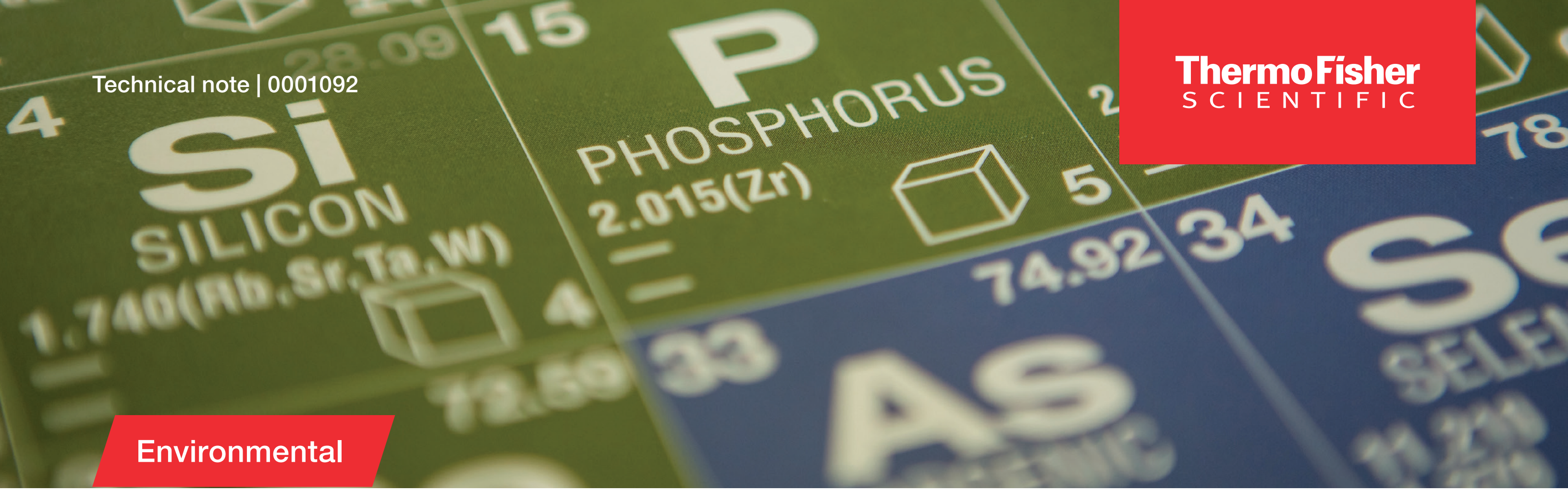

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Environmental

Addressing the challenge of measuring difficult elements using triple quadrupole ICP-MS

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Keywords

Interference removal, high IP elements, ICP-MS, triple quadrupole, silicon, sulfur, phosphorous, arsenic, selenium

Goal

This note will highlight how the analysis of the elements silicon, sulfur, phosphorous, arsenic, and selenium, often considered difficult to measure using ICP-MS, can be achieved with sub ng·mL^{-1} detection levels using triple quadrupole ICP-MS.

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is recognized as a key technique for the analysis of trace elements in a wide variety of sample types. This is due to its outstanding speed, detection sensitivity, and ability to achieve detection limits generally in the low ng·L^{-1} concentration range for most of the elements in the periodic table. For many elements, particularly metals with low ionization potentials and low natural backgrounds, detection limits in the pg·L^{-1} range can be achieved, even under normal laboratory conditions. However, there are certain elements that 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). Among these elements, non-metals with low atomic mass like silicon, phosphorous, or sulfur stand out, but arsenic and selenium are often considered challenging as well. This is particularly true when single quadrupole ICP-MS systems are employed for analysis.

Silicon (1st IP = 8.15 eV, most abundant isotope ^{28}Si, 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 $^{14}N_2^+$ (generated from air entrained into the plasma), which interferes with the major isotope of silicon, ^{28}Si.

Phosphorous (1st IP = 10.49 eV, monoisotopic at ^{31}P) is a highly relevant element in life science applications, as it can act as a proxy for DNA fragment analysis and is also important in industrial applications, for example, as a potential impurity in battery materials. However, due to its high ionization potential and significant polyatomic interferences (principally $^{14}N^{16}O^{1}H^{+}$), the analysis of phosphorous is often limited by reduced detection sensitivity and 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 ^{32}S, 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 $^{16}O_2^{+}$. The use of O_2 as a reactive cell gas leads to the formation of $^{32}S^{16}O^{+}$, which has proven to be a viable way for analyzing this element.[1]

The most common interferences on arsenic (monoisotopic at *m/z* 75, 1st IP = 9.82 eV) are chlorine based, such as either $^{40}Ar^{35}Cl^{+}$ or $^{40}Ca^{35}Cl^{+}$, but additional interferences such as $^{150}Nd^{++}$ or $^{150}Sm^{++}$ can be observed when rare earth elements are present.[2] The use of triple quadrupole technology removes all these interferences but most importantly also helps to reduce detection limits compared to single quadrupole ICP-MS systems operated using helium and kinetic energy discrimination (KED).

Similar considerations apply to selenium (1st IP = 9.75 eV), where the most abundant isotope, ^{80}Se, 49.80%, is not accessible for single quadrupole systems because of the intense $^{40}Ar_2^{+}$ interference. With triple quadrupole technology, this interference can be easily overcome using oxygen as the cell gas, as can a wide variety of other interferences.[3]

Experimental

A Thermo Scientific™ iCAP™ TQ ICP-MS was used for all experiments. 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 observed for silicon and is therefore instrumental in achieving the best possible detection limits for this element.[4] As oxygen has been used as the only reactive cell gas in this study, the Thermo Scientific™ iCAP™ TQe ICP-MS would also be able to deliver similar performance. A summary of the typical instrument parameters can be found in Table 1.

Table 1. Instrument parameters

Parameter	Value
Nebulizer	Borosilicate glass Micromist, 400 $\mu L \cdot min^{-1}$, pumped at 40 rpm
Spray chamber	Quartz cyclonic, cooled at 2.7 °C
Injector	Quartz, 2.5 mm i.d.
Torch	PLUS torch
Interface	Nickel sampler and nickel skimmer cone with high sensitivity insert
Plasma power	1,550 W
Nebulizer gas	1.09 $L \cdot min^{-1}$
QCell setting	TQ-O_2
Cell gas flow	100% O_2, 0.34 $mL \cdot min^{-1}$
Dwell time per isotope	0.1 s

Calibration standards were prepared by gravimetric dilution using single element standards (SPEX CertiPrep™, Metuchen, USA) and 2% (v/v) HNO_3 (Optima™ grade, Fisher Scientific). The respective concentration levels for all analytes under study are summarized in Table 2.

Table 2. Calibration ranges for all analytes. All concentrations are given in $\mu g \cdot L^{-1}$

<table>
<tr><th></th><th>Silicon</th><th>Phosphorous</th><th>Sulfur</th><th>Arsenic</th><th>Selenium</th></tr>
<tr><td>STD 1</td><td colspan="3">0.5</td><td colspan="2">0.005</td></tr>
<tr><td>STD 2</td><td colspan="3">1</td><td colspan="2">0.1</td></tr>
<tr><td>STD 3</td><td colspan="3">10</td><td colspan="2">1</td></tr>
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Results and discussion

Calibration curves for all analytes are shown in Figure 1 (A-E).

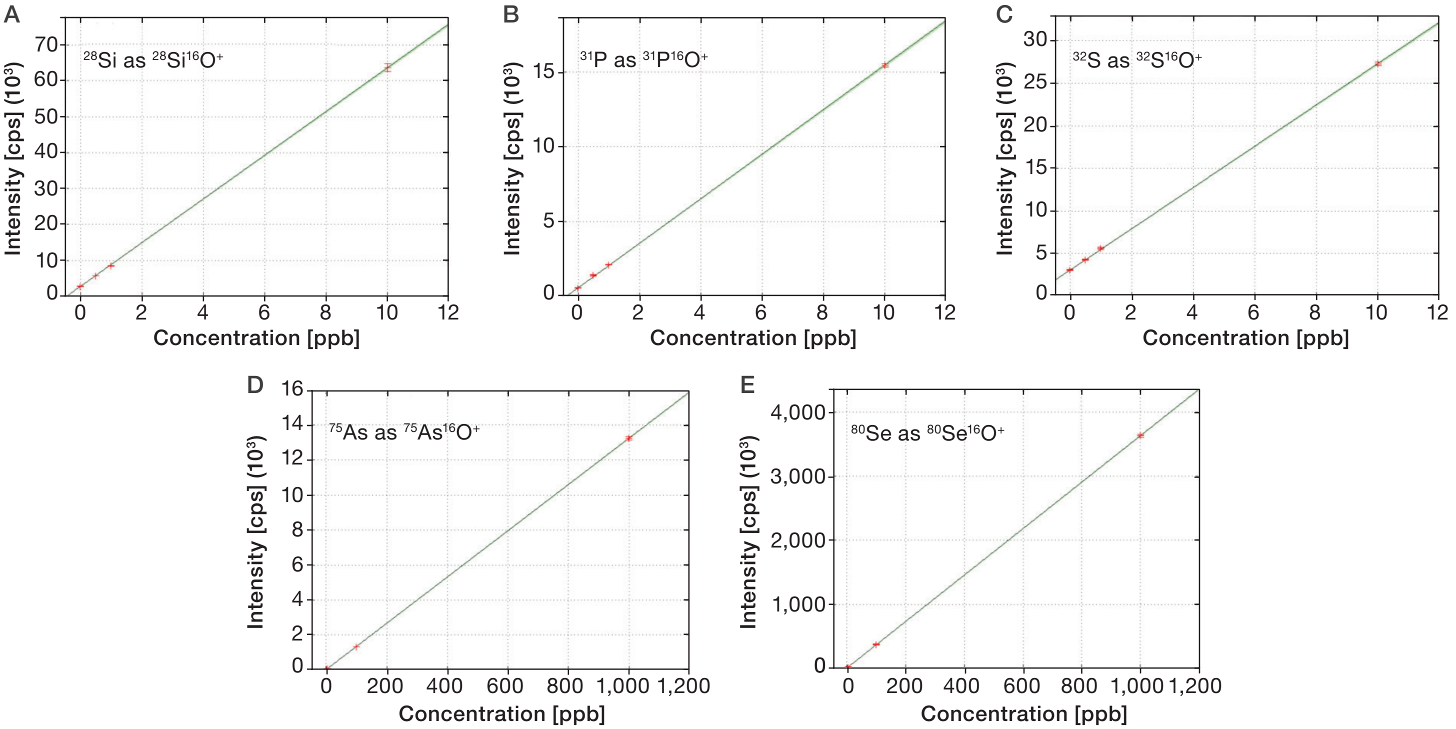
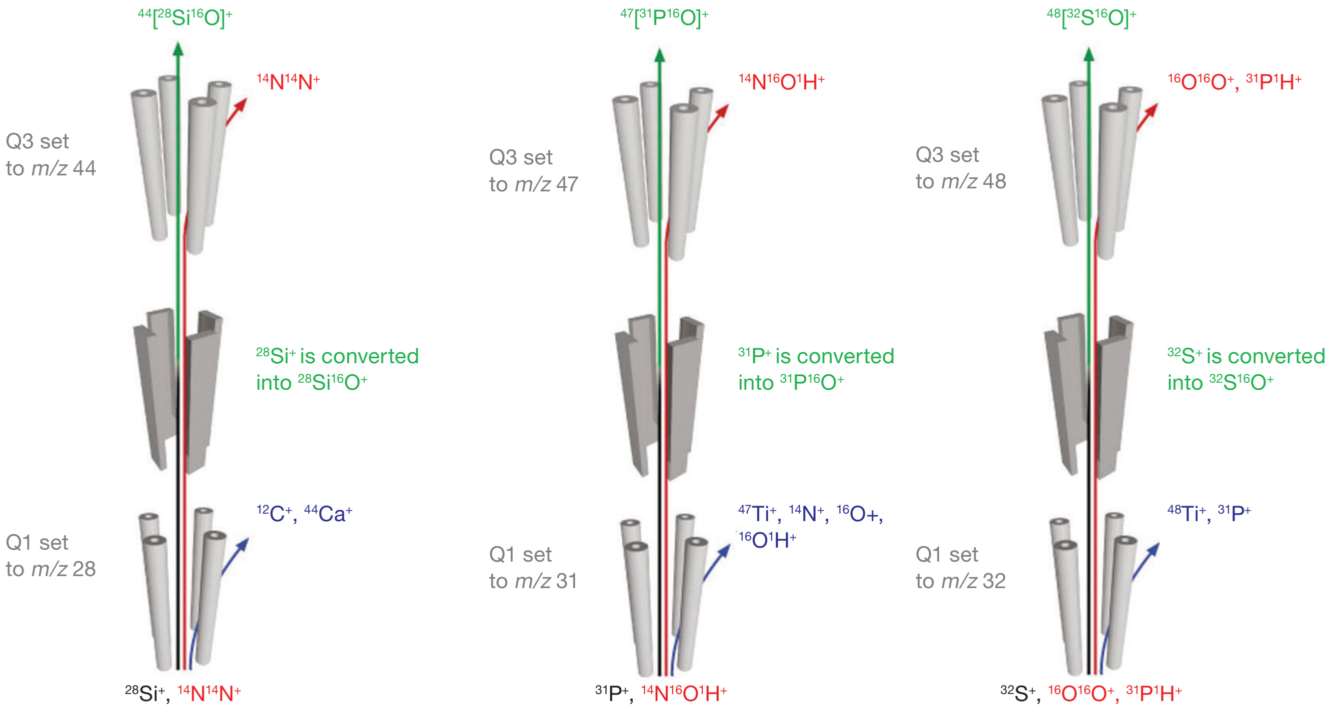


Figure 1. Calibration curves for all analytes investigated in this study (A – Si; B - P; C - S; D – As; E – Se)

In all cases, the use of oxygen as a reactive cell gas leads to a mass-shift reaction, in which the analyte is converted into a new molecular ion, while the (previously isobaric) interference does not react and can be subsequently filtered out in the third quadrupole. In all cases, the first quadrupole performs an additional mass filtration to remove other ions of both lower and higher mass than the target mass. This is essential to avoid unwanted side reactions that could lead to the formation of new interferences in the collision/reaction cell (CRC). This process is further illustrated for silicon, phosphorous, and sulfur in Figure 2.



CRC filled with reactive gas (O_2) in all cases

Figure 2. Schematic illustration of the settings for both quadrupoles when analyzing silicon, phosphorous and sulfur

The occurrence of a mass shift reaction is further confirmed when looking at survey scans, showing all signals recorded in a user defined mass range. Figure 3 shows a mass scan in the range of *m/z* 90–100, equivalent to the *m/z* range in which all isotopes of selenium would appear following a reaction with oxygen. Selenium was chosen for this test, as other elements under investigation in this study are either monoisotopic or have one isotope with an abundance of more than 90%. Selenium in turn has a total of six isotopes with abundance ranging between 0.86% and 49.80%. This rich isotopic pattern allows confirmation of the absence of interferences (caused, for example, by unwanted side reactions if mass filtration in the first quadrupole was not efficient enough).

The resulting instrumental limits of detection (IDL) as well as the blank equivalent concentrations (BEC) for all analytes under investigation are summarized in Table 3. The IDLs were calculated based on three times the standard deviation of three replicate concentration measurements of a 2% (v/v) HNO_3 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.

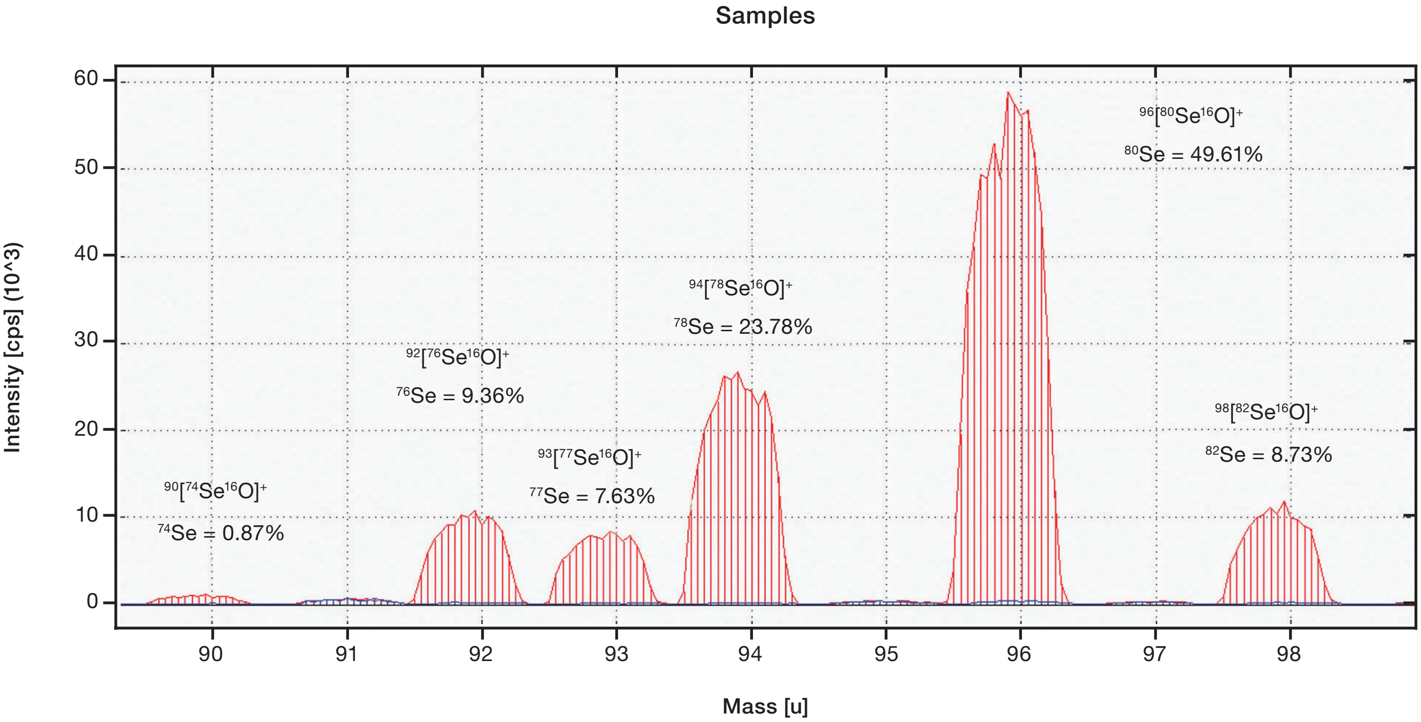


Figure 3. Full mass scan of the range between *m/z* 90 and 100 for a solution containing 20 µg·L^{-1} of Se (red) and a blank solution (blue). The correct isotopic pattern confirms full removal of all potential interferences.

Table 3. 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	Arsenic	Selenium
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 $^{32}S\|^{32}S.^{16}O$	^{75}As as $^{75}As\|^{75}As.^{16}O$	^{80}Se as $^{80}Se\|^{80}Se.^{16}O$
IDL	0.021	0.005	0.026	0.0004	0.0006
BEC	0.43	0.36	1.17	0.0004	0.0003

Finally, a series of ten solutions containing all five elements 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, and 5 ng·L^{-1} for arsenic and selenium. The results highlight the ability of the iCAP TQ ICP-MS to deliver accurate and precise results, even at ultra-trace concentrations (Figure 4). In all cases, the relative deviation between individual read outs of a given sample (%RSD) was found to be below 8% for 10 replicates.

Conclusion

This note highlights the benefits of using a triple quadrupole ICP-MS system in combination with oxygen as a reactive cell gas for the analysis of elements having high ionization potentials and numerous spectral interferences. The different reactivity of the analytes (to form new product ions with different masses than the interferences) not only allows significant reduction of background signals but also improves sensitivity. Further reduction of the background for silicon is possible when using the PLUS torch, so that significant improvements of the detection limits for this element can be achieved.

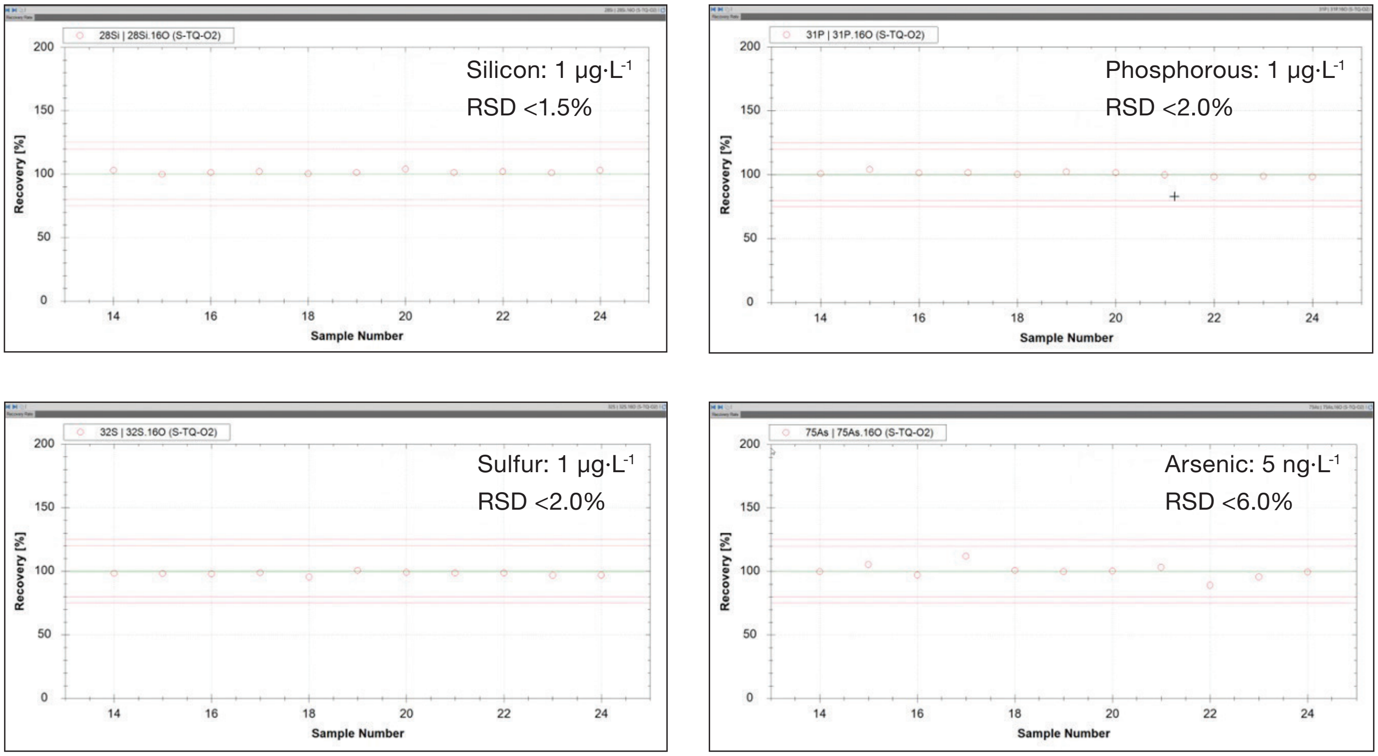


Figure 4. Results of repeated analysis of samples spiked with the analytes under study at a concentration range close to the background levels

References

1. Thermo Scientific Application Note 44465: Analytical testing of trace elements in refinery products using a robust ICP-MS approach. **https://appslab.thermofisher.com/App/4487/elemental-analysis-petroleum-products**
2. Thermo Scientific Application Note 44484: Overcome unexpected interferences and accelerate environmental analysis using triple quadrupole ICP-MS. **https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-44484-icp-ms-triple-quadrupole-unexpected-interferences-an44484-en.pdf**
3. Thermo Scientific Application Note 44478: Effectively increase sample turnover and boost data confidence using triple quadrupole ICP-MS. **https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-44478-icp-ms-triple-quad-increase-sample-turnover-an44478-en.pdf**
4. Thermo Scientific Product Spotlight 44485: Thermo Scientific iCAP Qnova Series ICP-MS: PLUS Torch for improved ICP-MS analysis of challenging samples PLUS Torch. **https://www.thermofisher.com/document-connect/document-connect.html?url=https%3A%2F%2Fassets.thermofisher.com%2FTFS-Assets%2FCMD%2FSpecification-Sheets%2Fsp-44485-icp-ms-icap-plus-torch-sp44485-en.f&title=U3BlY2lmaWNhdGlvbiBTaGVldDogUExVUyBUb3JjaCBmb3IgaUNBUCBRbm92YSBTZXJpZXMgSUNQLU1T**

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