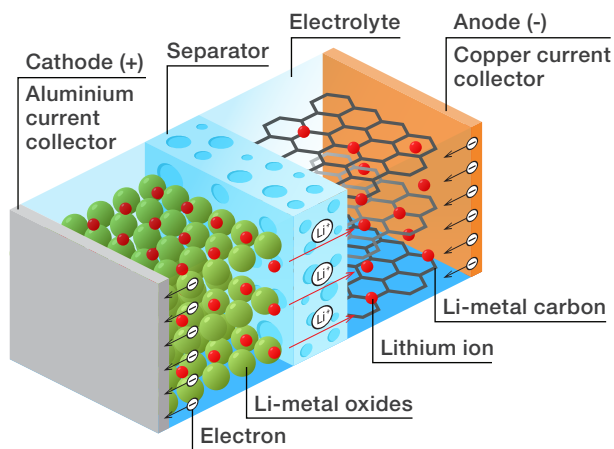


Figure 1. Lithium-ion battery diagram

This application note describes an optimized analytical method for the analysis of lithium battery cathode materials, as well as recycled battery materials. In this work, samples could be analyzed immediately following acid assisted dissolution, even though they contained elevated amounts of total dissolved solids (TDS), in this case up to 5.3% w/w. To overcome the analytical challenges described above, a triple quadrupole instrument, the Thermo Scientific™ iCAP™ TQe ICP-MS, was applied for the analysis. Use of triple quadrupole technology offered superior interference removal and operation using Argon Gas Dilution (AGD) facilitated direct analysis of concentrated sample solutions.

Experimental

Experimental optimization of the instrument parameters

An iCAP TQe ICP-MS, fitted with the AGD option was used for all analyses. In addition to the standard setup for AGD, the additional gas flow added to the sample aerosol before it enters the plasma was humidified. Use of a humidifier (pergo, Elemental Scientific (ESI), Omaha, NE, USA) significantly improves the analysis of elements with high ionization potentials, such as arsenic and selenium, which could otherwise suffer from reduced recovery in the matrix. The sample introduction system consisted of a Peltier cooled (at $2.7 \text{ }^\circ\text{C}$), baffled cyclonic spray chamber, PFA microflow nebulizer, and quartz torch with a 2.5 mm i.d. removable quartz injector. As well as using triple quadrupole mode operation with O_2 for key interfered analytes such as As and Se, the instrument was operated in single quadrupole mode using helium and kinetic energy discrimination (KED) to facilitate highest sensitivity, interference-free analysis of all the measured analytes over the full mass range. To allow the signal of the major component nickel to be monitored as well, the quadrupole resolution for this analyte was increased, so that the number of ions being detected was significantly reduced, thereby avoiding excessive lifetime-reducing signal impact on the detector. A Thermo Scientific™ iSC-65 Autosampler was employed to automate sample introduction. Table 1 summarizes the instrument configuration and analytical parameters. The selection of the most appropriate isotopes per analyte, as well as the optimum analysis conditions (i.e., KED mode versus reactive gas, on mass mode versus mass shift reaction mode) was automatically accomplished using the Reaction Finder Method Development Assistant available in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. Measurement modes were optimized using the autotune procedures available in the software.

Table 1. Instrument configuration and operating parameters

Parameter	Value	
Nebulizer	ESI PFA MicroFlow ST, orange cap, 400 $\mu\text{L}\cdot\text{min}^{-1}$	
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	Quartz torch	
Injector	2.5 mm i.d., Quartz	
Interface	Nickel sampler and skimmer cone with high matrix insert	
Plasma power	1,550 W	
Nebulizer gas	0.23 $\text{L}\cdot\text{min}^{-1}$	
Additional gas flow (Ar)	0.80 $\text{L}\cdot\text{min}^{-1}$	
QCell setting	He KED	TQ-O ₂
QCell gas flow	100% He 4.2 $\text{mL}\cdot\text{min}^{-1}$	100% O ₂ 0.32 $\text{mL}\cdot\text{min}^{-1}$
CR bias	-21 V	-6.3 V
Q3 bias	-18 V	-12 V
Scan setting	0.1 s dwell time, 5 sweeps, 3 main runs	
Analysis time per sample	Total 4 min 10 s: including uptake 80 s and wash out 30 s	

Sample preparation

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

The NMC 811 cathode solid standard (MSE Supplies, AZ, USA), a real ternary battery material (Figure 2A), and a real battery recycling solution (already digested with H_2SO_4 , detail is in Table 2) were prepared to evaluate the iCAP TQe ICP-MS system for this analysis. All samples were digested before analysis as described in Table 2. An aliquot of approximately 0.5–1.0 g of each sample was accurately weighed, and acid digested

using aqua regia. The acids employed for digestion were 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™). Two digestion procedures were tested, based on closed vessel digestion 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.) and alternatively, hot plate digestion (220 °C for 2 hours) as is shown in Figure 2B. Using microwave digestion, it was possible to achieve complete digestion of the NMC811 cathode standard, but the real ternary cathode material showed undigested particles, visible at the bottom of the vessel, which were removed by filtration using a 0.45 μm Teflon filter (as shown in Figure 2B). The hot plate digestion method was not able to digest the samples completely and black powder remained in the solution (Figure 2C), which was also filtered prior to analysis.

Detailed information on the digestion procedures used is summarized in Table 2 and Figure 2. After digestion, the samples were made up to a final volume of either 50 or 100 mL using 1% (m/v) HNO_3 , so that the amount of total dissolved solids was around 1.0% (m/v) in the measured sample solutions.

All blank, calibration standard, 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™)) and multi-element standards (SPEX™ CertiPrep™, Metuchen, NJ, USA) to result in the concentration ranges listed in Table 3. The details of the measurement modes, acquisition parameters, and internal standards used for each element are shown in Table 4.

To test the performance of the method for the analysis of such sample types over longer periods and to demonstrate analytical robustness for a high throughput orientated laboratory, battery matrix solutions with concentrations of 1.0% (m/v) and 5.3% (m/v) were analyzed over 14 hours. An internal standard solution containing 1,000 $\mu\text{g}\cdot\text{L}^{-1}$ Sc and 200 $\mu\text{g}\cdot\text{L}^{-1}$ Y, Rh, Te, and Lu 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.

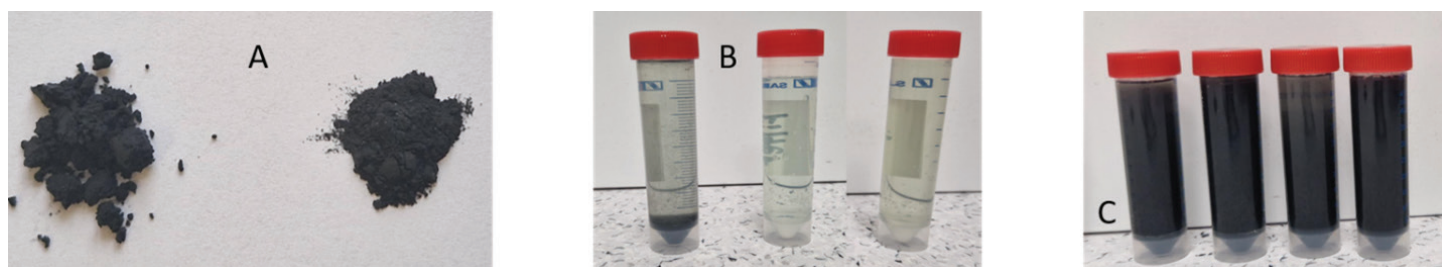


Figure 2. Battery materials investigated in this study. (A) Real ternary cathode sample (right) and cathode standard (left). (B) After the microwave sample preparation (from left to right: real ternary cathode sample, same sample after filtration, and cathode standard material). (C) Ternary cathode and cathode standard sample after hot plate digestion – incomplete with undigested material remaining.

Table 2. Details of the samples and preparation

I.D.	Sample	Preparation	Comment	Filtration	Collected sample	Acid (aqua regia)	Final volume	TDS (%) in final solution
1	Cathode standard	Microwave	Digestion completed	No	0.5 g	8 mL	50 mL	1.0%
2	Cathode standard	Hotplate	Not completed digestion	Yes	1 g	16 mL	100 mL	1.0%*
3	Real ternary cathode	Microwave	Not completed digestion	Yes	0.5 g	8 mL	50 mL	1.0%*
4	Real ternary cathode	Hotplate	Not completed digestion	Yes	1 g	16 mL	100 mL	1.0%*
5	Recycled battery solution	Dilution	Sample was already prepared using H ₂ SO ₄	No	10 mL	With 2% HNO ₃	50 mL	5.3%

* For these samples, the mentioned TDS content refers to a complete digestion. Actual TDS load is lower due to the fact that the digestion process was not complete.

Table 3. Summary of the concentration details of the standard calibration, CCV (continuing calibration verification), and matrix spike recovery test

Solution items	Sample type	Element	Concentration range (mg·L ⁻¹)	QC CCV (mg·L ⁻¹)
Standard A	Calibration curve	Ti, Ge, Hg, Au, Ce, Nd, Sm, Eu, Gd, Dy, Er, Tm, Yb, W, Ta, Hf, Sn, Sb	0.0002–0.001	0.0005
Standard B		Be, V, Cr, Cu, Zn, Ga, As, Se, In, Cd, Ag, Sr, Rb, Mo Cs, Ba, U, Pb, Bi, Tl	0.02–0.1	0.05
Standard C		Li, Al, Co, Mn	100–500	250
Standard D		S, P	0.1–10	0.5
Standard E		Na, Ca, K, Mg, Fe, Zr	2–10	5
Standard F		Ni	1,000–5,000	1,000
Spike recovery 1	Matrix spike recovery	Ti, Ge, Hg, Au, Ce, Nd, Sm, Eu, Gd, Dy, Er, Tm, Yb, W, Ta, Hf, Sn, Sb	0.0002	–
Spike recovery 2		Li, Al, Co, Mn, Ni	100	–
Spike recovery 3		Be, V, Cr, Cu, Zn, Ga, As, Se, In, Cd, Ag, Sr, Rb, Mo Cs, Ba, U, Pb, Bi, Tl	0.05	–
Spike recovery 4		S, P, Na, Ca, K, Mg, Fe, Zr	5	–

Results and discussion

Figure 3 shows the comparison of analytical results for the bulk elements in the cathode standard obtained by the microwave and hot plate digestion methods. Although the different digestion procedures produced different levels of undigested material, the overall results for the ratios of nickel to manganese and cobalt showed close agreement. In addition, different repeats of the measurement (N=24) showed excellent precision with an RSD of 1.4%.

The results between both sample preparation techniques may vary for certain elements. For example, elements such as titanium, zirconium, or hafnium may show insufficient recovery when using the proposed hot plate digestion method. This can be improved by the addition of hydrofluoric acid (HF), but this acid must be handled with great care.*

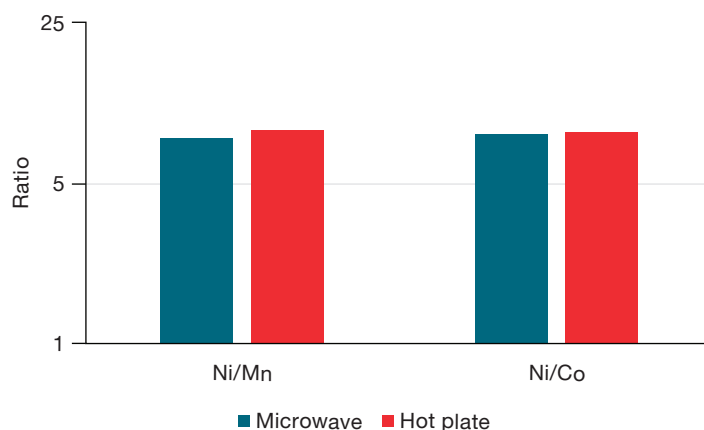


Figure 3. Comparison of the measured ratios of the bulk element concentrations for the cathode standard sample obtained by the microwave and hot plate digestion methods

*Use of full personal protective equipment (PPE), including gloves, lab coat, and safety glasses is essential when handling all acids. With hydrofluoric acid, it is also essential to have calcium gluconate gel on hand in case of contact of HF with skin. In the event of skin exposure to HF, wash the affected area immediately with copious amounts of water, dry and apply a liberal coating of calcium gluconate gel to the exposed area.

Sensitivity and linearity

Table 4 summarizes the instrument detection limits (IDLs) obtained, together with the coefficient of determination (R^2) for all 51 elements analyzed in this study. The IDLs were calculated as three times the standard deviation of ten replicate measurements of the calibration blank. Note that these detection limits include the dilution factor applied using AGD. No further liquid dilution other than what is mentioned in the sample preparation section was applied.

As illustrated in Table 4, using the He KED single quadrupole configuration achieved excellent performance in terms of sensitivity and linearity for many of the target analytes. However, as noted earlier, it is important to highlight that the analysis of some elements is challenging using a single quadrupole ICP-MS

strategy because of specific interferences created by the sample matrix. Figure 4 shows a full mass spectrum obtained during the analysis of the NMC 811 cathode material (diluted to 1% (m/v) TDS), clearly showing the high amounts of manganese, nickel, and cobalt. As mentioned before, the analysis of selenium in this matrix is considered difficult due to nickel-based interferences. Also, other elements, such as arsenic which is monoisotopic at m/z 75, can be highly interfered in this matrix, as a result of a false positive signal caused by cobalt oxide ($^{59}\text{Co}^{16}\text{O}$) formation.³ To address these challenges, using a triple quadrupole ICP-MS system, such as the iCAP TQe ICP-MS, is the perfect choice, as it offers the superior selectivity needed to efficiently eliminate these interferences.

Table 4. Summary of analysis modes, calibration results, and IDLs for all target analytes

Analyte	Measurement mode	Q3 analyte	Internal standard	Coefficient of determination (R^2)	IDL (mg·L ⁻¹)
⁷ Li	He KED	–	⁴⁵ Sc	0.9989	0.019
⁹ Be	TQ-O ₂	⁹ Be	⁴⁵ Sc	0.9960	0.022
²³ Na	He KED	–	⁴⁵ Sc	0.9991	0.020
²⁴ Mg	He KED	–	⁴⁵ Sc	>0.9999	0.002
²⁷ Al	He KED	–	⁴⁵ Sc	0.9989	0.003
³¹ P	TQ-O ₂	³¹ P. ¹⁶ O	⁴⁵ Sc	0.9950	0.099
³² S	TQ-O ₂	³² S. ¹⁶ O	⁴⁵ Sc	0.9357	0.398
³⁹ K	He KED	–	⁴⁵ Sc	>0.9999	0.031
⁴⁴ Ca	He KED	–	⁴⁵ Sc	0.9953	0.038
⁴⁸ Ti	TQ-O ₂	⁴⁸ Ti. ¹⁶ O	⁴⁵ Sc	0.9674	0.0004
⁵¹ V	TQ-O ₂	⁵¹ V. ¹⁶ O	⁴⁵ Sc	0.9996	0.0002
⁵² Cr	TQ-O ₂	⁵² Cr. ¹⁶ O	⁴⁵ Sc	0.9991	0.002
⁵⁵ Mn	He KED	–	⁴⁵ Sc	0.9983	0.001
⁵⁶ Fe	He KED	–	⁴⁵ Sc	>0.9999	0.001
⁵⁹ Co	He KED	–	⁴⁵ Sc	0.9998	0.001
⁶² Ni	He KED	–	⁴⁵ Sc	0.9994	0.016
⁶³ Cu	He KED	–	⁴⁵ Sc	0.9970	0.0002
⁶⁶ Zn	He KED	–	⁴⁵ Sc	0.9998	0.001
⁷² Ge	He KED	–	⁸⁹ Y	0.9984	<0.0001
⁷⁵ As	TQ-O ₂	⁷⁵ As. ¹⁶ O	¹²⁵ Te	0.9965	0.0003
⁸⁰ Se	TQ-O ₂	⁸⁰ Se. ¹⁶ O	¹²⁵ Te	0.9983	0.0004
⁸⁵ Rb	He KED	–	⁸⁹ Y	0.9997	0.0001
⁸⁸ Sr	TQ-O ₂	⁸⁸ Sr. ¹⁶ O	⁸⁹ Y	0.9993	<0.0001
⁹⁰ Zr	TQ-O ₂	⁹⁰ Zr. ¹⁶ O	⁸⁹ Y	0.9928	0.0003
⁹⁸ Mo	TQ-O ₂	⁹⁸ Mo. ¹⁶ O	¹⁰³ Rh	0.9939	<0.0001
¹⁰⁵ Pd	He KED	–	¹⁰³ Rh	0.9930	<0.0001

Table 4 continued. Summary of analysis modes, calibration results, and IDLs for all target analytes

Analyte	Measurement mode	Q3 analyte	Internal standard	Coefficient of determination (R ²)	IDL (mg·L ⁻¹)
¹⁰⁷ Ag	He KED	–	¹⁰³ Rh	0.9983	<0.0001
¹¹¹ Cd	TQ-O ₂	¹¹¹ Cd	¹⁰³ Rh	0.9994	<0.0001
¹¹⁵ In	He KED	–	¹²⁵ Te	0.9968	<0.0001
¹¹⁸ Sn	He KED	–	¹²⁵ Te	0.9933	0.0001
¹²¹ Sb	He KED	–	¹²⁵ Te	0.9981	0.0001
¹³³ Cs	He KED	–	¹²⁵ Te	0.9990	<0.0001
¹³⁸ Ba	TQ-O ₂	¹³⁸ Ba. ¹⁶ O	¹²⁵ Te	0.9995	0.0001
¹⁴⁰ Ce	TQ-O ₂	¹⁴⁰ Ce. ¹⁶ O	¹²⁵ Te	0.9994	<0.0001
¹⁴⁴ Nd	TQ-O ₂	¹⁴⁴ Nd. ¹⁶ O	¹⁵⁹ Tb	0.9920	<0.0001
¹⁴⁹ Sm	TQ-O ₂	¹⁴⁹ Sm. ¹⁶ O	¹⁵⁹ Tb	0.9878	<0.0001
¹⁵³ Eu	TQ-O ₂	¹⁵³ Eu	¹⁵⁹ Tb	0.9996	<0.0001
¹⁵⁷ Gd	TQ-O ₂	¹⁵⁷ Gd. ¹⁶ O	¹⁵⁹ Tb	0.9936	<0.0001
¹⁶³ Dy	TQ-O ₂	¹⁶³ Dy. ¹⁶ O	¹⁶⁵ Ho	0.9943	<0.0001
¹⁶⁶ Er	TQ-O ₂	¹⁶⁶ Er. ¹⁶ O	¹⁶⁵ Ho	0.9968	<0.0001
¹⁶⁹ Tm	TQ-O ₂	¹⁶⁹ Tm. ¹⁶ O	¹⁶⁵ Ho	0.9968	<0.0001
¹⁷² Yb	TQ-O ₂	¹⁷² Yb	¹⁷⁵ Lu	0.9850	<0.0001
¹⁷⁸ Hf	TQ-O ₂	¹⁷⁸ Hf. ¹⁶ O	¹⁷⁵ Lu	0.9981	<0.0001
¹⁸¹ Ta	TQ-O ₂	¹⁸¹ Ta. ¹⁶ O	¹⁷⁵ Lu	0.9917	0.0001
¹⁸² W	He KED	–	¹⁷⁵ Lu	0.9837	0.0003
¹⁹⁷ Au	He KED	–	¹⁷⁵ Lu	0.9655	0.0006
²⁰² Hg	He KED	–	¹⁷⁵ Lu	0.9524	<0.0001
²⁰⁵ Tl	He KED	–	¹⁷⁵ Lu	0.9987	<0.0001
²⁰⁸ Pb	He KED	–	¹⁷⁵ Lu	0.9979	<0.0001
²⁰⁹ Bi	He KED	–	¹⁷⁵ Lu	0.9988	<0.0001
²³⁸ U	He KED	–	²³² Th	0.9993	<0.0001

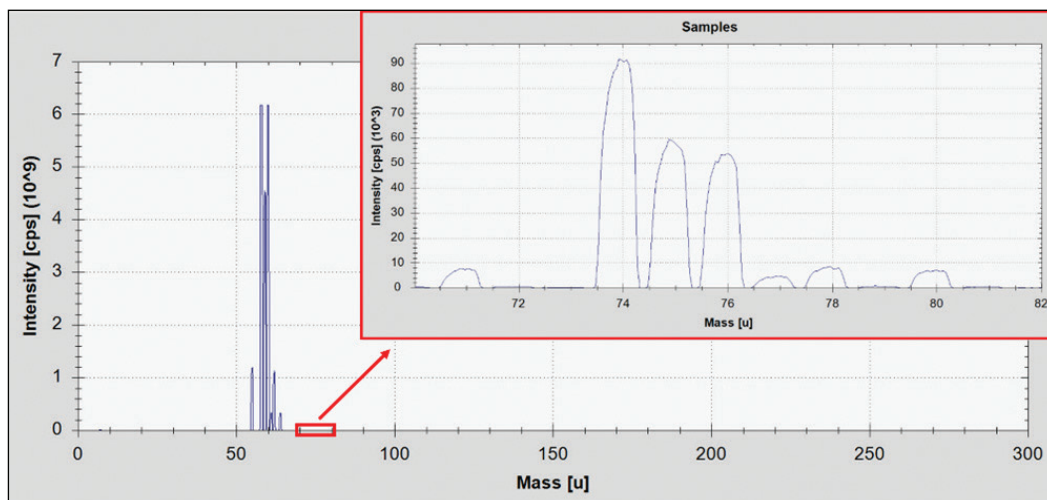


Figure 4. Survey scan spectra of a 1% (m/v) battery cathode standard sample

Table 5 shows the comparison of the results in the cathode standard between the He KED and TQ-O₂ modes. Although He KED mode is the default method of choice for suppressing polyatomic interferences, the high amounts of nickel present in the sample lead to a contribution of ⁶²Ni¹⁶O⁺, for example, on the signal recorded for ⁷⁸Se⁺, resulting in a false positive for selenium of 6.2 mg·kg⁻¹. Similarly, the result obtained for arsenic showed a false positive of 16.5 mg·kg⁻¹, caused by the polyatomic ⁵⁹Co¹⁶O⁺ interference on ⁷⁵As⁺, as a consequence of the high Co concentration in the sample matrix. In contrast, use of the TQ-O₂ mode eliminated these polyatomic ion species and produced interference-free results. The process of interference removal using oxygen is shown in Figure 5. In short, whereas the analyte of interest reacts with oxygen and forms a molecular ion with a new mass-to-charge ratio (referred to as a mass-shift reaction), the previously isobaric (i.e., having the same nominal mass) interference does not react in a similar way and can therefore be eliminated in the third quadrupole of the system. The first quadrupole provides an additional mass filtration before the collision/reaction cell, so that unwanted side reactions with other components present in the ion beam, are effectively suppressed.

Table 5. Comparison results of the cathode standard sample between the two measurement modes

Measurement mode	Arsenic (mg·kg ⁻¹)*	Selenium (mg·kg ⁻¹)*
He KED	16.5	6.2
TQ-O ₂	0.3	<0.04 (MDL)

*Results calculated back to the solid material

The results obtained for the lithium battery samples and the method detection limits (MDLs) of the analysis are summarized in Table 6. MDLs for all 51 elements measured are based on the instrumental detection limits summarized above but including the dilution factor (100-fold for cathode solid samples and 5-fold for the recycled battery solution) incurred during the sample digestion process.

In addition, to evaluate the accuracy and precision of the analysis, spike recovery testing (the detail of spike concentration list is at Table 3) was performed on the cathode standard solution. In general, the recovery was found to be between 83% and 115% and achieved reliable results.

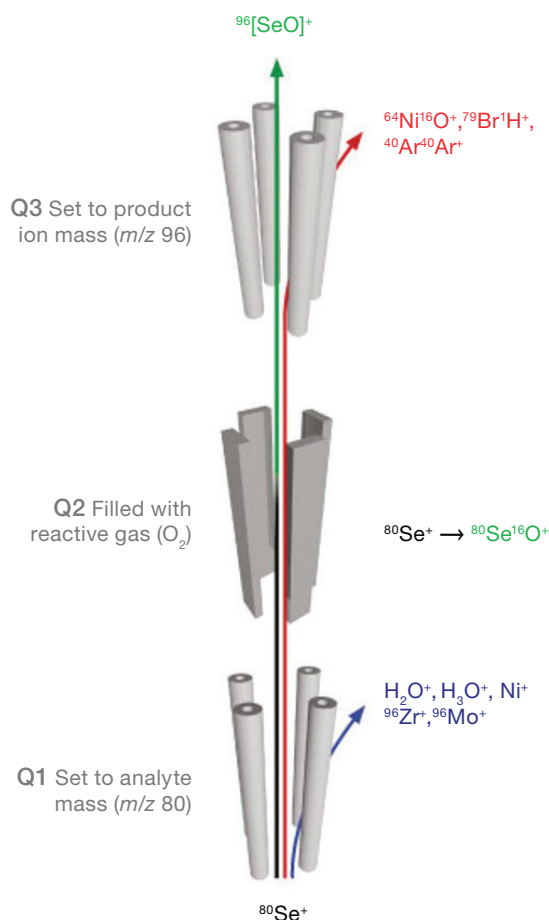


Figure 5. Schematic showing TQ mass shift modes for selenium

Table 6. Quantification results for the cathode matrix samples (sample I.D. 1–4 at Table 2, in mg·kg⁻¹) and for the recycled battery solution (sample I.D. 5 in Table 2, in mg·L⁻¹)

	Solid cathode samples		Recycled battery solution	
	MDL (mg·kg ⁻¹) for solid samples	Concentration range in the four cathode battery samples and standards (mg·kg ⁻¹)	MDL (mg·L ⁻¹) for solution sample	Concentration in the recycled battery solution (mg·L ⁻¹)
⁷ Li	1.9	28,823–66,422	0.10	>1,000
⁹ Be	2.2	<MDL	0.11	<MDL
²³ Na	2	125–1,345	0.10	>2,000
²⁴ Mg	0.22	19–101	0.01	>1
²⁷ Al	0.32	242–18,138	0.02	<0.1
³¹ P	9.9	3–5,011	0.49	>1
³² S	39.8	838–2,085	1.99	>20,000
³⁹ K	3.1	16–207	0.15	<10
⁴⁴ Ca	3.8	16–167	0.19	<10
⁴⁸ Ti	0.04	5–80	0.002	<1
⁵¹ V	0.02	0.03–1.2	0.001	<MDL
⁵² Cr	0.17	1–24	0.01	<MDL
⁵⁵ Mn	0.13	40,366–82,215	0.01	<2,000
⁵⁶ Fe	0.09	6–788	0.005	<0.1
⁵⁹ Co	0.06	46,329–81,406	0.00	<2,000
⁶² Ni	1.6	193,839–427,549	0.08	>20,000
⁶³ Cu	0.02	1–50724	0.001	<1
⁶⁶ Zn	0.09	1–26	0.004	<MDL
⁷² Ge	0.001	<MDL	<0.001	<MDL
⁷⁵ As	0.03	0.09–0.8	0.002	<MDL
⁸⁰ Se	0.04	<MDL	0.002	<MDL
⁸⁵ Rb	0.01	<MDL	<0.001	<MDL
⁸⁸ Sr	0.001	1–3	<0.001	<MDL
⁹⁰ Zr	0.03	7–1,254	0.001	<MDL
⁹⁸ Mo	0.001	<MDL	<0.001	<MDL
¹⁰⁵ Pd	0.001	<MDL	<0.001	<MDL
¹⁰⁷ Ag	0.005	0.5–1.6	<0.001	<MDL
¹¹¹ Cd	0.001	0.06–0.6	<0.001	<MDL
¹¹⁵ In	0.001	<MDL	<0.001	<MDL
¹¹⁸ Sn	0.01	<MDL	<0.001	<MDL
¹²¹ Sb	0.01	<MDL	<0.001	<MDL
¹³³ Cs	0.002	<MDL	<0.001	<MDL
¹³⁸ Ba	0.01	1–160	0.001	<MDL
¹⁴⁰ Ce	0.003	<MDL	<0.001	<MDL
¹⁴⁴ Nd	0.002	<MDL	<0.001	<MDL
¹⁴⁹ Sm	0.001	<MDL	<0.001	<MDL

Table 6 continued. Quantification results for the cathode matrix samples (sample I.D. 1–4 at Table 2, in mg·kg⁻¹) and for the recycled battery solution (sample I.D. 5 in Table 2, in mg·L⁻¹)

	Solid cathode samples		Recycled battery solution	
	MDL (mg·kg ⁻¹) for solid samples	Concentration range in the four cathode battery samples and standards (mg·kg ⁻¹)	MDL (mg·L ⁻¹) for solution sample	Concentration in the recycled battery solution (mg·L ⁻¹)
¹⁵³ Eu	0.001	<MDL	<0.001	<MDL
¹⁵⁷ Gd	0.001	<MDL	<0.001	<MDL
¹⁶³ Dy	0.002	<MDL	<0.001	<MDL
¹⁶⁶ Er	0.001	<MDL	<0.001	<MDL
¹⁶⁹ Tm	0.002	<MDL	<0.001	<MDL
¹⁷² Yb	0.002	<MDL	<0.001	<MDL
¹⁷⁸ Hf	0.003	16–36	<0.001	<MDL
¹⁸¹ Ta	0.01	<MDL	0.001	<MDL
¹⁸² W	0.03	<MDL	0.001	<MDL
¹⁹⁷ Au	0.06	<MDL	0.003	<MDL
²⁰² Hg	0.004	<MDL	<0.001	<MDL
²⁰⁵ Tl	0.001	<MDL	<0.001	<MDL
²⁰⁸ Pb	0.004	0.1–0.5	<0.001	<MDL
²⁰⁹ Bi	0.001	<MDL	<0.001	<MDL
²³⁸ U	0.001	<MDL	<0.001	<MDL

Evaluation of long-term robustness

To simulate high-throughput analysis, a larger batch of samples containing the 1.0% (m/v) and 5.3% (m/v) lithium battery solutions previously analyzed were scheduled for analysis. After generating calibration standard curves, the batch contained several blocks containing the battery samples together with the required QC checks. The total number of solutions analyzed was 202 (including 148 unknown samples and 54 calibrants and QC checks), requiring a total analysis time of approximately 14 hours.

Figure 6 shows the relative standard deviation of all CCVs (n=7) for all 51 elements indicating excellent recovery (within 89% to 117%) with a relative standard deviation of $\pm 5.2\%$ within the batch. The iCAP TQe ICP-MS therefore allows for robust and reliable long-term analysis even for samples containing a high and variable composition of the sample matrix.

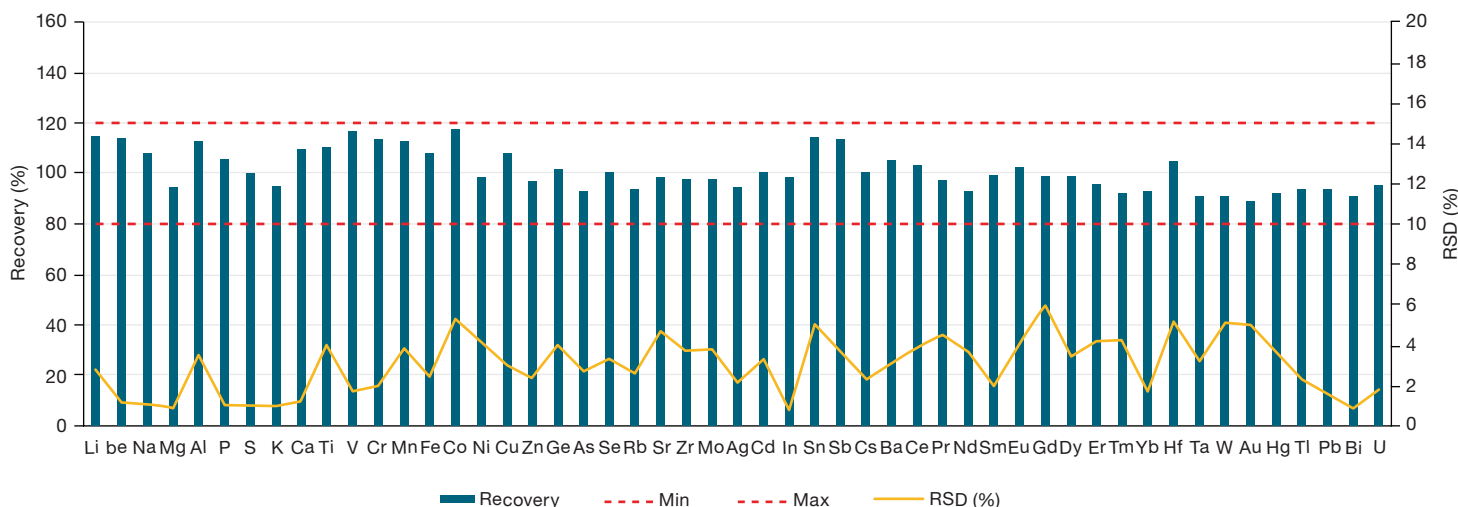


Figure 6. QC calibration verification results with the 51 elements measured

All internal standards showed reliable and predictable recovery (within approximately 72% to 124%) over the entire runtime of the batch, demonstrating robust analytical performance. While an internal standard recovery of around 72% still allows for accurate correction of matrix effects and potential drift, which ultimately demonstrates the ability of the system to effectively analyze a variety of different sample types with vastly different dissolved solids load in a single batch.

Conclusions

The iCAP TQe ICP-MS, operated using AGD, enables analysts to perform accurate and reliable elemental analysis in challenging samples such as battery cathode solutions. This was demonstrated by the analysis of 51 elements in a large number of lithium battery samples with high concentrations. The analytical method was rigorously tested for performance, and the results obtained clearly demonstrated the following analytical advantages for battery cathode sample analysis:

- AGD mode allowed the aspiration of up to 5.3% (m/v) lithium battery cathode solutions and allowed excellent MDLs to be obtained, eliminating the need for labor-intensive manual sample dilution and accelerating sample throughput.
- High sensitivity TQ-O₂ mode provided the advanced performance required for the accurate determination of As, Se, interference free in complex, lithium battery matrix samples showing outstanding analysis performance.
- Excellent CCV recovery and spike recovery results, as well as stable and consistent internal standards response, were obtained across a batch containing 202 samples of 1% (m/v) and 5.3% (m/v) lithium battery cathode solutions, demonstrating the reliability of the method.

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