

Analysis of Selenium in Difficult Samples

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Introduction

Selenium is an essential element for humans and most other living organisms; its most relevant chemical form in biological systems is Selenocysteine, an amino acid found in a variety of enzymes like the Glutathion peroxidases that protect body tissues from oxidative stress. Low Selenium intake in humans may lead in to serious illnesses. High regular doses, however, can be highly toxic.

For drinking water, foodstuff, and many environmental regulations, limit values have been implemented that must not be exceeded. Therefore, the analysis of Selenium has become an important application in routine laboratory work.

ICP-MS is today's method of choice for multi-element analysis. With its unique features, e.g. detection power, sample throughput and dynamic working range, ICP-MS appears to be the perfect analytical tool for all detectable elements. However, attention must be directed to both spectral and non-spectral interferences that can impact on the accuracy of Selenium analysis.

Interferences on Selenium

Non-spectral interferences

Non-spectral interferences on Selenium are related to its high ionization potential (I.P.=9.75 eV). Under the standard operating conditions of an Argon-based ICP, the ionization degree of Selenium is limited to a few percent, leading to poor sensitivity. Additionally, the distribution of total element sensitivity across several isotopes (Figure 1.) makes it challenging to reach detection limits for some analytical requirements. As well as the low Selenium sensitivity in simple aqueous solutions, sample matrix can contribute to either poorer or better ionization. In a previous work¹ the impact of refractory matrix elements and the presence of Carbon was investigated. An increase of Selenium ionization and improved matrix tolerance was found when either CH₄ was added to the nebulizer gas flow or high-purity organic solvents, e.g. 2-Propanol, was continuously mixed with the sample flow. Compared with aqueous solutions the introduction of Carbon to the ICP can improve sensitivity of Selenium by a factor of up to 8.

Spectral interferences

Selenium analysis can suffer from a number of spectral interferences. Even in aqueous solutions without additional sample matrix, significant overlaps of ArAr⁺ occur on all Selenium isotopes. With modern reaction/collision cell designs they can be significantly attenuated. The best working mechanism was found in reaction cell mode based on 8% H₂/He premixed reaction gas (Figure 1 and 2).

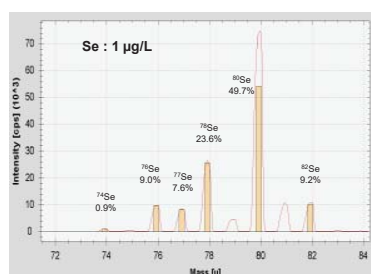


FIGURE 1. Selenium isotopes

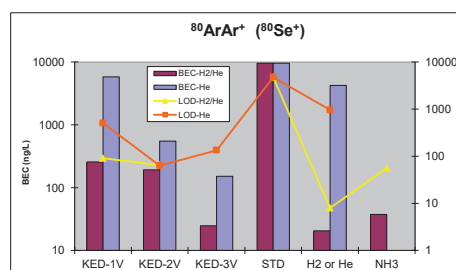


FIGURE 2. Interference removal on ⁸⁰Se

In addition to the predominating ArAr⁺ molecular ions, there are some other interfering species affecting the accurate analysis of Selenium. Table 1 shows a list of typical sample-specific interfering candidates. Krypton may be difficult to control, because this gas is a contaminant of the Argon used for the ICP, namely liquid Argon may show high levels of Krypton. The listed molecular ions can be attenuated successfully by KED while sacrificing Selenium sensitivity.

Doubly charged Rare Earth Elements (REE) cannot be removed or attenuated by collision or reaction cell processes. Although not commonly present, in particular Gadolinium has to be considered in several applications. In clinical samples, namely whole blood and serum, Gadolinium can be present due to the application of Gadoteric acid and related contrast media for MRI examinations. Environmental samples, especially surface and urban waste waters, are increasingly contaminated with Gadolinium due to MRIs conducted in hospitals. Also in other biological materials, e.g. plant leaves, Gadolinium is sometimes present, either by co-absorption from soil or environmental contamination.

| Mass (a.m.u.) | Selenium Interference | relative abundance (%) |
|---------------|-----------------------|------------------------|
| 74 | Ge | 36.5 |
| 74 | ArS | 4.2 |
| 74 | FeOH | 2.2 |
| 74 | Sm ⁺⁺ | 11.3 |
| 76 | Ge | 7.8 |
| 76 | Sm ⁺⁺ | 26.7 |
| 77 | ArCl | 24.1 |
| 77 | Sm ⁺⁺ | 22.7 |
| 78 | Gd ⁺⁺ | 20.5 |
| 78 | Kr | 0.4 |
| 80 | ArCa | 96.6 |
| 80 | Gd ⁺⁺ | 21.9 |
| 80 | Kr | 2.3 |
| 82 | BrH | 49.3 |
| 82 | Kr | 11.6 |
| 82 | ArCa | 0.6 |
| 82 | Dy ⁺⁺ | 28.2 |

TABLE 1. Interferences on Se isotopes

Solving the Gd⁺⁺ problem

Instrumentation

All investigations were carried out using a Thermo Scientific™ iCAP™ Qc ICP-MS (Thermo Fisher Scientific, Bremen, Germany) in standard configuration. For sample introduction, a FAST module (Elemental Scientific, Omaha, NE, USA) equipped with a 1 mL sample loop was used. ¹⁰³Rh was used for internal standardization and mixed online with the sample flow combined with 10 per cent (v/v) semiconductor grade 2-Propanol, (Alfa Aesar GmbH & Co. KG, Karlsruhe, Germany). The operating conditions of the iCAP Qc ICP-MS are listed in Table 2.

Reaction cell with Oxygen

Oxygen can help transfer native Selenium into its oxides which in turn can be analyzed at masses 16 a.m.u. higher, e.g. ⁷⁸Se¹⁶O⁺ and ⁸⁰Se¹⁶O⁺, respectively. The SeO⁺ molecular ions are isobaric with Molybdenum isotopes. Although in some cases Molybdenum can be completely oxidized to either MoO⁺ or MoOO⁺, this effect is strongly dependent on the reaction cell settings and on the Molybdenum concentration present in the sample. Not enough Oxygen in the cell and the Molybdenum oxidation will be incomplete. Too high Oxygen flows will reduce Selenium sensitivity and sacrifice detection power.

Reaction cell with Hydrogen and interference correction

The use of Hydrogen is one of the best studied regimes in reaction cell technology. It can eliminate ArAr⁺ signals very efficiently, but is not capable of removing the Gd⁺⁺ overlap on Selenium isotopes. However, at a mass resolution of ca. 0.4 a.m.u. ¹⁵⁵Gd⁺⁺ can be mass resolved from the signals at 77 and 78 a.m.u. (see Figure 3).

| Parameter | Units | KED | 10% O ₂ / He | 8% H ₂ / He | STD |
|----------------|--------|------|-------------------------|------------------------|------|
| Sampling Depth | mm | 5 | 5 | 5 | 5 |
| Plasma Power | W | 1550 | 1550 | 1550 | 1550 |
| Cool Flow | L/min | 14 | 14 | 14 | 14 |
| Auxiliary Flow | L/min | 0,65 | 0,65 | 0,65 | 0,65 |
| Nebulizer Flow | L/min | 0,84 | 0,84 | 0,84 | 0,84 |
| CCT Bias | V | -21 | -13 | -10,01 | -2 |
| Pole Bias | V | -18 | -20 | -16 | -1 |
| CCT1 Flow | mL/min | 5,0 | 0,0 | 5,0 | 0,0 |
| CCT2 Flow | mL/min | 0,0 | 3,4 | 0,0 | 0,0 |

TABLE 2. Settings for measurement modes.

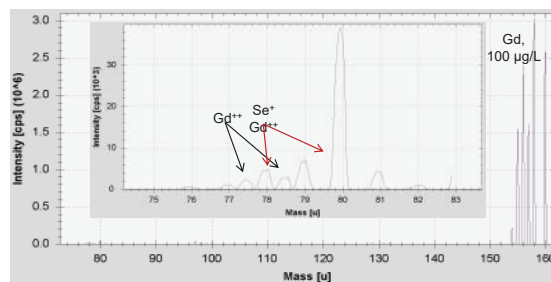


FIGURE 3. Mass resolution of Gd²⁺ interferences from Selenium isotopes

Since the abundances of ¹⁵⁵Gd and ¹⁵⁶Gd are well known and it can be assumed that all Gadolinium isotopes form the same level of doubly charged ions, a mathematical interference correction can be applied to subtract the Gd⁺⁺ contribution from the signal measured at mass 78 and obtain the net Selenium intensity.

Results

Although Selenium analysis can be difficult when Molybdenum and Gadolinium are also present in the sample, there is an easy way to accomplish accurate analysis. Table 3 lists the results from a multi-mode analysis of variant test samples as well as a NIST certified reference material², known for problematic Selenium analysis. Test solutions with different spike amounts of Molybdenum and Gadolinium demonstrate the applicability of the operating conditions of an iCAP Qc ICP-MS and tolerance against high excess of these interfering species. Highlighted in green are well-matching results, while Selenium recoveries in NIST-1547 highlighted in red indicate unacceptable agreement. Reactive mode with H₂/He and the application of interference correction based on half-mass measurement of ¹⁵⁵Gd⁺⁺ results in superb detection limits and excellent agreement with certified values as well as high tolerance against Gadolinium spikes on the analytical results for Selenium.

| Measurement Mode | NIST-1547 certified (µg/kg) | STD | | | 8% H ₂ /He | | | | KED | | | | 10% O ₂ /He | |
|--------------------------------|-----------------------------|------------------|------------------|------------------|-----------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|----------------------------------|----------------------------------|
| | | ⁷⁷ Se | ⁷⁸ Se | ⁸² Se | ⁷⁷ Se | ⁷⁸ Se | ⁸⁰ Se | ⁸² Se | ⁷⁷ Se | ⁷⁸ Se | ⁸⁰ Se | ⁸² Se | ⁷⁸ Se ¹⁶ O | ⁸⁰ Se ¹⁶ O |
| 10µg/kg Mo | | 0.002 | -0.028 | 0.000 | -0.025 | -0.004 | -0.104 | -0.002 | 0.033 | 0.022 | 0.018 | -0.052 | 68.473 | 56.259 |
| 10µg/kg Gd | | 0.053 | -0.062 | 0.003 | 0.063 | -0.010 | 0.045 | -0.002 | 1.127 | -0.598 | 1.650 | 0.001 | 0.180 | 0.164 |
| 1µg/kg Se+ 10µg/kg Mo | | 0.991 | 0.898 | 1.015 | 0.976 | 0.996 | 0.953 | 0.980 | 0.987 | 1.041 | 1.053 | 1.225 | 69.925 | 57.744 |
| 1µg/kg Se+ 10µg/kg Gd | | 1.043 | 0.858 | 1.037 | 1.060 | 0.991 | 1.014 | 0.967 | 2.245 | 0.824 | 2.779 | 1.120 | 1.174 | 1.139 |
| 1µg/kg Se+ 100µg/kg Gd | | 1.664 | 0.651 | 1.038 | 1.814 | 0.977 | 2.118 | 0.968 | 12.526 | -2.342 | 17.992 | 1.144 | 1.035 | 1.024 |
| 1µg/kg Se+10µg/kg Mo&Gd | | 1.036 | 0.894 | 1.042 | 1.053 | 0.999 | 1.010 | 0.989 | 2.121 | 0.938 | 2.832 | 1.067 | 69.023 | 57.281 |
| NIST 1547 (Peach Leaves) | 0.120 +/- 0.009 | 0.300 | 0.049 | 0.172 | 0.747 | 0.126 | -0.243 | 0.190 | 2.972 | 0.052 | 0.299 | 0.857 | 0.580 | 0.446 |
| LOD as 3 * SD _{blank} | | 0.030 | 0.019 | 0.014 | 0.086 | 0.001 | 0.061 | 0.044 | 0.020 | 0.024 | 0.110 | 0.086 | 0.047 | 0.026 |

TABLE 3. Comparison of analytical results for multi-mode analysis of Selenium.

Conclusions

- The iCAP Q ICP-MS has high detection power for selenium, boosted to up to 8 times the standard sensitivity by the addition of methane gas to the plasma
- High mass resolution capabilities enable the resolution of Gd⁺⁺ interferences from selenium isotopes
- A H₂/He gas mixture provided the best interference reduction and sensitivity combination for selenium analysis, enabling accurate analysis of selenium in samples with high REE content

References

1. M. Paul, Removing spectral interferences in ICP-QMS by collision/reaction cell technology - is there a "best" way ?, Poster presentation at 2011 Winter Conference on Plasma Spectrochemistry, Budapest, Hungary
2. NIST-1547 "Peach Leaves", Certificate of Analysis, National Bureau of Standards & Technology, 1991, Gaithersburg, MD, USA

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