

Dramatically improved selenium analysis with the Thermo Scientific iCAP RQ ICP-MS using pure hydrogen CRC gas

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Keywords

BEC, LOD, Hydrogen Gas, KED, Selenium

Goal

To demonstrate the performance for selenium analysis that can be achieved with the Thermo Scientific™ iCAP™ RQ ICP-MS using kinetic energy discrimination (KED) mode and pure hydrogen as the collision/reaction cell (CRC) gas.

Introduction

Selenium is a metalloid element that has varied uses in industry ranging from processing and manufacturing glass, photovoltaic cells, circuit rectifiers, stainless steel and even some anti-dandruff shampoos. It is also an essential trace element for some plants and animals, including humans, which occurs naturally in many environmental sources. Analysis of selenium is, therefore, important in both an industrial and biological context.

Selenium is one of the most challenging elements to be analyzed by ICP-MS because it has a relatively high ionization energy and suffers from high intensity interferences on the major selenium isotopes originating from the argon gas of the ICP-MS plasma source, namely $^{40}\text{Ar}^{40}\text{Ar}$ on ^{80}Se and $^{38}\text{Ar}^{40}\text{Ar}$ on ^{78}Se . In addition to this, typical sample matrices of environmental, clinical and semiconductor samples usually produce additional interferences on the selenium masses.

To remove these polyatomic interferences, usually an ICP-MS equipped with a collision/reaction cell (CRC) before the analyzer quadrupole is used. One common CRC approach is the use of helium gas and Kinetic Energy Discrimination (KED). In this mode, the CRC is pressurized with a low flow of helium that collides with the ions in the CRC and reduces their kinetic energy. Applying an electrical potential difference between the CRC and mass analyzer quadrupole sets up a potential energy barrier that only ions with a certain amount of kinetic energy can overcome and then enter the mass analyzer quadrupole as part of the ion beam. Since the polyatomic interference ions have a larger collisional cross section, they collide with the helium more frequently and lose more kinetic energy than the analyte ions, and they are therefore preferentially rejected from the ion beam.

Using pure helium as the KED cell gas does improve the accuracy and detection limits for selenium compared to standard, non-collision operation, but the sensitivity for Se is considerably reduced in the process. In addition, He-KED is not effective at removing doubly charged interferences, which is a common requirement in clinical research when Gd-based MRI contrast agents are used prior to obtaining a biological sample for analysis. In applications such as this and other advanced applications requiring sub $\text{ng}\cdot\text{L}^{-1}$ Se measurements, further enhancement in Se detection capabilities is needed.

Replacing the CRC gas with pure hydrogen has some benefits over using helium. Firstly, hydrogen is reactive: it reacts with both polyatomic ions and doubly charged species via charge transfer and cluster-ion formation reactions that generate neutral species and side-product ions respectively. The neutral species formed are removed from the ion beam since they are unaffected by the deflector lens before the mass analyzer, and side product ions are rejected from the ion beam through KED.

The second benefit is that hydrogen is a lighter gas than helium, so collisions with selenium ions results in a lower loss of kinetic energy. This allows selenium to be measured with higher sensitivity than He-KED can achieve, consequently reducing limits of detection further. This technical note demonstrates the performance achievable for selenium analysis using pure hydrogen gas as the CRC gas using the Thermo Scientific™ iCAP™ RQ ICP-MS.

Instrumentation

The instrument configuration and operation parameters are shown in Table 1. It should be noted that the iCAP RQ ICP-MS used for these experiments was installed in a normal lab environment and not in a clean room.



Table 1. Operation parameters and configuration for iCAP RQ ICP-MS.

Parameter	Value
Spraychamber	Quartz cyclonic, cooled at 2 °C
Nebulizer	100 μL PFA concentric, self-aspirating
Injector	2.0 mm sapphire injector
Interface	Ni sample cone and high sensitivity skimmer insert
Plasma Power	1550 W
Nebulizer Gas	1.1 $\text{L}\cdot\text{min}^{-1}$
CRC Gas	Pure hydrogen gas 4.5 $\text{mL}\cdot\text{min}^{-1}$
KED	3 V
Lens Setting	Auto tuned
Dwell Time	0.2 sec at ^{78}Se

Sample preparation

Standard solutions at concentrations of 0, 2, 4, 6, 8 and 10 $\text{ng}\cdot\text{L}^{-1}$ were prepared gravimetrically by adding the appropriate quantity of a 1000 $\text{mg}\cdot\text{L}^{-1}$ SPEX CertiPrep™ Se single element stock solution directly to 2% m/m HNO_3 (65% HNO_3 Optima™ grade from Fisher Chemical) and 0.5% m/m HCl (32-35% HCl Optima™ grade from Fisher Chemical).

Results

Figure 1 shows that an excellent calibration curve can be obtained using the H₂-KED mode. The sensitivity of this calibration was over 19 kcps per µg·L⁻¹ for ⁷⁸Se, with a corresponding detection limit (based on 3x the standard deviation of the calibration blank) of 0.2 ng·L⁻¹. In comparison, the typical detection limit for ⁷⁸Se using He-KED mode is 25 ng·L⁻¹.

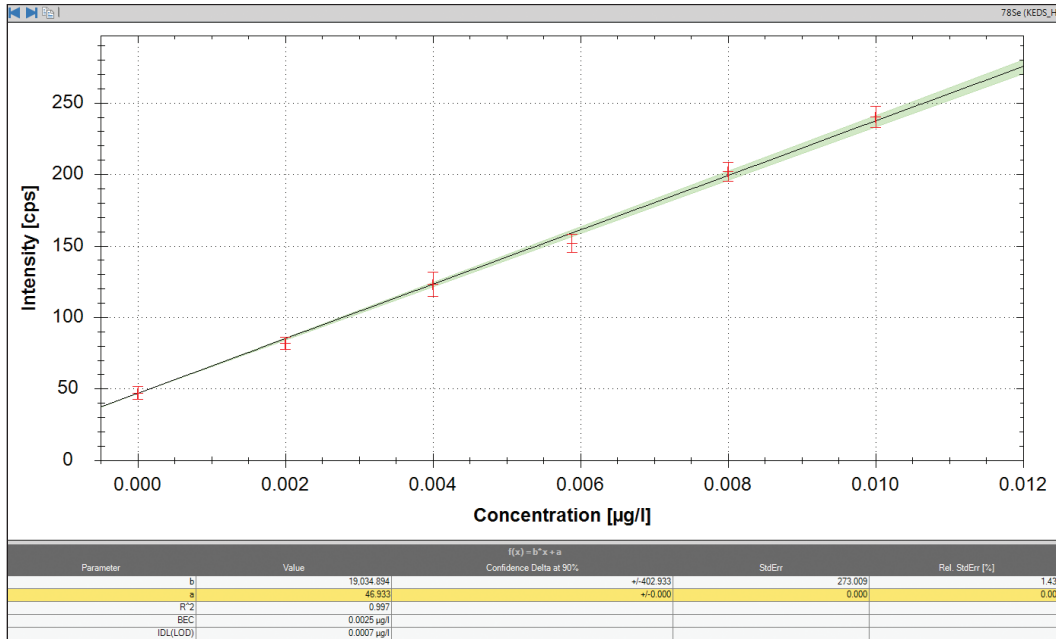


Figure 1. Calibration curve for ⁷⁸Se using H₂-KED mode.

To evaluate the stability of this approach and its potential for extended application to multi-element analysis results were collected over 10 hours with a 100 ng·L⁻¹ tuning solution using three different modes within a single analytical run (Figure 2).

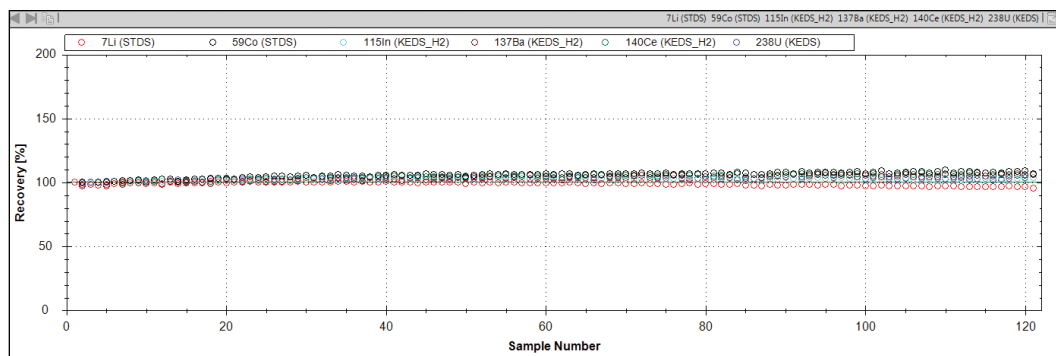
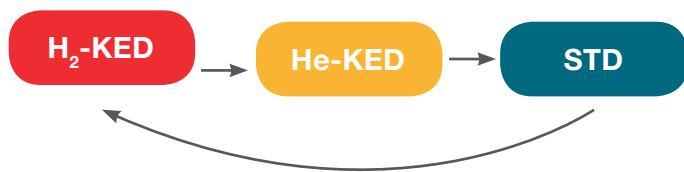


Figure 2. 10 h stability data for a 100 ng·L⁻¹ tuning solution, using multiple measurement modes (H₂-KED, He-KED, STD).

To demonstrate the achievable productivity and accuracy, a short switching time of only 15 seconds was applied for each mode. The switching time cannot be set too short, since this would sacrifice the completeness of interference removal and ultimately the stability of the results as well.

The sequence of measurement modes was first H₂-KED mode, followed by He-KED mode and then Standard mode without a CRC gas). Excellent precision was achieved for the 10 hour run, with all analytes being below 2% RSD. This finding implies that H₂ can be successfully implemented into routine analytical work flows in order to benefit from this novel approach for high performance analysis of selenium using ICP-MS.

Conclusion

The Thermo Scientific iCAP RQ ICP-MS provides excellent performance for ultratrace determination of selenium using pure hydrogen CRC gas while simultaneously maintaining high productivity and accuracy for routine multi-elemental analysis.

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