

Rolling over interferences: How triple quadrupole ICP-MS facilitates the analysis of challenging samples for electric vehicles

Tomoko Vincent¹, Sukanya Sengupta¹, Bhagyesh Surekar¹, Simon Nelms², Daniel Kutscher¹
1: Thermo Fisher Scientific, Hanna-Kunath-StraÙe 11, Bremen, Germany, 28199
2: Thermo Fisher Scientific, Stafford House, Boundary Way, Hemel Hempstead, United Kingdom, HP2 7GE

Abstract

Purpose: This presentation will give an overview of how triple quadrupole ICP-MS is able to resolve the analytical challenges found when analyzing battery material samples resulting from the large-scale growth in the electric vehicle sector.

Methods: Different components of a battery, for example cathode materials, were analyzed for potentially difficult analytes to highlight the superior interference removal capability of a triple quadrupole ICP-MS compared to a single quadrupole instrument for such applications.

Results: Consistent interference removal and often superior detection limits could be confirmed.

Introduction

The continuous development of lithium-ion battery technology is a key step to move away from the combustion of fossil fuels at point of use. Lithium based batteries are the most promising, as they provide high capacity, good cycle stability, at moderate cost. To achieve the intended performance, it is of high importance to assure consistent quality and especially purity of the raw materials used. This includes specifically the cathode material (like binary or ternary alloys containing lithium, cobalt, manganese and nickel) and the electrolyte (lithium hexafluorophosphate and organic compounds), but also other components of the battery. This presentation will provide an overview of how triple quadrupole ICP-MS is able to resolve the analytical challenges encountered when analyzing battery material samples. The presentation will include examples from different components of a battery, including raw materials, electrolytes and cathode materials.

Materials and methods

Sample Preparation

An aliquot of approximately 0.5 – 1.0 g of a ternary cathode material (NMC 811 cathode solid standard, MSE supplies®, AZ, USA) was acid digested using aqua regia. A microwave assisted procedure was employed to achieve complete dissolution of the solid material. After digestion, the samples were made up to a final volume of 50 or 100 mL using 1% (m/v) HNO₃, so that the amount of total dissolved solids was around 1.0% (m/v) in the measured sample solution. Calibration standards and quality control checks for all measurements were prepared by gravimetric dilution using single element standards (SPEX CertiPrep™, Metuchen, USA) and 2% (v/v) HNO₃ (Optima™ grade, Fisher Scientific).

Instrumentation

A Thermo Scientific™ iCAP™ TQe ICP-MS system was used for all analyses. To facilitate the direct analysis of highly concentrated solutions, as typically found when working with cathode materials, the instrument was operated using Argon Gas Dilution (AGD) to automatically dilute the sample aerosol using a clean stream of argon gas, delivered directly from the instrument.

To achieve the best possible detection limits on typically challenging elements, a slightly different configuration was applied to the same instrument. For these measurements, the instrument was equipped with a PLUS torch, a direct replacement for the standard torch made from a high purity ceramic material. The PLUS torch helps to reduce the backgrounds typically observed for silicon when using quartz torches and is therefore instrumental in achieving the best possible detection limits for this element.¹

Table 1 gives an overview of the most important instrument parameters and their corresponding values.

Table 1. Typical instrumental parameters applied for the analysis of NCM cathode materials and all other analyses

Parameter	Value	
	Analysis of cathode materials	Other analyses
Nebulizer*	ESI PFA MicroFlow ST	Borosilicate glass, Micromist
Spray chamber	Quartz cyclonic, cooled at 2.7 ° C	
Torch	Quartz torch	PLUS Torch
Injector	2.5 mm I.D., Quartz	
Interface	Nickel sampler and skimmer cone	High Sensitivity Insert
Plasma power	1550 W	
Nebulizer Gas	0.23 L·min ⁻¹	1.09 L·min ⁻¹
Additional gas flow (Ar)	0.80 L·min ⁻¹	N/A
Collision/Reaction Cell (CRC) Parameters		
QCell setting	He KED	TQ-O ₂
QCell gas flow	100% He 4.2 mL·min ⁻¹	100% O ₂ 0.32 mL·min ⁻¹
CR bias	-21 V	-6.3 V
Q3 bias	-18 V	-12 V

Data Analysis

Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution Software was used to operate the instrument and all peripherals, acquire the data and evaluate the results. Qtegra software offers

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Results

Analysis of NCM cathode materials

The most common cathode materials used today consist of a ternary mixture of Nickel, Cobalt and Manganese (NCM). A consistent stoichiometric composition of the cathode is of high importance, and so is the control of impurities, which could lead to unwanted side reactions and battery performance degradation over time. However, the control of elemental impurities may be severely affected by interferences created by the sample matrix – in this case, high concentrations of the major components, which are often present in the g·L⁻¹ concentration range.

Selenium is an element generally considered as difficult to analyze using ICP-MS. Common interferences can be reduced or eliminated using an inert collision gas such as helium and kinetic energy discrimination (KED). However, in the case of a nickel matrix, additional polyatomic interferences (mainly NiO⁺) occur on the different Se isotopes, with the ⁸²Se isotope being the least interfered. The most abundant polyatomic interferences are summarized in table 2.

In a similar way, the presence of high amounts of cobalt may interfere with the detection of (monoisotopic) arsenic, through the formation of ⁵⁹Co¹⁶O⁺ on ⁷⁵As.

Selenium Isotope	Abundance [%]	Typical Interferences	Interferences in high Nickel matrices
74	0.9	³⁷ Cl ₂ ⁺	⁵⁸ Ni ¹⁶ O ⁺
76	9.00	⁴⁰ Ar ³⁶ Ar ⁺	⁶⁰ Ni ¹⁶ O ⁺
77	7.60	⁴⁰ Ar ³⁷ Cl ⁺	⁶⁰ Ni ¹⁶ O ¹ H ⁺
78	23.60	⁴⁰ Ar ³⁸ Ar ⁺ ; ⁷⁸ Kr ⁺	⁶² Ni ¹⁶ O ⁺
80	49.70	⁴⁰ Ar ⁴⁰ Ar ⁺ ; ⁸⁰ Kr ⁺ ; ⁷⁹ Br ¹ H ⁺	⁶⁴ Ni ¹⁶ O ⁺
82	9.20	⁸² Kr ⁺ ; ⁸¹ Br ¹ H ⁺	⁶⁴ Ni ¹⁸ O ⁺ ; ⁶⁴ Ni ¹⁷ O ¹ H ⁺

The impact of the additional interferences is shown in figure 1, showing a survey scan of a typical NCM cathode material.

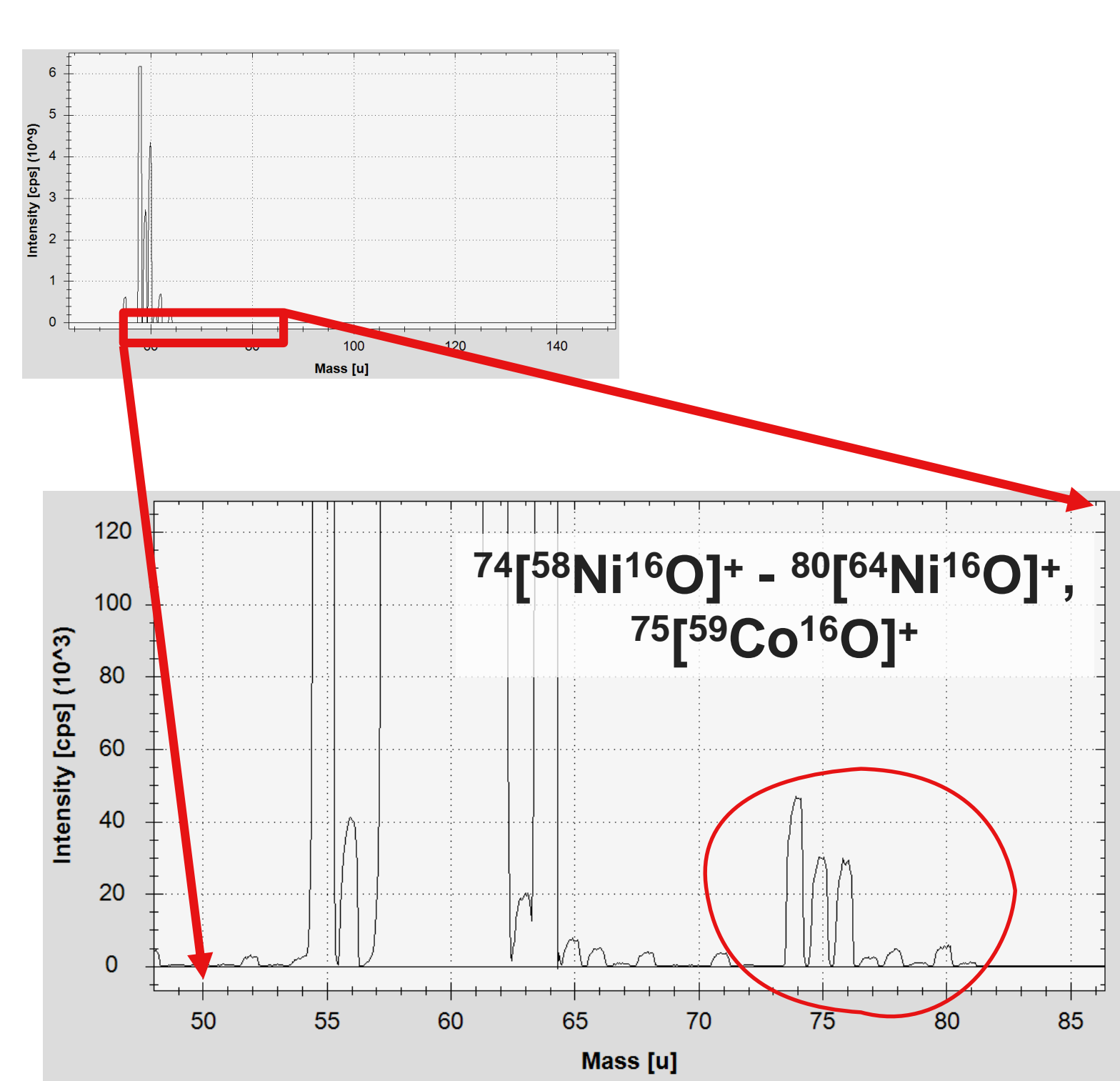


Figure 1. Survey scan showing the mass range between m/z 0 to 150, with a close-up of the range m/z 55-85, highlighting the abundant interferences formed from a typical NCM cathode material.

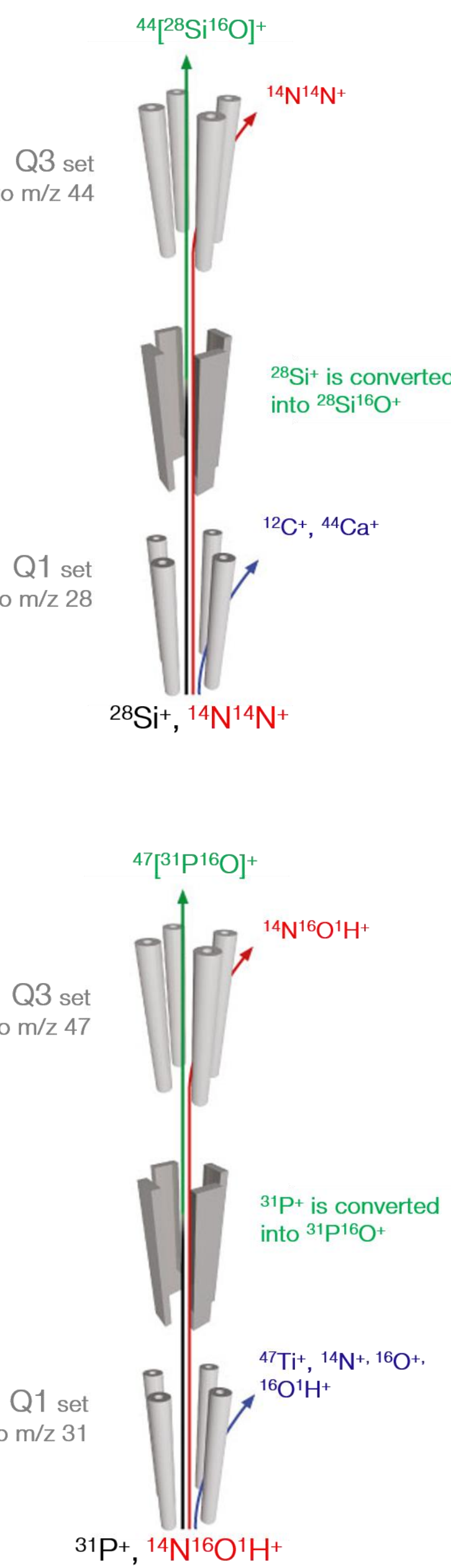
The NiO derived interferences can easily be removed using oxygen as a reaction gas, but only following a mass filtration step before the CRC, in order to avoid unwanted reactions with other ions present in the ion beam. However, if uncorrected for, i.e. when using a single quadrupole ICP-MS system, they can lead to significant false positive bias. The results of the quantitative analysis of the material for arsenic and selenium are summarized in table 3 (calculated back to the original solid material).

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

Even though He KED mode is the usual method of choice to suppress polyatomic interferences, the high amounts of Nickel present in the sample lead to a contribution of, for example, ⁶²Ni¹⁶O⁺ on the signal recorded for ⁷⁸Se⁺, so that the result obtained for selenium was a false positive of 6.2 mg·kg⁻¹. Similarly, the result obtained for arsenic showed a false positive of 16.5 mg·kg⁻¹, again caused by a polyatomic interference formed from the matrix. In contrast, TQ-O₂ mode eliminated the interferences and returned the correct result.

Highly sensitive detection of challenging elements²

Certain elements are often classified as “difficult to analyze” using ICP-MS, mainly due to their elevated 1st ionization potential (IP, reducing the number of ions that are formed in the plasma) or the interferences potentially present (causing elevated backgrounds and therefore increased detection limits). However, for a comprehensive characterization and elucidation of degradation processes, these elements are of high importance. Figure 2 illustrates how these elements can be measured, interference-free, using triple quadrupole ICP-MS.



Silicon (1st IP = 8.15 eV, most abundant isotope ²⁸Si, at 92.2%) is one of the most difficult elements for ICP-MS analysis, mainly because of the ubiquitous nature of this element and the need to carefully control blank levels. The main interference on Si is ¹⁴N₂⁺ (generated from air entrained into the plasma), which interferes with the major isotope of silicon, ²⁸Si.

Phosphorous (1st IP = 10.49 eV, monoisotopic at ³¹P) is important in industrial applications, and, due to its presence in LiPF₆, commonly found in degradation products in cycled batteries. However, due to its high ionization potential and significant polyatomic interferences (principally ¹⁴N¹⁶O¹H⁺), its analysis is often limited by elevated detection limits. Because of its monoisotopic nature, there are no other, less interfered alternative isotopes available.

Sulfur (1st IP = 10.36 eV, most abundant isotope ³²S, at 95.02%): is one of the most difficult elements to be analyzed using ICP-MS. Its high ionization potential means that the ion yield is generally low and in aqueous media, there are highly abundant interferences, such as ¹⁶O₂⁺.

Figure 2. Schematic illustration of the settings for both quadrupoles when analyzing silicon, phosphorous and sulfur (top to bottom)

The resulting instrumental limits of detection (IDL) as well as the blank equivalent concentrations (BEC) for all analytes under investigation are summarized in Table 4. The IDLs were calculated based on three times the standard deviation of three replicate concentration measurements of a 2% (v/v) HNO₃ solution, which was the same solution used for the preparation of the calibration standards. For most elements, with the exceptions of arsenic and selenium, the background is still a limiting factor. Even though the level of interferences is reduced by several orders of magnitude, the high ionization potential and hence low ion yield, lead to a blank equivalent concentration that is above the instrumental detection limit. Nevertheless, the achieved IDLs support the fact that stable signals can be detected even at sub-µg·L⁻¹ concentration levels.

Table 4. Instrumental detection limit (IDL) and blank equivalent concentration (BEC) results for all analytes measured. All data are given in µg·L⁻¹.

	Silicon	Phosphorous	Sulfur
Masses selected Q1/Q3	²⁸ Si as ²⁸ Si ²⁸ Si ¹⁶ O	³¹ P as ³¹ P ³¹ P ¹⁶ O	³² S as ³² S ³² S ¹⁶ O
IDL	0.021	0.005	0.026
BEC	0.43	0.36	1.17

Finally, a series of ten solutions containing all elements under investigation at similar concentrations were analyzed to determine the accuracy and precision of the analysis. The purpose of this test was to evaluate the performance of the instrument at concentrations close to the background level limit. The concentration levels tested were 1 µg·L⁻¹ for silicon, phosphorous and sulfur. The results are graphically displayed in Figure 3.

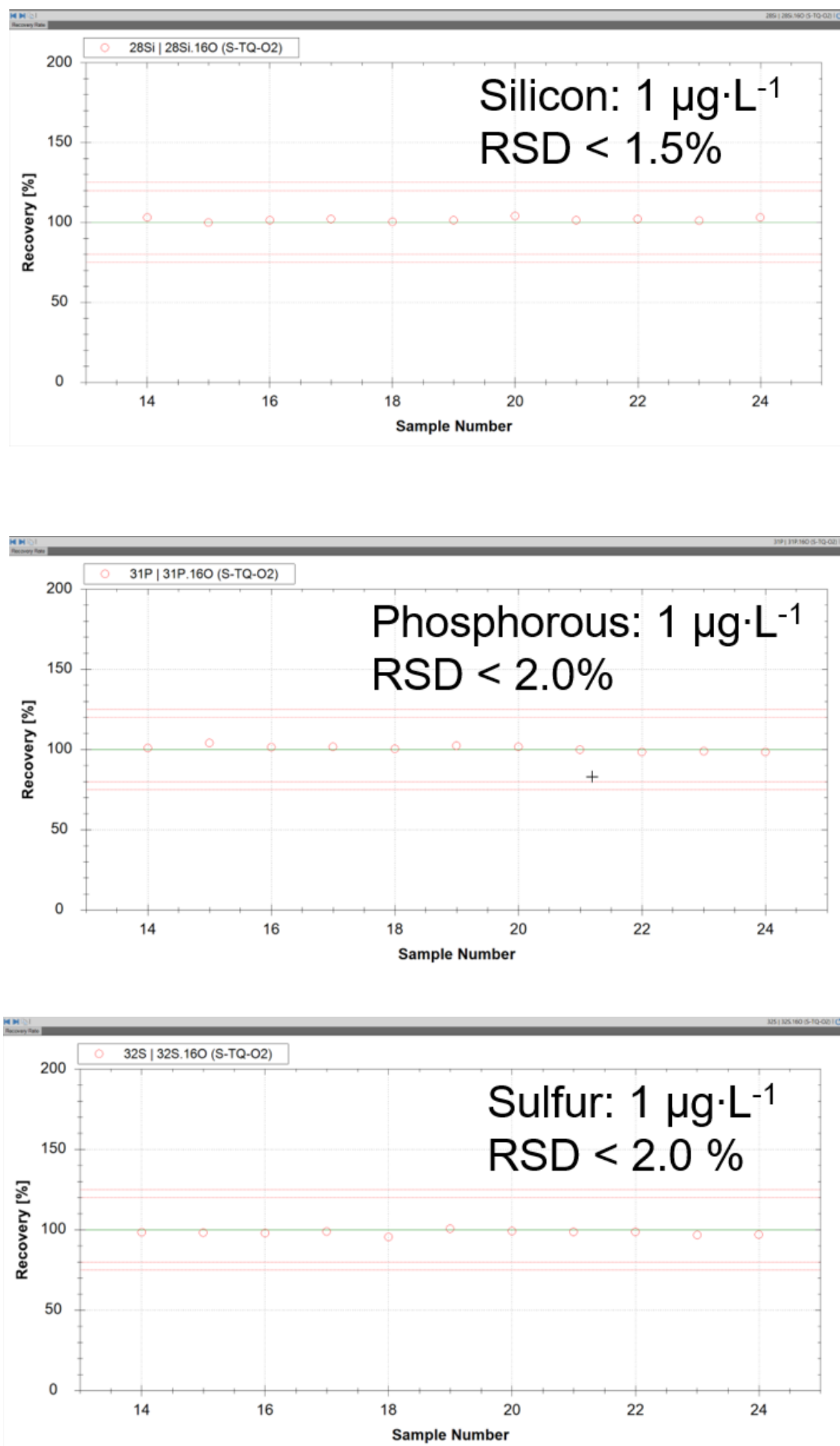


Figure 3. Results of repeated analysis of samples spiked with the analytes under study at a concentration range close to the background levels

The results highlight the ability of the iCAP TQe ICP-MS to deliver accurate and precise results, even at ultra-trace concentrations. In all cases, the relative deviation between individual read outs of a given sample (%RSD, n = 10) was found to be below 2%.

Conclusions

- The use of triple quadrupole ICP-MS and oxygen as a reactive gas provided the advanced performance required for the accurate determination of critical elements, such as arsenic and selenium free from polyatomic interference in a highly complex lithium battery matrix samples showing outstanding analysis performance.
- Triple quadrupole ICP-MS in combination with oxygen as a reactive cell gas is a powerful tool for the analysis of elements having high ionization potentials and numerous spectral interferences.
- Further reduction of the background for silicon is possible when using the PLUS torch, so that significant improvements of the detection limits for silicon can be achieved.

References

- Product Spotlight 44485: Thermo Scientific iCAP Qnova Series ICP-MS: PLUS Torch for improved ICP-MS analysis of challenging samples.
- Technical Note 1092: Addressing the challenge of measuring difficult elements using triple quadrupole ICP-MS

Acknowledgements

Dr. Mikael Axelsson (Thermo Fisher Scientific, Sweden) is acknowledged for useful exchange and discussions around the analysis of lithium battery materials.

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