

Accurate determination of arsenic and selenium in environmental samples using triple quadrupole ICP-MS

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Goal

To demonstrate the accurate determination of arsenic and selenium in sediments and rocks that contain elevated levels of rare earth elements using triple quadrupole ICP-MS.

Introduction

Due to the impact arsenic and selenium can have in the environment at low levels, as a toxin or essential nutrient respectively, it is important to be able to quantify them accurately.



Selenium for example is an essential element that is necessary for normal thyroid function and due to its antioxidant properties, is associated with several health benefits. Diseases associated with selenium deficiency such as Keshan disease and symptoms of hypothyroidism, are most commonly found in areas where levels of selenium in soil are particularly low. Supplementation as a remedy is common practice and is not isolated to humans. Understanding where soil selenium deficiencies occur for example supports the correct supplementation of cattle grazing in those areas to prevent white muscle disease (a cattle specific selenium deficiency disease).

Arsenic on the other hand, in its inorganic forms (the most common forms found in ground water and soils) is classified as carcinogenic. Arsenic can be found at natural, elevated levels or highly enriched in ground waters (e.g. in Bangladesh) and in soils from irrigation with arsenic contaminated ground water. In this case, accurate analysis of arsenic is key to understanding whether crops, such as rice grown in these areas could contain an elevated level of arsenic and be a potential risk for consumption.

In addition to assessing the exposure implications of these elements, their accurate analysis is vital to understanding their geochemical cycling processes and impact on the environment.

Analysis of these two elements by ICP-MS is challenging due to multiple spectral interferences, and becomes especially challenging in the presence of high amounts of rare earth elements (REEs) such as dysprosium, gadolinium, neodymium, samarium or terbium due to the formation of doubly charged ions. These doubly charged REEs lead to false positive results on arsenic and selenium and as such lead to incorrect conclusions and actions based on that data.

Triple quadrupole (TQ) ICP-MS offers improved interference removal for such challenging applications through the use of selective reaction chemistry to produce higher mass ions, which can either mass shift analytes into an interference free region of the mass spectrum or mass shift interferences away from analytes. This application note evaluates the efficiency of TQ-ICP-MS measurement modes and compares them to single quadrupole (SQ) ICP-MS measurement modes with the Thermo Scientific™ iCAP™ TQ ICP-MS for the quantification of arsenic and selenium in the presence of REEs. To test the robustness and the accuracy of the approach, two samples, a deep sea sediment and a geochemical reference standard, were analyzed under optimal conditions.

Instrumentation

An iCAP TQ ICP-MS was used to analyse all samples. The system was configured with a high matrix interface (Table 1) for improved handling of the high amounts of total dissolved solids (TDS) encountered in the samples and a 200 $\mu\text{L}\cdot\text{min}^{-1}$ free aspirating, glass, concentric nebulizer due to the limited volume of digested sample.

Four different measurement modes were evaluated:

SQ-STD – single quadrupole mode with no collision/reaction cell (CRC) gas.

SQ-H₂ – single quadrupole mode with CRC pressurized with pure hydrogen as a reaction gas. Please note that hydrogen is not available on the Thermo Scientific™ iCAP™ TQe ICP-MS.

SQ-KED – single quadrupole mode with CRC pressurized with helium as a collision gas and Kinetic Energy Discrimination (KED) applied.

TQ-O₂ – triple quadrupole mode with CRC pressurized with oxygen as a reaction gas, Q1 set to analyte mass (M^+) and Q3 set to product ion mass (MO^+).

All parameters within each of the measurement modes were defined automatically by using the autotune procedures provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software. The autotune functionality ensures that plasma and interface related settings, such as nebulizer flow and extraction lens voltage are automatically applied across all associated measurement modes so that the sample is processed in exactly the same way in the plasma, independent of the CRC and quadrupole settings. Details about the settings used for the different modes are shown in Table 1.

Table 1. Instrument parameters for all measurement modes

Parameter	Value			
Nebulizer	MicroMist quartz nebulizer 0.2 mL·min ⁻¹ , free aspirating			
Spraychamber	Quartz cyclonic spraychamber cooled to 2.7 °C			
Injector	2.5 mm id, quartz			
Interface	High Matrix (3.5 mm) insert, Ni cones			
RF Power	1,550 W			
Nebulizer Gas Flow	1.04 L·min ⁻¹			
Modes	SQ-STD	SQ-H ₂	SQ-KED	TQ-O ₂
Mass shift applied	No	No	No	Yes
Mass shift over x mass units	-	-	-	16
Gas Flow	-	9.0 mL min ⁻¹	4.65 mL min ⁻¹	0.35 mL min ⁻¹
CR Bias	-2	-7.55	-21 V	- 7.0 V
Q3 Bias	-1	-12 V	-18 V	-12 V
Scan Settings	0.2 s dwell time per analyte, 10 sweeps			

The method development assistant in the Qtegra ISDS Software, Reaction Finder, automatically selects the best mode to use for the analyte measurements. In this evaluation exercise, in which the effectiveness of different measurement modes for the same analyte was investigated, replicate analytes were added and the measurement modes selected manually.

The formation of doubly charged ions and the resulting interferences in ICP-MS are known issues. There are several ways to mitigate these interferences on the analyte signals, including:

- Interference correction equations
- Tuning of the instrument to reduce formation of doubly charged ions within the plasma
- Mass shift reactions that move the analyte of interest to a different m/z

Many laboratories prefer to avoid the approach of using interference correction equations as it is possible that due to small daily changes in plasma conditions, they need to be calculated or checked on a daily basis to verify their accuracy. Mass shift reactions show promise but have limitations with SQ-ICP-MS due to the complex mixture of ions in the CRC that can cause other potential interferences. With TQ-ICP-MS, the pre-selection of the mass of interest in Q1 enables a more controlled reaction for the analytes and removes interferences that could still be problematic in SQ-ICP-MS.

The Reaction Finder tool selects TQ-O₂ mode automatically for ⁷⁵As and ⁸⁰Se. To be able to compare different modes and the results for different isotopes, the same measurement mode was also selected for ⁷⁸Se and ⁸²Se. This mode uses pure O₂ in the CRC to create oxide ions of the arsenic and selenium isotopes. Arsenic was measured at m/z 91 as ⁷⁵As¹⁶O and the selenium isotopes ⁷⁸Se, ⁸⁰Se and ⁸²Se were measured at m/z 94 as ⁷⁸Se¹⁶O, at m/z 96 as ⁸⁰Se¹⁶O and at m/z 98 as ⁸²Se¹⁶O respectively.

Figure 1 demonstrates how Q1 (when set to the analyte mass), effectively removes the singly charged REEs and any ions that would eventually interfere with the product ions, such as ⁹¹Zr and ⁹⁴Mo for ⁷⁵As and ⁷⁸Se respectively. Q2 (the CRC) is filled with O₂ and creates the product ions ⁹¹[AsO]⁺ and ⁹⁴[SeO]⁺ for ⁷⁵As and ⁷⁸Se respectively. In Q3, any remaining doubly charged REE are rejected and the product ion is isolated for measurement.

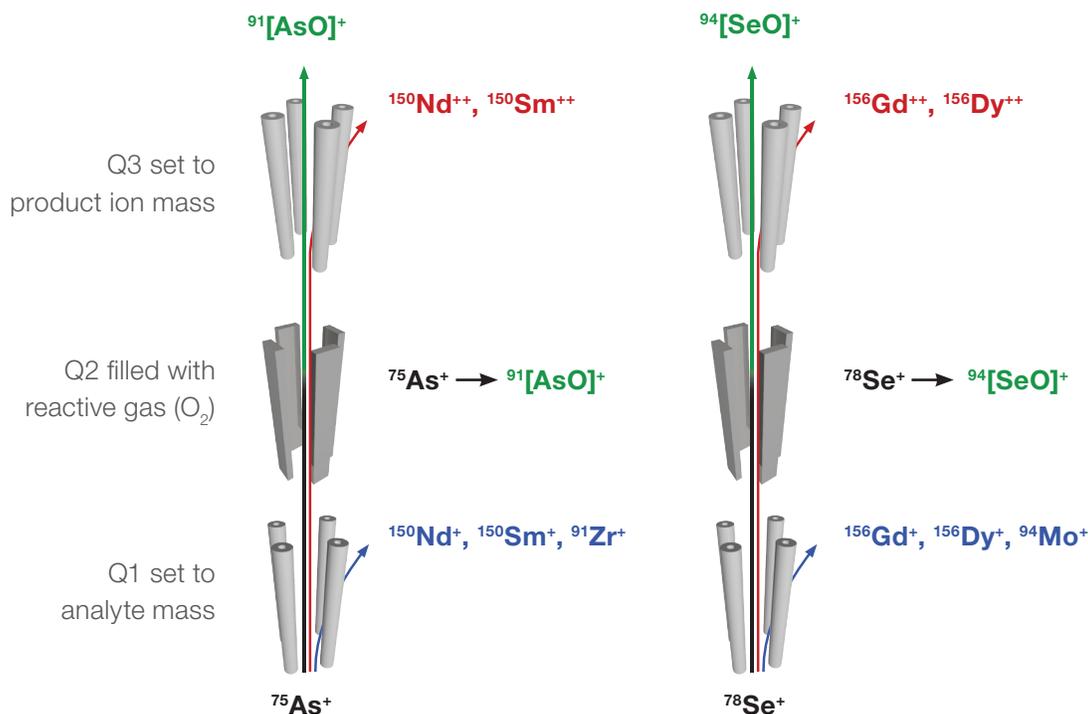


Figure 1. TQ mass shift modes for arsenic and selenium

Sample preparation

Calibration standards of arsenic and selenium at concentrations of 0.2, 0.5, 1, 2 and 5 $\mu\text{g}\cdot\text{L}^{-1}$ were prepared by diluting the appropriate volume of single element standards (SPEX CertiPrep) in a mixture of 2% (v/v) HNO_3 and 2% (v/v) methanol (MeOH) (OPTIMA LC/MS grade, Fisher Scientific). Mixtures of REE for interference evaluation were prepared by diluting appropriate volumes of the single element standards (SPEX CertiPrep) dysprosium, gadolinium, neodymium, samarium and terbium in 2% (v/v) HNO_3 /2% (v/v) MeOH. The final solution contained 1 $\text{mg}\cdot\text{L}^{-1}$ of each REE.

Approximately 35 mg of a marine sediment sample, collected from the deep Pacific Ocean (supplied by the University of Oldenburg, Germany) and 50 mg of the andesite reference standard AGV-1 (United States Geological Survey) were weighed and treated in closed PTFE vessels with concentrated HNO_3 (1 mL, OPTIMA grade, Fisher Scientific) overnight to oxidize any organic matter (if present). In the next step, concentrated HF (1.5 mL, OPTIMA grade, Fisher Scientific) and HClO_4 (1.5 mL, OPTIMA grade, Fisher Scientific) were added and the vessels then heated in a hot block for 12 h at 180 °C. After digestion, the acids were evaporated on a hot plate at 180 °C to near dryness. The residues were

re-dissolved, fumed off three times with 6N HCl to near dryness and finally taken up in 10 mL 1N HNO_3 . Prior to analysis, both samples were further 1:10 diluted with 1% (v/v) HNO_3 /2% (v/v) MeOH. The dilution protocol resulted in final TDS levels of 500 ppm for AGV-1 and 348 ppm for the sediment sample. Lutetium was added at a concentration of 1 $\mu\text{g}\cdot\text{L}^{-1}$ as an internal standard to all blanks, standards and samples prior to analysis.

The use of methanol (or other suitable carbon source) is important in the analysis of arsenic and selenium due to the effect of carbon enhancement in the plasma which increases the ionization of both elements. This will correct for over recovery in the case of external calibration and also leads to higher sensitivity and improved detection limits.

Results

External calibrations for arsenic and selenium in the range 0.2 to 5 $\mu\text{g}\cdot\text{L}^{-1}$ show excellent linearity and LODs of 0.17 $\text{ng}\cdot\text{L}^{-1}$ and 2.02 $\text{ng}\cdot\text{L}^{-1}$ for ^{75}As (Figure 2, left) and ^{78}Se (Figure 2, right) respectively, when using TQ- O_2 mode. The carbon enhancement effect of methanol in the samples is seen as an approximate 2-fold increase in sensitivity for both analytes, compared to typical sensitivities without methanol.

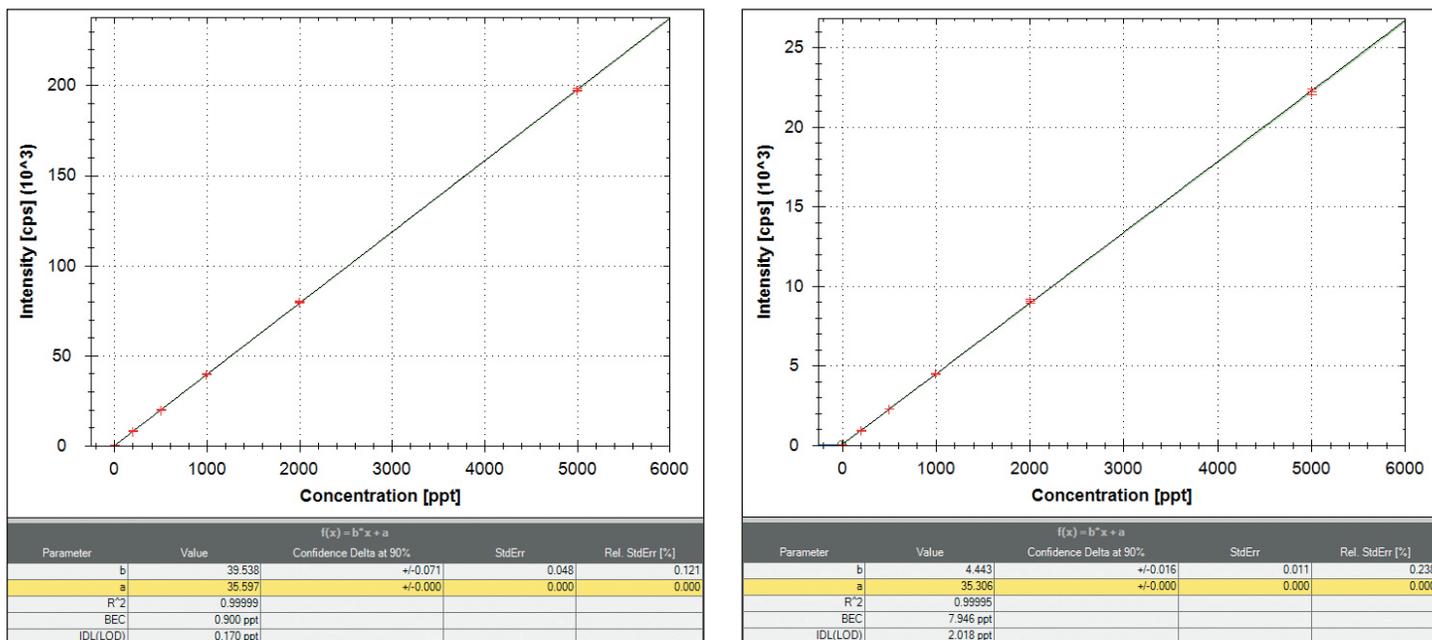


Figure 2. Screenshots from Qtegra ISDS Software. Calibration curves for ^{75}As measured as $^{91}[\text{AsO}]^+$ (left) and ^{78}Se measured as $^{94}[\text{SeO}]^+$ (right) in TQ- O_2 mass shift mode.

To demonstrate the efficiency of interference removal with TQ- O_2 mass shift mode, it was compared to three different SQ modes: SQ-STD (no gas), SQ- H_2 and SQ-KED (He gas). The background equivalent concentrations (BECs) of arsenic and the 3 isotopes of selenium (at masses 78, 80 and 82) were determined in a solution containing $1 \text{ mg}\cdot\text{L}^{-1}$ each of the REEs dysprosium, gadolinium, neodymium, samarium and terbium (to give a total REE concentration of $5 \text{ mg}\cdot\text{L}^{-1}$) (Figure 3).

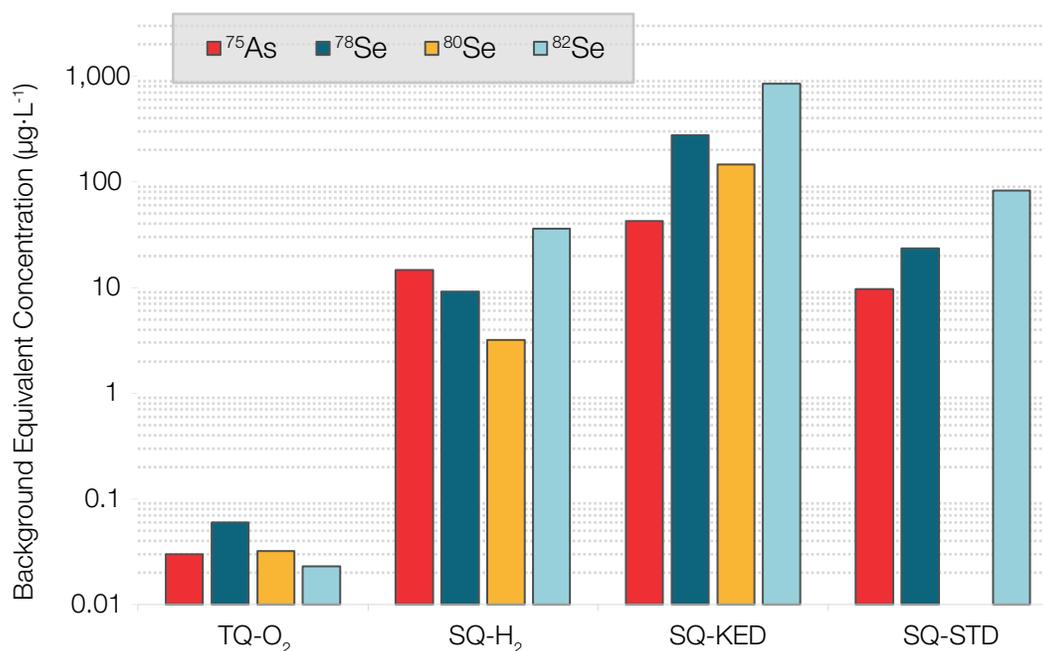


Figure 3. BECs of arsenic and selenium isotopes in a $5 \text{ mg}\cdot\text{L}^{-1}$ REE solution using four different measurement modes. The y-axis for the BEC is reported in logarithmic scale for clarity. The BEC of ^{80}Se for SQ-STD mode is not reported because of the large interference from $^{40}\text{Ar}^{40}\text{Ar}$.

In SQ-STD mode, the BEC for ^{75}As was $9.7 \mu\text{g}\cdot\text{L}^{-1}$ and for the selenium isotopes all BECs were between 23 and $142 \mu\text{g}\cdot\text{L}^{-1}$ due to the non-filtered doubly charged interferences from the REEs. While SQ-KED is a powerful tool for the removal of polyatomic interferences, it suffers from an increased transmission of doubly charged ions relative to other ions in the mass range where these doubly charged ions are detected, due to their higher kinetic energy. This is reflected in the increased BEC. Although SQ- H_2 mode is effective for removing argon based polyatomic interferences, it is not suitable for removing doubly charged interferences resulting in BECs in the single to double digit $\mu\text{g}\cdot\text{L}^{-1}$ range.

TQ- O_2 mode showed the lowest BECs for all of the isotopes investigated. In this mode, BECs of $30 \text{ ng}\cdot\text{L}^{-1}$ for ^{75}As and 23, 32 and $60 \text{ ng}\cdot\text{L}^{-1}$ for ^{82}Se , ^{80}Se and ^{78}Se respectively, were achieved.

To evaluate the accuracy of the TQ- O_2 mode, the $5 \text{ mg}\cdot\text{L}^{-1}$ REE solution was spiked with $1 \mu\text{g}\cdot\text{L}^{-1}$ arsenic and selenium, and spike recoveries were determined (Figure 4). All recoveries were within 99 to 102% of the spiked value, demonstrating good accuracy for the method.

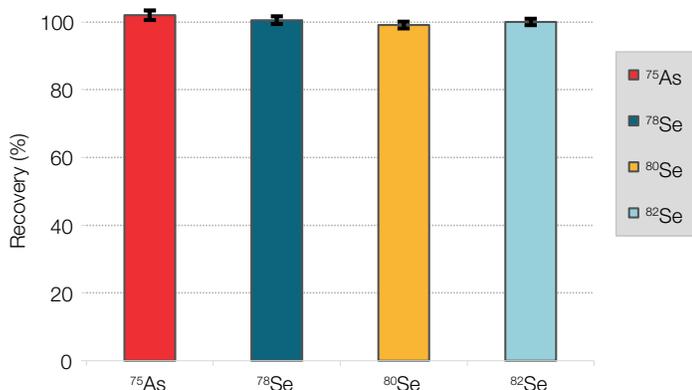


Figure 4. Spike recoveries of $1 \mu\text{g}\cdot\text{L}^{-1}$ arsenic and selenium from a $5 \text{ mg}\cdot\text{L}^{-1}$ REE solution in TQ- O_2 mode

Table 2. Quantitative data for arsenic and selenium in AGV-1 and a deep sea sediment using TQ- O_2 mode (calculated back to the solid and reported in $\mu\text{g}\cdot\text{g}^{-1}$)

AGV-1	Content in original sample ($\mu\text{g}\cdot\text{g}^{-1}$)	Certified content ($\mu\text{g}\cdot\text{g}^{-1}$)	Recovery
^{75}As	0.892	0.88	101%
^{78}Se	< LOQ	-	-
Deep Sea Sediment			
^{75}As	1.303	-	-
^{78}Se	0.109	-	-

TQ- O_2 mode provides the best BECs for arsenic and selenium in a complex matrix so this mode was applied for the analysis of two different samples, a certified standard (AGV-1) and one deep sea sediment sample.

AGV-1 is an andesite geochemical reference standard, with principal matrix components of silicon, aluminum and iron and with gadolinium at $5 \mu\text{g}\cdot\text{g}^{-1}$, samarium at $5.9 \mu\text{g}\cdot\text{g}^{-1}$, dysprosium at $3.6 \mu\text{g}\cdot\text{g}^{-1}$ and neodymium at $33 \mu\text{g}\cdot\text{g}^{-1}$. After digestion and dilution of the raw material the concentrations of gadolinium, samarium, dysprosium and neodymium in the analyzed sample were 2.5, 2.95, 1.8 and $16.5 \mu\text{g}\cdot\text{L}^{-1}$, respectively. The deep sea sediment was collected as part of a collection of samples along a transect in the deep Pacific Ocean as part of an independent study. Although not certified, the sediment is expected to contain elevated levels of REEs.

The quantitative data for arsenic and selenium measured in the AGV-1 CRM and the deep seas sediment are shown in Table 2. The measured concentration of $0.446 \mu\text{g}\cdot\text{L}^{-1}$ As in the diluted AGV-1 sample corresponds to a recovery of around 100% of the certified value. The limit of quantification (LOQ) was calculated by multiplying the standard deviation of the blank signal by a factor of 10, then dividing this result by the slope of the calibration.

Both samples were also spiked with $1 \mu\text{g}\cdot\text{L}^{-1}$ of arsenic and selenium after the digestion and dilution steps to determine analyte recovery and accuracy of the method. The spike recoveries for arsenic and all selenium isotopes (93–98%) demonstrate good accuracy for arsenic and selenium determination in these complex samples (Table 3). The internal standard recovery of lutetium (measured as $^{175}\text{Lu}^{16}\text{O}$) was in the range of 90–107% throughout the sample analysis when compared to the calibration blank.

Table 3. Spike recovery of arsenic and selenium in AGV-1 and the marine sediment sample using TQ-O₂ mode. Both samples were spiked with 1 µg·L⁻¹ of arsenic and selenium after digestion and 1:10 dilution.

AGV-1	Measured concentration (µg·L ⁻¹)	Measured concentration in spiked sample (µg·L ⁻¹)	Spike recovery (%)
⁷⁵ As	0.446	1.392	94.6
⁷⁸ Se	< LOQ	0.939	93.4
⁸⁰ Se	< LOQ	0.935	93.1
⁸² Se	< LOQ	0.944	93.6
Deep Sea Sediment	Measured concentration (µg·L ⁻¹)	Measured concentration in spiked sample (µg·L ⁻¹)	Spike recovery (%)
⁷⁵ As	0.454	1.429	97.6
⁷⁸ Se	0.038	1.014	97.6
⁸⁰ Se	0.037	1.016	97.9
⁸² Se	0.037	1.001	96.4

Conclusion

The iCAP TQ ICP-MS was used to measure trace levels of arsenic and selenium in complex environmental matrices. The measured concentration for arsenic in the certified geological material was in agreement with reference values and the spike recoveries for both arsenic and selenium in both samples were determined in the range 93–98%. The TQ-O₂ mode shows the lowest BECs for arsenic and selenium in the presence of high concentrations of REEs when compared to the other analysis modes. The TQ-O₂ mode is an ideal mode for interference removal in rocks, soil and sediment samples where high REE concentrations can be expected. The Reaction Finder tool offers the user the ability to set up methods easily by automatically determining the optimum measurement modes for the analysis and reduces the time spent on the daily method set-up.

References

1. http://crustal.usgs.gov/geochemical_reference_standards/andesite1.html

Find out more at thermofisher.com/TQ-ICP-MS

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