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

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Introduction

Selenium Isotope Dilution Analysis using Innovative Reaction cell ICP-MS

Selenium (Se) is one of major elements required to be quantified in various types of samples due to its essentiality in animal/human and toxicity when ingested in excess. However it is a difficult element to accurately quantify. There would be three reasons. The first is that required Limit of Quantification (LOQ) for Se is commonly as low as ppb to sub ppb range. The second is Se has high ionization potential (IP=9.75eV), causing low sensitivity due to poor ionization in plasma, susceptibility to matrix suppression and difficulty in finding suitable Internal Standard (ISTD) element. The third is that all Se isotopes suffer severe interference as summarized in table 1. Isotope Dilution (ID) method is well known technique for its absolute accuracy, however it is also a method that is least susceptible to signal drift and matrix suppression, which are common problems in ICP-MS, deteriorating accuracy of quantification. However application of ID method to Se quantification has been limited because of the third reason stated above; interference.

Table 1: Interference on major Se Isotopes

m/z	Abundance %	Isobar	argide	oxide	hydride	chloride	doubly charged	dimer
77	7.63		$^{37}Cl^{40}Ar^+$, $^{39}K^{38}Ar^+$	$^{61}Ni^{16}O^+$, $^{60}Co^{16}OH^+$	$^{76}GeH^+$,$^{76}SeH^+$	$^{37}Cl^{40}Ca^+$	$^{154}Sm^{++}$, $^{154}Gd^{++}$	
78	23.77	$^{78}Kr^+$	$^{38}Ar^{40}Ar^+$, $^{38}K^{40}Ca^+$	$^{62}Ni^{16}O^+$	$^{77}SeH^+$	$^{42}K^{37}Cl^+$	$^{156}Gd^{++}$, $^{156}Dy^{++}$	$^{39}K_2^+$
80	49.61	$^{80}Kr^+$	$^{40}Ar^{40}Ar^+$, $^{40}Ca^{40}Ca^+$	$^{64}Zn^{16}O^+$, $^{64}Ni^{16}O^+$	$^{79}BrH^+$	$^{45}Sc^{35}Cl^+$	$^{160}Gd^{++}$, $^{160}Dy^{++}$	$^{40}K_2^+$
82	8.73	$^{82}Kr^+$	$^{42}Ca^{40}Ar^+$	$^{66}Zn^{16}O^+$	$^{81}BrH^+$	$^{47}Ti^{35}Cl^+$	$^{164}Dy^{++}$, $^{164}Er^{++}$	$^{41}K_2^+$

The innovative reaction cell of ICP-QQQ allows us to measure more than one Se isotopes free from interference, making it possible to quantify Se using ID method. Recently Giuseppe et al.[1] applied ID method for multi element analysis focusing on less susceptibility to matrix suppression rather than the absolute accuracy. They proposed Online Isotope Dilution Analysis (OIDA) that removes time consuming step for spiking enriched-isotope standard into samples.
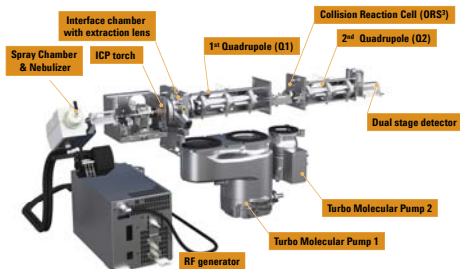
Experimental

Agilent ICP-QQQ

Figure 1: Configuration of Agilent ICP-QQQ

Agilent Technologies developed a new high-end ICP-MS, Triple Quadrupole ICP-MS (ICP-QQQ). As shown in Fig.1, it has two Quadrupoles before and after Collision/Reaction Cell. The 1st Quadrupole selects ions entering the cell, providing **consistent reaction condition** to changing sample composition. It solves problem of current reaction cell technologies, allowing analyst to use reaction cell for more elements/applications, more effectively. The Agilent ICP-QQQ has following features.

- The best performance cell for solving interference problem.
  - ➢ Advanced reaction cell overcoming weak point of existing reaction cell due to unique QQQ configuration.
  - ➢ Versatile He collision cell. The performance is better than Agilent 7700 due to MS/MS scan.
- Sensitivity is much higher than Agilent 7700 series ICP-MS. A lab-prototype achieved 810 Mcps/ppm with oxide ratio (CeO^+/Ce^+) of 1.47% by x-lens and 1.2 Gcps/ppm with oxide ratio of 2.47% by s-lens for Yttrium.
- Random back ground noise is as low as <0.2cps .
- Abundance sensitivity is immeasurably low; <10-9
- It keeps Agilent 7700 compatible robustness and durability, being applicable to developed Agilent 7700 applications.

Results and Discussion

1/Cell gas mode investigation

Interference removal capability was studied to determine optimum cell gas condition and the best isotopes of Se for ID method. An experimental result is given in Fig.2. The Figure shows Background Equivalent Concentration (BEC) of four reaction gas modes in various synthetic matrix samples. All modes used MSMS scan that operates the 1st Quad as 1 amu-window band pass mass filter, selecting ions entering reaction cell. While Se isotopes were detected at the nature 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 to SeO^+ . We call it mass shift method. Fig. 3 illustrates the mass shift method. Reaction between Se^+ and O_2 is endothermic though ($\Delta Hr=0.769eV$), the reaction was promoted at octopole bias of -18V effectively forming SeO^+. Addition of small amount of H_2 into cell was found effective for further reducing BEC.
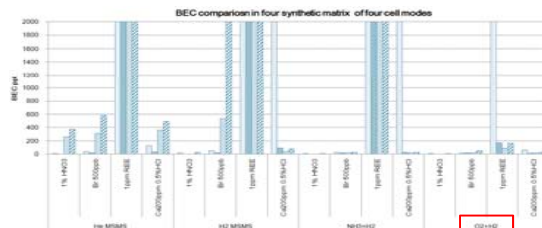

Fig.2 Result of interference removal capability study

From Fig.2 we can see O_2+H_2 mass shift method gives the best interference removal capability , allowing us to measure three Se isotopes, $^{78}Se,^{80}Se$ and ^{82}Se nearly free from interference. O_2 cell gas can be used with existing cell-ICP-MS though, the method doesn't work fine when sample contains either Zr, Mo or Ru since their isotopes overlaps SeO^+. With ICP-QQQ, due to ion selection by Q1, the method can be applied to samples regardless of the composition. It is clear advantage of ICP-QQQ over existing cell ICP-MS, allowing us to apply the developed method to various types of samples.
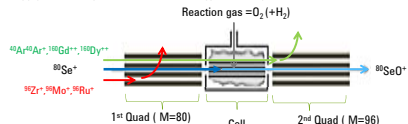

Fig.3 Illustration of O_2 mass shift method of ICP-QQQ

2/ Selenium Online Isotope Dilution Analysis (OIDA)

^{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 HNO3, and diluted to be appropriate concentration. It was spiked to all tested samples online using Agilent online-ISTD mixing kit (IPA was added to the spike solution to enhance Se^+ signal) . Please refer to reference 1) for detail of OIDA. Se concentration of sample is calculated by formula [1] using measured isotope ratio, ^rR_m . I determined Se concentration in samples using two isotope ratios, ratio of ^{82}Se to ^{80}Se and ratio of ^{82}Se to ^{78}Se for comparison.

$$C_x = C_r \left(\frac{^rR_m - R_m}{R_m - R_n} \right) \left(\frac{R_n - R_m}{R_m - ^rR_m} \right) \qquad [1]$$

R_m : measured isotope ratio of mixed reference standard and spike solution

^rR_m : measured isotope ratio of mixed unknown sample and spike solution

C_x : concentration of unknown sample

R_n : natural isotope ratio

C_r : concentration of natural reference standard

R_s : isotope ratio of spike

3/ Quantification Error study in ID method

For accurate quantification, ID method normally needs correction of measured isotope ratio such as mass bias correction and dead time correction. However we can expect good accuracy with OIDA method without corrections when Cx ≒ Cr is met [2]. Theoretically Error =0 is achieved when Cx = Cr without correction. I investigated the accuracy of measurement without correction. I analyzed 0.1,0.2,2 and 20 ppb natural Se solution using 2ppb solution as natural reference standard. From Fig.4 it is found that quantification error becomes significant when Cx <<Cr and Cx>>Cr and accuracy of 95-105% would be achievable to concentration ranging from 100ppt to 5ppb without correction. Since accuracy of measured isotope ratio of $^{82}Se/^{78}Se$ suffer severer mass bias effect , it gave larger uncertainty in determined concentration.
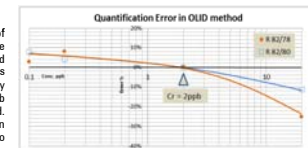

Fig.4 Quantification error of ID method

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

Se concentration was determined in various Certified Reference Material (CRM) using developed method. Analyzed CRM contain environmental water, rock, sediment, food, bio-sample and plant. Those CRM are all prepared in 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 expected Se concentration falls between 100ppt and 5ppb. Integration time of 1 sec. was applied to three Se isotopes measurement and ten replicates were done for averaging. Se concentration is calculated by formula [1] using measured isotope ratio, ^rR_m.

Fig.5 shows Se quantification result in recovery % to certified value. The developed method determined Se concentration of all CRM with good accuracy except two milk samples. At this moment , I have no clear idea to explain the result. It may be simply because of human error during sample prep, or due to unknown interference or signal enhancement. One of plan I have for next step is to utilize ID method spiking isotope-enriched standard before sample preparation.
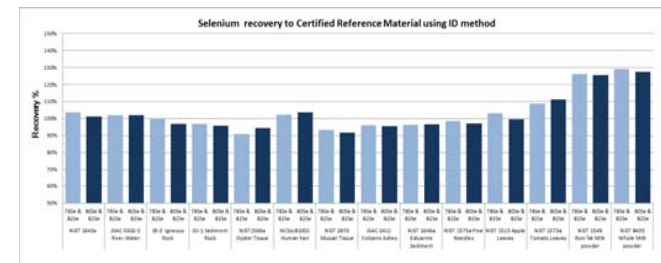

Fig.5 Result of Se analysis in CRM by OIDA using O_2+H_2 mass shift method of ICP-QQQ

Conclusions

1/We found that reaction cell using O_2+H_2 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 Quad.
2/ We demonstrated the OIDA using O2+H2 mass shift method of ICP-QQQ can be used for Se quantification in wide range of samples.
3/ Next our plan is to investigate the high recovery of Se in milk samples.

Reference
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