Reaction Cell Frontier: Selenium Isotope Dilution Analysis using Innovative Reaction Cell ICP-MS

Naoki Sugiyama, Agilent Techonologies, Inc., 9-1 Takakura-cho, Hachioji-shi,Tokyo 192-0033 JAPAN.

Introduction

Selenium Isotope Dilution Analysis using Innovative Reaction cell ICP-MS

Selenium (Se) is one of the major elements required to be quantified in various types of samples due to its nutritional essentiality in animals and humans, and its toxicity when ingested in excess. However, for several reasons, it is a difficult element to accurately quantify. The first is that the required Limit of Quantification (LOQ) for Se is commonly as low as ppb to sub ppb levels. The second is that Se has high ionization potential (IP=9.75e V), causing low sensitivity due to poor ionization in plasma, susceptibility to matrix suppression, and difficulty in finding suitable Internal Standard (ISTD) elements. The third is that all Se isotopes suffer from severe interferences as summarized in Table 1. Isotope Dilution (ID) methodology is well known for its absolute accuracy due to its ability to minimize the effects of signal drift and matrix suppression, which are common problems in ICP-MS. However the application of isotope dilution to Se quantification has been limited because of the third reason stated above: interferences.

Introduction

The innovative reaction cell of the new Agilent triple quadrupole ICP-MS, enables measurement of more than one Se isotope free from interferences, making it possible to quantify Se using isotope dilution. Recently, Giuseppe et al.[1] applied the ID method for multi element analysis focusing on less susceptibility to matrix suppression, rather than on absolute accuracy. They proposed Online Isotope Dilution Analysis (OIDA) which removes the time-consuming step of spiking enriched-isotope standards into the samples.

Experimental

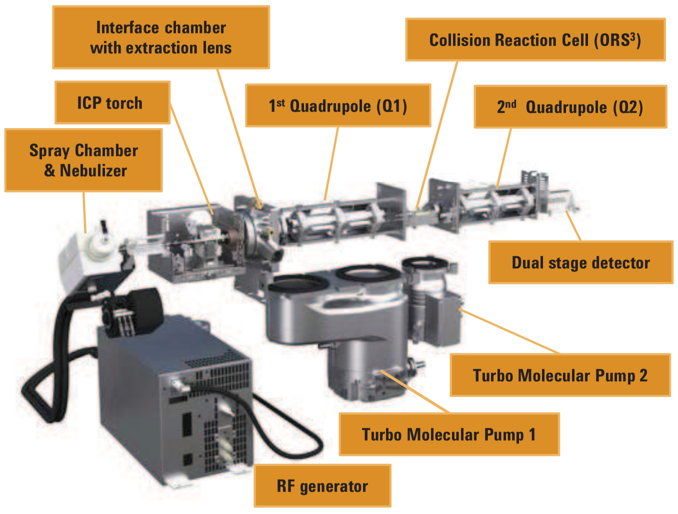

Figure 1. Configuration of Agilent ICP-QQQ

Table 1. Interference on major Se Isotopes

m/z	Abundance %	Isobar	argide	oxide	hydride	chloride	doubly charged	dimer
77	7.63		^{37}Cl^{40}Ar+, ^{39}K^{38}Ar+	^{61}Ni^{16}O+, ^{59}Co^{18}O+	^{76}GeH+, ^{76}SeH+	^{37}Cl^{40}Ca+	^{154}Sm++, ^{154}Gd++	
78	23.77	^{78}Kr+	^{38}Ar^{40}Ar+, ^{38}Ar^{40}Ca+	^{62}Ni^{16}O+	^{77}SeH+	^{41}K^{37}Cl+	^{156}Gd++, ^{156}Dy++	^{39}K^{39}K+
80	49.61	^{80}Kr+	^{40}Ar^{40}Ar+, ^{40}Ca^{40}Ar+	^{64}Ni^{16}O+, ^{64}Zn^{16}O+	^{79}BrH+	^{45}Sc^{35}Cl+	^{160}Gd++, ^{160}Dy++	^{39}K^{41}K+
82	8.73	^{82}Kr+	^{42}Ca^{40}Ar+	^{66}Zn^{16}O+	^{81}BrH+	^{45}Sc^{37}Cl+	^{162}Dy++, ^{162}Er++	

Experimental

Agilent Technologies has developed a new triple quadrupole ICP-MS (ICP-QQQ). As shown in Figure 1, it has two quadrupoles, one before and one after the collision/reaction cell. The first quadrupole selects ions entering the cell, providing **consistent reaction conditions** during changing sample composition. It solves the problems associated with current reaction cell technologies, allowing the analyst to use the reaction cell for more elements and applications, more effectively. The Agilent ICP-QQQ has the following features:

- Superior interference removal:
  - Advanced reaction cell technology overcomes the weaknesses of existing reaction cell instruments due to the unique QQQ configuration.
  - Versatile He collision mode with performance better than the Agilent 7700 Series ICP-MS due to MS/MS scanning ability.
- Sensitivity is much higher than the single quadrupole 7700 ICP-MS. A lab-prototype achieved 810 Mcps/ppm for Yttrium with oxide ratio (CeO+/Ce+) of 1.47% when using the high matrix x-lens and 1.2 Gcps/ppm with oxide ratio of 2.47% when using the high sensitivity s-lens.
- Random background noise is as low as <0.2cps
- Abundance sensitivity is immeasurably low: <10-9
- Maintains Agilent 7700 compatible robustness and durability, being applicable to developed Agilent 7700 applications

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Results and Discussion

Cell gas mode investigation

The interference removal capability was studied to determine the optimum cell gas conditions and the best Se isotopes for the ID method. Experimental results are given in Figure 2. The figure shows the background equivalent concentrations (BECs) using four reaction gas modes in various synthetic matrix samples. All modes used MS/MS scanning that operates the first Quad as a 1 amu-wide bandpass filter, selecting ions entering reaction cell. While Se isotopes were detected at the natural mass in the three cell gas modes, He, H_2 and NH_3+H_2 modes, they were detected as SeO^+ in O_2+H_2 mode. In this mode, Se^+ reacts with O_2, converting Se^+ to SeO^+. We refer to this as the mass shift method. Figure 3 illustrates the mass shift method. The reaction between Se^+ and O_2 is endothermic (ΔHr=0.769 eV), however, the reaction was promoted through the application of an octopole bias of -18 V, effectively forming SeO^+. Addition of small amount of H_2 into the cell was found to be effective at further reducing the BEC.

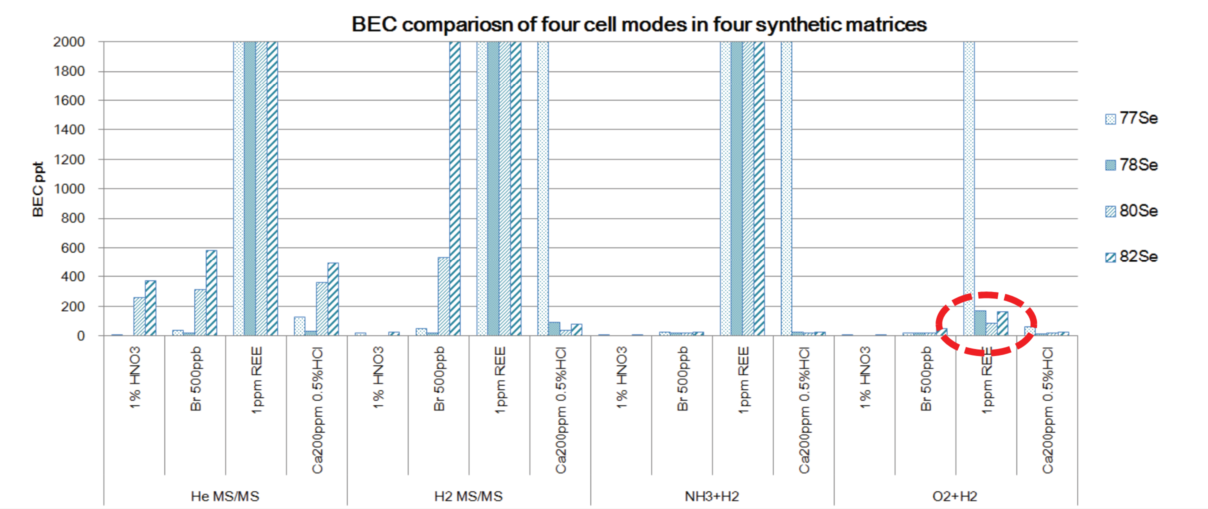


Figure 2. Result of interference removal capability study

From Figure 2, we can see O_2+H_2 mass shift method gives the best interference removal capability, allowing for the measurement of three Se isotopes, ^{78}Se,^{80}Se and ^{82}Se nearly free from interference. O_2 cell gas can be used with existing single-quadrupole cell ICP-MS, though the method does not work well when the sample contains either Zr, Mo or Ru, as their isotopes overlap SeO^+. With ICP-QQQ, due to ion selection by Q1, the method can be applied to samples regardless of the composition. This is a clear advantage of ICP-QQQ over existing cell ICP-MS, with the developed method being applicable to a variety of sample types.

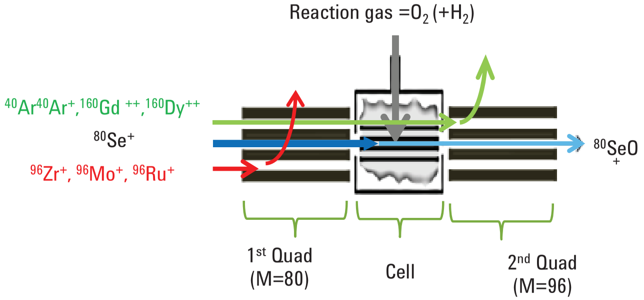
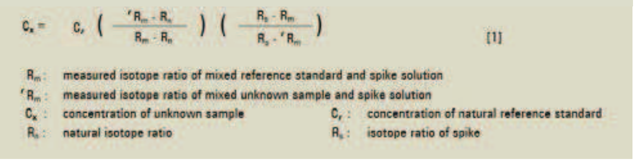


Figure 3. Illustration of O_2 mass shift method of ICP-QQQ

Selenium Online Isotope Dilution Analysis (OIDA)

A ^{82}Se enriched standard (^{82}Se 97.43%, ^{80}Se 1.65% and ^{78}Se 0.51%) was purchased from Oak Ridge National Laboratory. The standard was dissolved in ultrapure HNO_3, and diluted to the appropriate concentration. It was spiked to all tested samples online using the Agilent online-ISTD mixing kit. Isopropyl alcohol (IPA) was added to the spike solution to enhance Se^+ signal. Refer to Reference 1 for details of OIDA. The Se concentration of the sample was calculated using the measured isotope ratios of two Se isotopes according to the formula presented below.



$$C_x = C_y \left(\frac{{}'R_m - R_n}{R_m - R_n} \right) \left(\frac{R_s - R_m}{R_s - {}'R_m} \right) \qquad [1]$$

R_m : measured isotope ratio of mixed reference standard and spike solution
$'R_m$: measured isotope ratio of mixed unknown sample and spike solution
C_x : concentration of unknown sample
R_n : natural isotope ratio
C_y : concentration of natural reference standard
R_s : isotope ratio of spike

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Results and Discussion

Quantification error study using ID method

For accurate quantification, the ID method normally needs correction of the measured isotope ratios for mass bias and dead time. However we can expect good accuracy with the OIDA method without corrections when Cx ≒ Cr is met[2)]. Theoretically the error = 0 when Cx = Cr without correction. The accuracy of the measurement without correction was investigated. 0.1, 0.2, 2 and 20 ppb natural Se solutions were analyzed using a 2 ppb solution as the natural reference standard. Figure 4 shows that the quantification error becomes significant when Cx << Cr or Cx >> Cr. Accuracy of 95–105% would be achievable with concentrations ranging from 100 ppt to 5 ppb without correction. Since the accuracy of the measured isotope ratio of $^{82}Se/^{78}Se$ suffers from a severe mass bias effect, there was a larger uncertainty in the determined concentration.

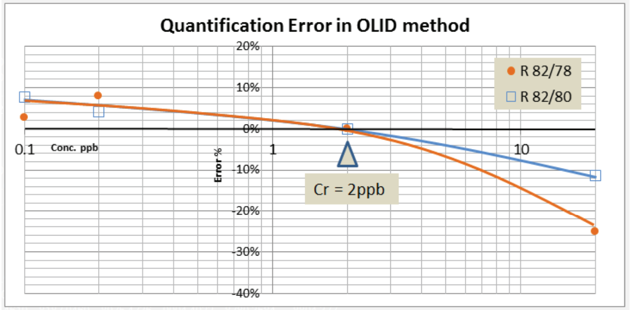

Figure 4. Quantification error of ID method

Se analysis by OIDA using O_2+H_2 mass shift method of ICP-QQQ

Se concentration was determined in various certified reference materials (CRMs) using the developed ID method. The analyzed CRMs included environmental water, rock, sediment, food, bio-sample and plant materials. These CRMs were all prepared in the appropriate way, i.e. ,some of them were microwave digested with HNO_3, HCl and H_2O_2. The tested samples were all diluted so that the expected Se concentration fell between 100 ppt and 5 ppb. An integration time of 1 second was applied to the three Se isotopes measured and ten replicates were acquired for averaging. Se concentration is calculated by formula [1] using measured isotope ratio, ^rRm.

Figure 5 shows the Se quantification results expressed as recovery % relative to the certified value. The developed method determined Se concentration of all CRMs with good accuracy, except two milk samples. Further investigation will be necessary to determine the cause of the poor results in the milk samples. One possibility for next step is to utilize the ID method after spiking the isotope-enriched standard before sample preparation.

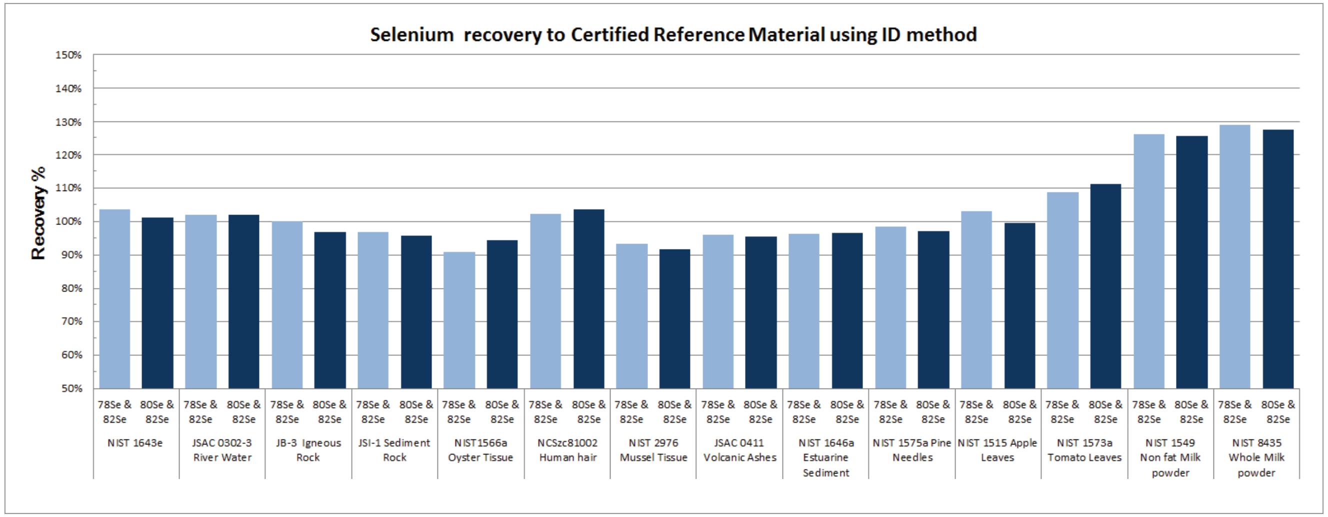

Figure 5. Results of Se analysis in CRMs by OIDA using O_2+ H_2 mass shift method of ICP-QQQ

Conclusions

- We found that a reaction cell using O2+H2 can effectively solve the interference by REE++ on Se isotopes. The developed method on ICP-QQQ can be applied to samples containing Zr, Mo and Ru, since they are removed by the first quadrupole.
- We demonstrated that OIDA using the O2+H2 mass shift method of the ICP-QQQ can be used for Se quantification in wide range of samples.
- Next our plan is to investigate the high recovery for Se in milk samples.

References

1. Giuseppe Centineo, Jose Angel, Rodriguez Castrillon and Esther Munoz Agudo, Agilent Technologies application note 5990-9171EN
2. A. Henrion , Fresenius J Anal Chem,1994, 350,657-658