

**AGILENT 8800 TRIPLE QUADRUPOLE ICP-MS
WINTER PLASMA CONFERENCE 2012 POSTERS**

Compendium

The Measure of Confidence



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Introduction

ICP-MS is an analytical technique capable of achieving detection limits in the part per trillion (ppt) or sub-ppt range for most elements. However, its excellent detection capability is often limited in real applications by two major factors: contamination and spectral interference. Collision/reaction cell technology, which had been routine in LC/MS, was applied to ICP-MS and proved effective at resolving most interference problems. This technology relies on one of two types of cells in ICP-MS: collision cells or reaction cells. Collision cells remove interfering polyatomic ions using the size difference between the analyte ion and interfering polyatomic ion and so are effective on all interferences caused by polyatomic ions. Since collision cells do not sacrifice the multi-element capability of ICP-MS, they have been widely accepted for many applications. However, for some interferences, the effectiveness of collision cells is limited. Interference by metal oxide ions is a common example. In this work, we applied novel reaction cell technology based on a triple quadrupole configuration to ICP-MS in order to remove interferences due to oxide ions such as $^{59}\text{Co}^{16}\text{O}^+$ on $^{75}\text{As}^+$ with excellent results.

Experimental

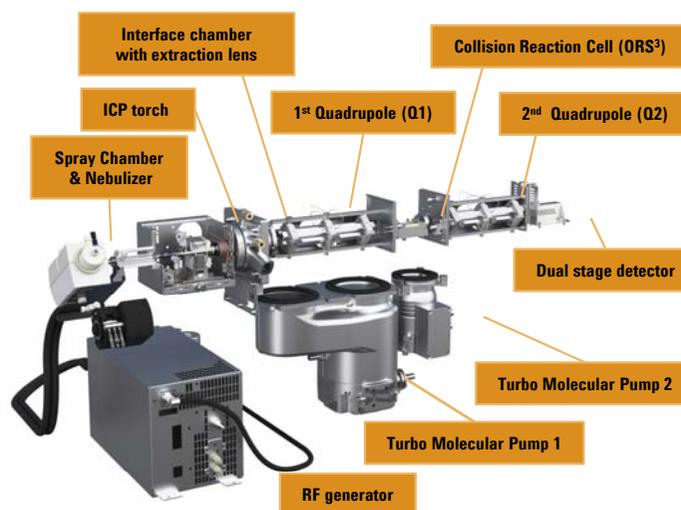
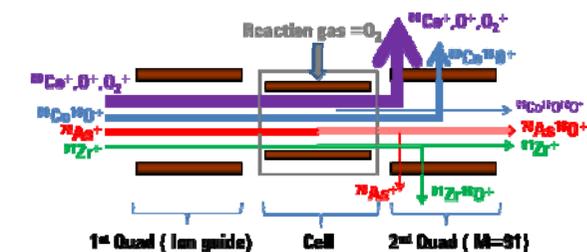


Figure 1. Configuration of Agilent ICP-QQQ

Agilent ICP-QQQ

Agilent Technologies has developed a new high-end, 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 1st quadrupole selects ions to enter the cell, providing consistent reaction conditions to changing sample composition (Figure 2 (2) MS/MS mode). It solves the problem of current cell technologies using reaction gas, allowing analysts to use reaction mode for more elements/applications, more effectively. Figure 2 illustrates the principle of two different modes for ICP-QQQ. One is (1) Single-Quad mode and the other is (2) MS/MS mode. The comparison of the two modes is discussed in this paper. In both cases, standard plasma conditions ($\text{CeO}^+/\text{Ce}^+=0.9\%$) were employed.

(1) Single-Quad mode (Q1 as an ion guide)



(2) MS/MS mode (Q1 as 1amu-window (m/z 75) band pass)

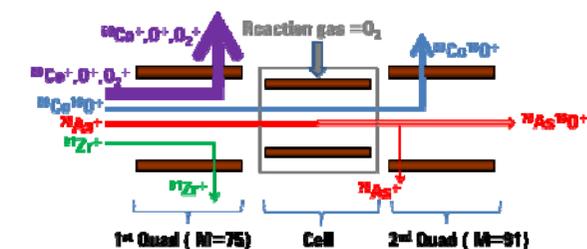
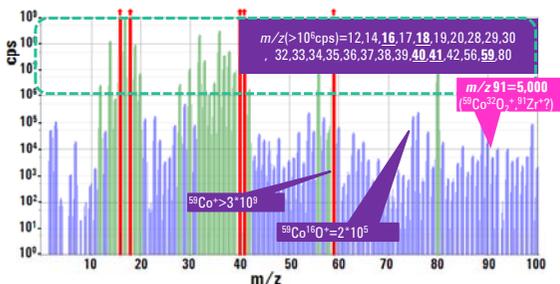


Figure 2. Illustration of the O_2 mass shift method of ICP-QQQ using two different modes (^{75}As as $^{75}\text{As}^{16}\text{O}^+$ at m/z 91)

- (1) Single-Quad mode: allows all ions through to the collision/reaction cell (as an ion guide), with the system acting as a single-quad ICP-MS (functioning like the octopole-based cell of the current Agilent 7700 series ICP-MS)
- (2) MS/MS mode: operates the 1st Quad as 1 amu-window band pass mass filter, selecting ions entering the reaction cell.

Results and Discussion

(1) Single-Quad mode (Q1 as an ion guide)



(2) MS/MS mode (Q1 as 1amu-window (m/z 75) band pass)

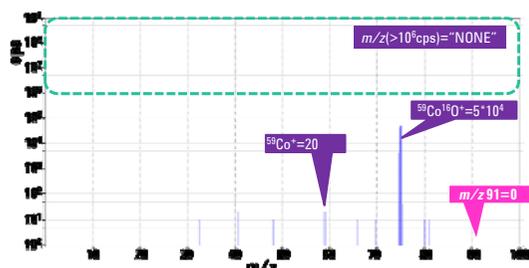


Figure 3. ICP-QQQ mass spectra for 100ppm (mg L^{-1}) Co in 1% HNO_3 by no gas mode (Octopole bias: -8 V, Q2 bias: -5 V)

- (1) Single-Quad mode: Red color spectrum (m/z 16,18,40,41,59) was measured as "EM protection ($> 3 \times 10^9$ cps)
- (2) MS/MS mode: Q1 rejected all masses except target mass (m/z 75). Only target-mass ions (m/z 75) entered the cell

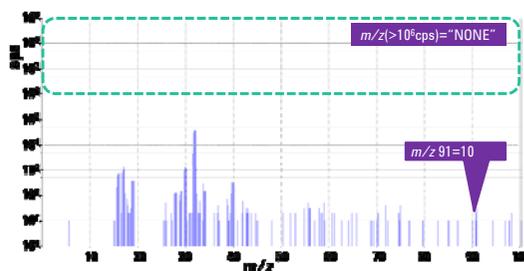
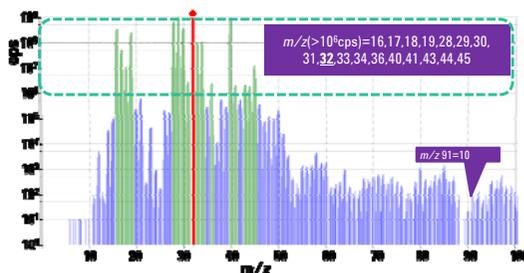


Figure 4. ICP-QQQ mass spectra for 1% HNO_3 by O_2 mode (Octopole bias: -16 V, Q2 bias: -26 V)

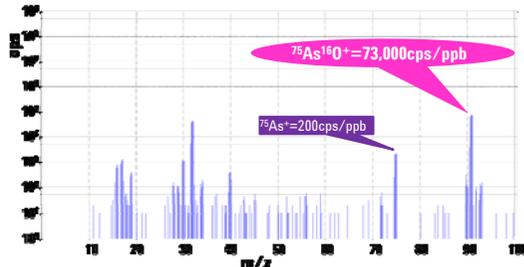
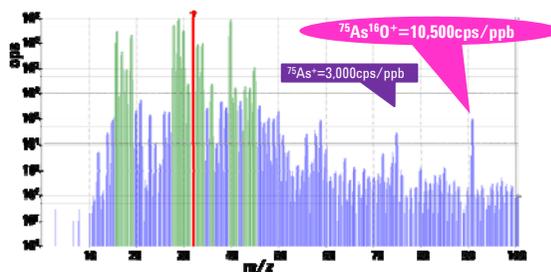


Figure 5. ICP-QQQ mass spectra for 10 ppb ($\mu\text{g L}^{-1}$) As in 1% HNO_3 by O_2 mode (Octopole bias: -16 V, Q2 bias: -26 V)

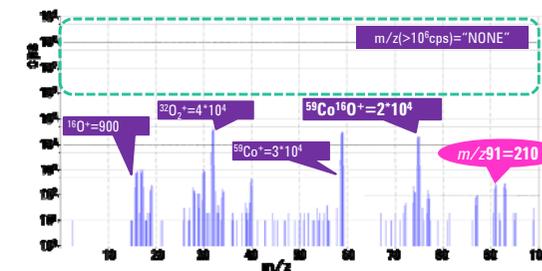
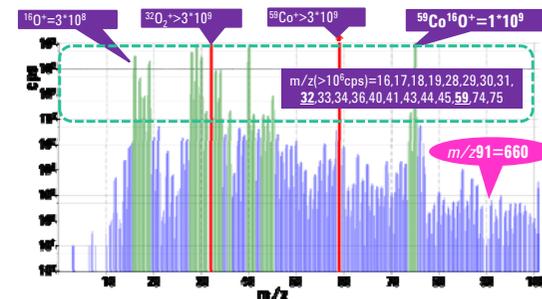


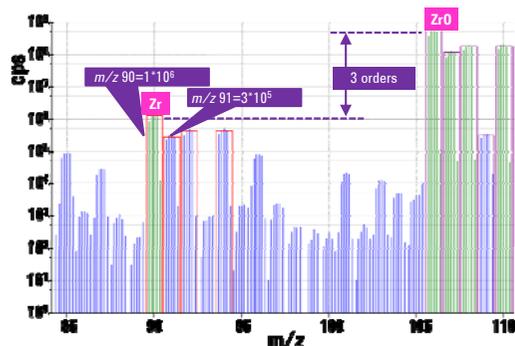
Figure 6. ICP-QQQ mass spectra for 100 ppm (mg L^{-1}) Co in 1% HNO_3 by O_2 mode (Octopole bias: -16 V, Q2 bias: -26 V)

- (1) Single-Quad mode: m/z 91 = 660 cps (As 63 ppt as AsO)
- (2) MS/MS mode: m/z 91 = 210 cps (As 29 ppt as AsO)

1) Single-Quad mode \rightarrow 34 (=63-29)ppt interference by CoO_2^+
 2) MS/MS mode \rightarrow The lowest BEC

Results and Discussion

(1) Single-Quad mode (Q1 as an ion guide)



Mass	Zr Abundance(%)
90	51.45
91	11.22
92	17.15
94	17.38
96	2.80

(2) MS/MS mode (Q1 as 1amu-window (m/z 75) band pass)

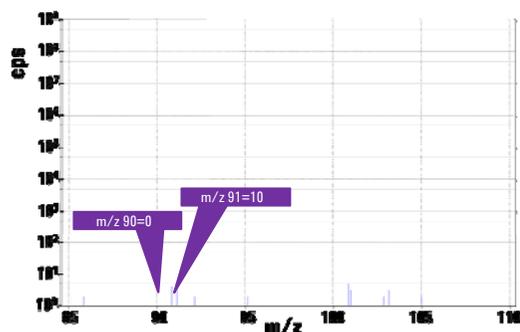


Figure 7. ICP-QQQ mass spectra for 10ppm(mg L^{-1}) Zr in 1% HNO_3 by O_2 mode (Octopole bias: -16 V, Q2 bias:- 26 V)

- (1) Single-Quad mode: Correct match with isotopic template confirms presence of Zr and ZrO
- (2) MS/MS mode: No Zr interference on m/z 91 (AsO^+)

Table 1. Kinetic rate constant and the enthalpy⁽¹⁾

Reaction	Kinetic Rate Constant/ $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	ΔH_r (enthalpy) kJ/mol(eV)
$^{75}\text{As}^+ + \text{O}_2 \rightarrow ^{75}\text{As}^{16}\text{O}^+ + \text{O}$	$4 \cdot 10^{-10}$ (\rightarrow Rapid)	-928(-9.6)
$^{59}\text{Co}^+ + \text{O}_2 \rightarrow ^{59}\text{Co}^{32}\text{O}_2^+ + \text{O}$	$1.5 \cdot 10^{-13}$ (\rightarrow Slow)	No data
$\text{Zr}^+ + \text{O}_2 \rightarrow \text{ZrO}^+ + \text{O}$	$5 \cdot 10^{-10}$ (\rightarrow Rapid)	-705(-7.3)

Figure 3 shows the mass spectrum for a 100 ppm Co solution. A lot of spectra signals were observed for (1) Single-Quad mode. On the other hand, almost no signal except the target mass (m/z 75) was observed for (2) MS/MS mode. When O_2 is introduced into the reaction cell, a new ion is produced at m/z 91 ($^{75}\text{As}^{16}\text{O}^+$) from a solution containing As (Figure 4 (blank), Figure 5 (10ppb As)). The reaction is exothermic (-928kJmol^{-1}) as shown in Table1. Bohme et al. report that the reaction of As^+ with O_2 to form AsO^+ is efficient, with a kinetic rate constant around $4 \cdot 10^{-10} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. On the other hand the reaction of Co^+ with O_2 to form CoO_2^+ is very slow, with a kinetic rate constant around $1.5 \cdot 10^{-13} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$.¹⁾

Table 2 shows the comparison of As quantitative results in a 100 ppm cobalt solution based on an external calibration in 1% HNO_3 . In no gas mode (#1), serious interference from $^{59}\text{Co}^{16}\text{O}$ resulted in a measured value for As of 32 ppb. The result using Helium mode (#2) was 3.7 ppb. While helium collision was able to reduce the interference about 1 order of magnitude better than no gas mode, it was still incapable of sufficiently removing the interference. On the other hand, using oxygen reaction mode (#3) (1) Single-Quad mode to convert $^{75}\text{As}^+$ to $^{75}\text{As}^{16}\text{O}^+$ was effective at separating the $^{59}\text{Co}^{16}\text{O}$ interference from the As measurement of 63 ppt. Moreover, the result of (#4) (2) MS/MS mode using Q1 as 1 amu-window band pass filter showed the best overall reduction of interference at 29 ppt.

The result difference was 34 ppt (63-29). In the case of (1) Single-Quad mode, it is probable that slight CoO_2^+ was generated in the cell because the signals of Co^+ and CoO^+ are higher than that of (2) MS/MS mode, as shown in Figure 6. **Figure 7** shows a mass spectrum of the m/z 85–110 region for 10 ppm Zr solution because ^{91}Zr (11.22% abundance) could cause a spectral overlap with $^{75}\text{As}^{16}\text{O}$. The reaction of Zr^+ with O_2 to form ZrO^+ is effective, as the signal due to ZrO^+ is approximately 3 orders of magnitude higher than that of Zr^+ . However, the As quantitative result was 30 ppb for (1) Single-Quad mode because of the residual $^{91}\text{Zr}^+$ interference. On the other hand the result of (2) MS/MS mode was 0 ppt because Zr^+ was completely eliminated by Q1.

Table 2. Comparison of As quantitative results in 100 ppm Co and 10 ppm Zr (ppt)

#	Collision/Reaction	Mass	Co(100ppm)	Zr (10ppm)	Interference
1	No gas	75	32000	0(**)	CoO
2	Helium	75	3700	0(**)	CoO
3	Oxygen(1) Single-Quad mode	91(*)	63	30000	CoO_2 (Slight), Zr
4	Oxygen(2) MS/MS mode	91(*)	29	0	Lowest BEC

(*) $\text{As}^{75}\text{As}^{16}\text{O}$,(**) as theoretical value (no experimental data)

Conclusions

Trace level arsenic measurement in high concentrations of cobalt is not possible using conventional techniques with quadrupole ICP-MS. This poster has demonstrated the following:

- ICP Triple Quad can provide a solution
- MS/MS mode using O_2 reaction was effective at solving the interference by CoO_2 , Zr etc., because the 1st Quadpole (set to 1 amu-window band pass filter) rejected all ions except the target mass (m/z 75) ions such as As^+ and CoO^+ .
- The result of MS/MS mode showed the best overall reduction of interference at 29 ppt.

Reference

1) John W. Olesik and Deanna R. Jones, J. Anal. At. Spectrom., 2006 ,21, 141-159

Introduction

The use of a collision/reaction cell, which is located between the ion extraction lenses and the quadrupole mass filter and pressurized using various inert or reactive gases, is now widely accepted in quadrupole ICP-MS as a means to reduce spectroscopic interferences. However, depending on the sample to be analyzed (analytes of interest, matrix species and their concentration), accurate quantification of analytes by collision/reaction cell ICP-MS is still sometimes problematic due to persistent interferences which cannot be removed by the current configuration.

In this study a triple quadrupole ICP-MS system, (Agilent 8800 Triple Quadrupole ICP-MS), has been developed based on the Agilent 7700 Series ICP-MS. The proposed system has a configuration of quadrupole - collision/reaction cell – quadrupole that follows the off-axis extraction lenses (Omega Lens). Employed in the cell (ORS: Octopole Reaction System) is an octopole ion guide. The first quadrupole, having unit mass resolving power, can select ion species that enter the cell. In contrast to the conventional cell-based quadrupole ICP-MS, where all of the ionic species generated in the plasma ion source region enter the cell, the new triple quad configuration can dramatically reduce the spectroscopic interferences as well as background noise.

In addition to the improvement of the ion optics arrangement, an improved vacuum system tailored to this configuration has been developed resulting in sensitivity comparable to single quad ICP-MS even though the additional first quadrupole operates as a unit mass resolving filter which does not have perfect ion transmission efficiency.

Introduction

This poster explains the hardware configuration, vacuum system, and the principles of operation using some experimental results obtained from the prototypes.

Hardware Configuration

Ion Optics Arrangement

Figure 1 shows a comparison of the hardware configurations between a conventional cell-based ICP-MS system (a) Agilent 7700 Series ICP-MS and the proposed triple quadrupole system (b) Agilent 8800 Triple Quadrupole ICP-MS. As mentioned above, the

Hardware Configuration

proposed system has a first quadrupole termed as “Quadrupole1 (Q1)” and related electrostatic ion lenses at the entrance and the exit of Q1, which are located between the ion extraction lenses and the collision/reaction cell (ORS). The quadrupole downstream of the cell is termed “Quadrupole2 (Q2)”, whose design is the same as that of 7700’s quadrupole. All the ion lenses including the off-axis ion extraction lenses and collision reaction cell which are used in 7700 are also used in the new system, so that the tuning parameters of the new system except for Q1 are almost identical to those of the 7700.

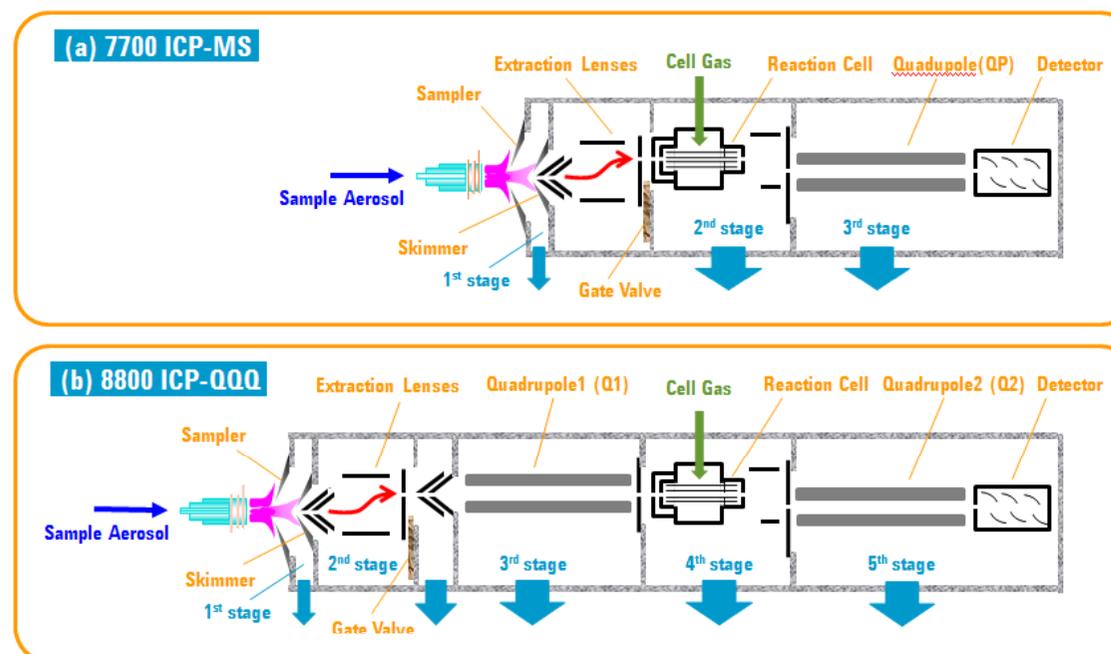


Figure 1. Comparison of hardware configuration between the conventional cell-based ICP-MS(a) and the proposed ICP-QQQ(b).

Hardware Configuration

Vacuum System

The ion source of the ICP-MS is an inductively coupled plasma (ICP) at atmospheric pressure. The analyte ions generated in the plasma are sampled and extracted through the interface region into the vacuum pressure region where the quadrupoles and the cell are located. In order to match such requirements, a new differential pumping system which reduces the pressure gradually along the ion flight direction by separating multiple vacuum stages was developed. Usually, a rotary oil pump is used to evacuate the interface region roughly down to the order of hundreds of Pascals, and a turbo molecular pump (TMP) evacuates the subsequent vacuum stages to the pressures in the order of 10^{-2} ~ 10^{-5} Pa. Another point is that various collision/reaction gases are introduced into the cell which is located at the intermediate vacuum stage in the differential pumping system. In ICP-MS, the relatively high flow rate (~15mL/min) and low-molecular-weight of gases such as H₂ or He which are often used as reaction or collision gases are problematic for turbo molecular pumps. Furthermore the ion source (ICP) generates a lot of heat which degrades the pump reliability, so the TMPs used in ICP-MS are exposed to severe pumping and thermal conditions.

The vacuum system for the new system was tailored to the ICP-QQQ configuration, and a 5 stage vacuum system was adopted while that of 7700 is 3 stage as indicated in Figure 1. In the new system, the chambers where the extraction lenses and Q1 are installed are divided and pumped down independently as the 2nd and 3rd stages, while the extraction lenses and cell are installed in the same vacuum stage on 7700 ICP-MS.

Hardware Configuration

Table 1 shows a comparison of the pressure and mean free path of Ar ions colliding with Ar gas molecules at each vacuum region. Compared to the cell, the quadrupole requires a longer axial length to ensure the mass resolution and abundance sensitivity, however, the mean free path of analyte ions is comparable with the ion flight path in the Q1 chamber if a 4 stage vacuum system is adopted. By dividing the chamber for the extraction lenses and Q1, the Ar gas flow into the 3rd stage can be dramatically reduced because most of the Ar gas entering the 2nd stage through the skimmer orifice is evacuated by the pump attached to 2nd stage, so that the pressure in the 3rd stage can be approximately 5×10^{-4} Pa which is about 40 times lower compared to that of the 4 stage vacuum system. As a result the mean free path in Q1 chamber becomes sufficiently long in this 5 stage vacuum system so that the ion transmission efficiency in Q1 and the sensitivity can be improved without compromising the mass filtering function of Q1 (mass resolution, abundance sensitivity, etc.).

Table 1. Pressure and mean free path at each vacuum region. Mean free path is calculated assuming the collision of an Ar ion with an Ar gas molecule.

	5 stage vacuum system		4 stage vacuum system	
	Pressure [Pa]	Mean free path [m]	Pressure [Pa]	Mean free path [m]
Interface chamber	500	--	500	--
Ion lens chamber	0.13	7.5×10^{-2}	0.2	5×10^{-2}
Q1 chamber	5×10^{-4}	19	2×10^{-2}	0.44
ORS chamber	2×10^{-4}	48	5×10^{-4}	19
Q2 chamber	5×10^{-4}	19	2×10^{-4}	48

Principle of Operation

MS/MS Mode

Figure 2 shows a comparison of the principles of operation between the new system and a conventional cell-based ICP-MS. In conventional ICP-MS, all ions generated in the ion source enter the cell pressurized by various cell gases, and some of the interference ions are removed. On the other hand, the new system places Q1 in front of the cell. In MS/MS mode, Q1 is driven as mass filter with unit mass resolving power. As a result, only the selected ions whose mass is the same as the targeted analyte ion can pass through Q1 and enter the cell. The target masses of Q1 and Q2 can be set independently because analyte ions often produce product ions by reacting with the cell gas in the cell.

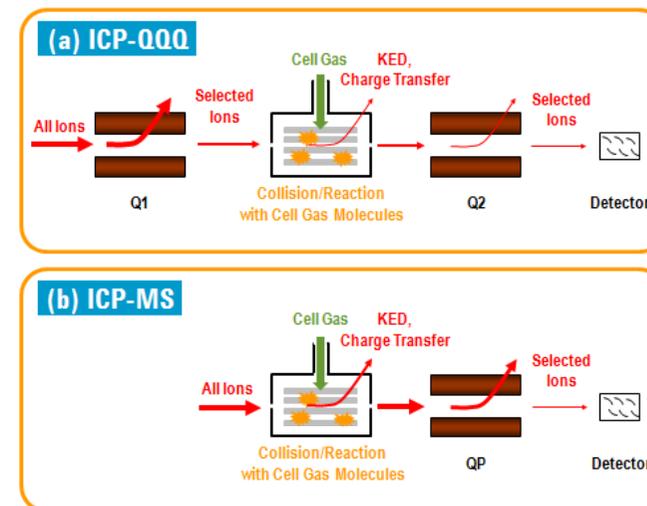


Figure 2. Comparison of principle of operation between the new ICP-QQQ (a) and the conventional cell-based ICP-MS (b).

Principle of Operation

Single Quad Mode

Not all analytes suffer from spectral interferences that need to be removed by MS/MS operation. However, their sensitivity would be compromised in MS/MS mode compared with the conventional ICP-MS due to the decrease in ion transmission through Q1 driven as a unit mass resolving filter. Single Quad mode in which Q1 is driven as an RF only quadrupole or low resolution bandpass filter improves ion transmission efficiency at Q1 and works as a conventional ICP-MS without sacrificing sensitivity of the analytes which do not suffer from spectral interferences.

Figure 3 shows the scan line of Q1 working in Single Quad mode and the stability diagram of the quadrupole. Two parameters, termed "Scan Line Slope (SLS) factor" and "Scan Line Gain (SLG) factor", determine the operating conditions of Q1 in Single Quad mode. For the SLS factor, setting the U voltage relative to that for unit mass resolution governs the degree of bandpass mass width. In general the lower the SLS factor is set, the broader the bandpass mass width is obtained. If the SLS factor is set to be 0, Q1 is driven as an RF only quadrupole, that is, a high pass filter with no low mass cut-off. For the SLG factor, setting V voltage relative to that for unit mass resolution governs the position of the bandpass window. The lower the SLG factor is set, the lower the mass band pass window moves. If Q1 is driven as RF only quadrupole, the lower the SLG factor, the lower the cut-off mass of this high pass filter.

Principle of Operation

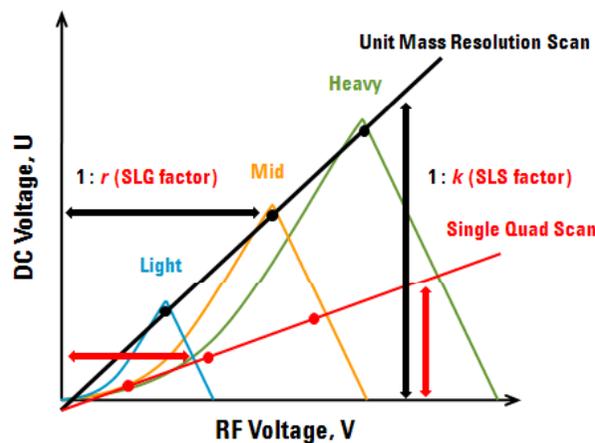


Figure 3. Scan line and stability diagram of quadrupole.
Black line; scan line for unit mass resolution scan
Red line; scan line of Q1 for single quad scan

Experimental

Titanium(Ti) Detection by O₂ Gas Mode

Figure 5 shows the principle of detection for ⁴⁸Ti by the ICP-QQQ system and a conventional ICP-MS using O₂ as cell gas. One of the challenges to detect Ti as TiO is the measurement of samples in which zinc (Zn) or nickel (Ni) coexist with Ti. Ti whose major isotope is 48amu is detected as its oxide (TiO), whose mass is 64amu. However, Zn and Ni also have isotopes whose mass is 64amu and overlap the analyte (TiO+) spectrum as atomic interferences on a conventional ICP-MS. On the new system, Q1, whose mass setting (m/z) is 48 ensures the elimination of Ni and Zn, so it can measure Ti as TiO+ without suffering from those interferences. In order to check the benefit of MS/MS capability, a 1ppb Ti sample, and a 1ppb Ti with 1ppb Cu and Zn sample were prepared and measured using MS/MS mode (a) and Single Quad mode (b) on the

Experimental

new ICP-QQQ system. In Single Quad mode (b) emulating the conventional ICP-MS, Cu and Zn interferences overlap all of the isotopes of the TiO⁺ spectrum. On the other hand, MS/MS mode removes such interferences using Q1, and the spectrum agrees with the natural isotopic abundance of Ti.

Another challenge is to measure Ti as a trace impurity in sulfuric acid (H₂SO₄) because Ti⁺ is subject to intense sulfur-based interference ions (SO⁺). However, on the new system, the ion-molecule reactions in the cell are predictable to the fact that Q1 can control the ion species entering the cell. The following are the thermochemical equations of reaction between relevant ions and O₂ cell gas:

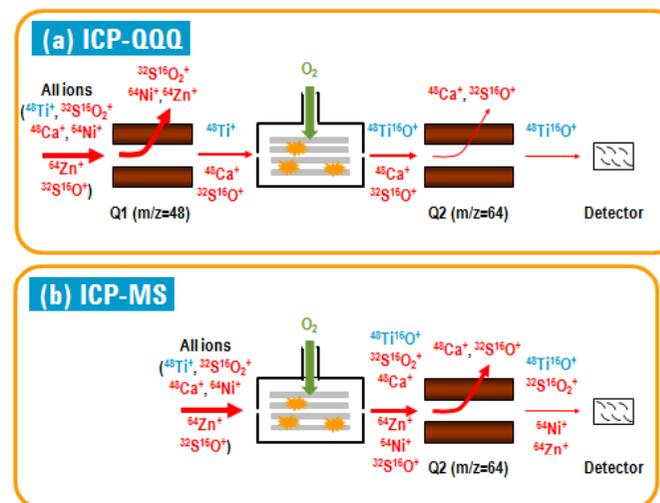
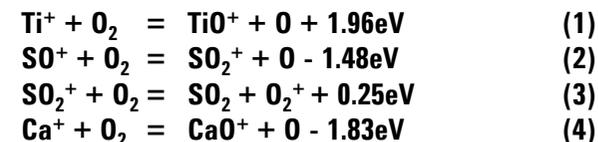


Figure 4. Principle of operation to detect ⁴⁸Ti by O₂ mode.

Experimental

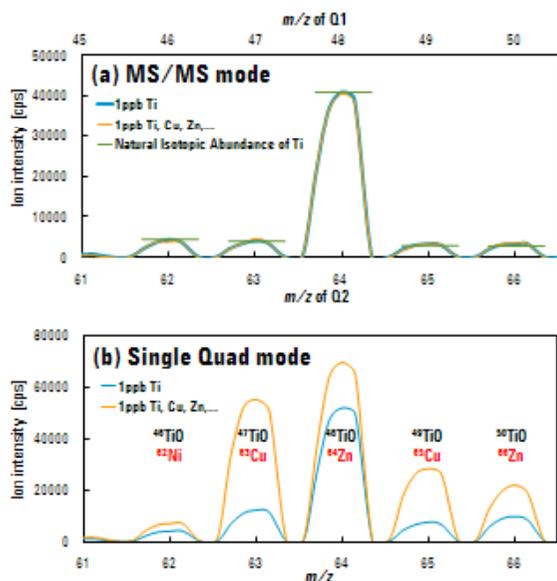


Figure 5. Spectra to measure Ti. Blue line; 1ppb Ti in 1% HNO_3
Orange line; 1ppb Ti, Cu, Zn, ... in 1% HNO_3
(a) MS/MS mode, (b) Single Quad mode

In general exothermic reactions are promoted in the cell while endothermic reactions are not. So Ti^+ reacts with O_2 cell gas to form TiO^+ rapidly (1) while SO^+ does not react (2). Once SO_2^+ is formed in the plasma, it is difficult to remove it in the cell (3), but the proposed system ensures its elimination by Q1 whose mass setting (m/z) is 48. Calcium (Ca) also has an isotope whose mass is the same as Ti, but Ca^+ doesn't react with O_2 cell gas rapidly due to its exothermic reaction under appropriate lenses and cell gas conditions (4).

Figure 6 shows the optimization of cell gas flow rate to minimize the background equivalent concentration (BEC) of ^{48}Ti . O_2 and He cell gases were swept while monitoring signal intensity of the standard (10ppb Ti in 10% H_2SO_4) and the blank (10% H_2SO_4). Minute O_2 gas flow less than 0.1 mL/min was sufficient to react Ti^+ with O_2 to form TiO^+ . Interestingly, He gas contributed to the reduction of background originating from sulfur-based interference (SO_2^+), dramatically maintaining the Ti sensitivity. The higher the He flow was set, the lower the background and BEC was achieved. This is because SO^+ is thermalized by collisions with He, which leads to suppression of the formation of SO_2^+ through the reaction (2). He gas also promotes the reaction (1) at a minute O_2 gas flow rate. Optimized O_2 and He cell gas flow rates were 0.07 mL/min and 12 mL/min respectively. Octopole bias voltage is also an important parameter to optimize the analytical conditions, and Figure 7 shows the BEC and sensitivity of Ti in 10% H_2SO_4 under various octopole bias conditions. Energy discrimination (voltage difference between octopole bias and Q2 bias) and deflector lens voltage are optimized to minimize the BEC at each octopole bias condition. As a result, the lowest BEC (~10ppt) was obtained at c.a. -20V octopole bias. At octopole bias voltages lower than -20V, the lower the voltage applied, the higher the resulting background count, which aggravated the BEC. This may be because interfering ions (SO_2^+) were not sufficiently thermalized at octopole bias conditions lower than -20V. At octopole bias voltages higher than -20V, the signal intensity of TiO^+ decreased significantly, which aggravated the BEC. Table 2 and Figure 8 show the experimental conditions and the calibration curve of ^{48}Ti respectively, which indicates strict linearity over very wide dynamic range (50ppt~10ppb).

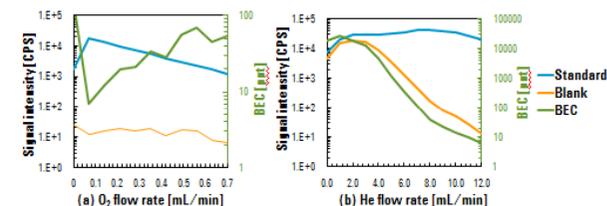


Figure 6. Cell gas flow rate vs. BEC and signal intensity of standard (10ppb Ti in 10% H_2SO_4) and blank (10% H_2SO_4) solution.

- (a) O₂ flow sweep, He flow rate is 12 mL/min (fixed)
- (b) He flow sweep, O₂ flow rate is 0.07 mL/min (fixed)

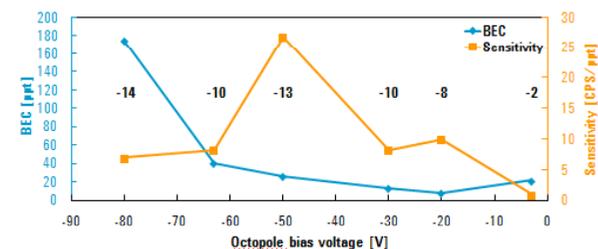


Figure 7. Octopole bias vs. BEC and sensitivity of Ti. Numbers described on each point are optimized energy discrimination. [V]

Table 2. Experimental conditions

Instrument	Agilent 8800 Breadboard
Nebulizer	MicroFlow PFA-100
Extraction lenses	s-model lens
RF power [W]	1550
Carrier gas flow [L/min]	0.73
Makeup gas flow [L/min]	0.47
Sampling depth [mm]	8.0
QP1 bias [V]	-5
Octopole bias [V]	-20
Energy discrimination [V]	-8
O₂ flow [mL/min]	0.07
He flow [mL/min]	12.0

Experimental

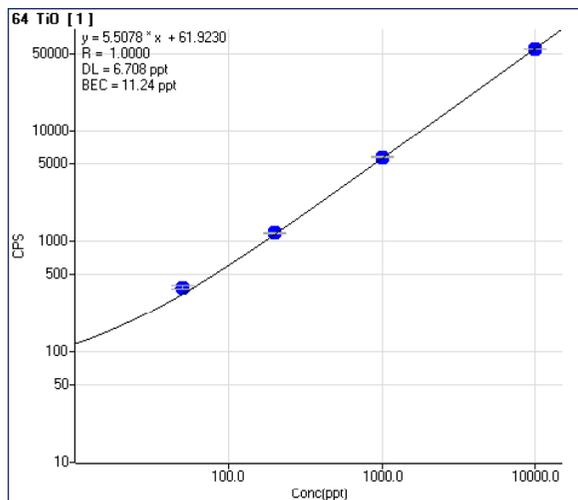
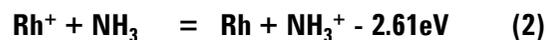
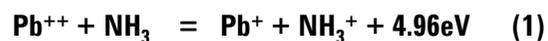


Figure 8. Calibration curve for Ti in 10% H₂SO₄

Rhodium (Rh) Detection in Lead (Pb) matrix by NH₃ Gas Mode

Rh is one of the platinum group elements(PGE) and typically low content of it is analyzed. Especially Rh determination in Pb button obtained via fire assay by ICP-MS is challenging because intense doubly charged Pb interference(²⁰⁶Pb⁺⁺) overlaps analyte Rh ion(¹⁰³Rh⁺). Figure 9 shows the principle of determination of Rh in Pb matrix by the proposed system. The following is the thermochemical equations of reaction between relevant ions and NH₃ cell gas:



Q1 whose mass setting(m/z) is 103 ensures the transmission of both Rh⁺ and Pb⁺⁺ and the elimination of the other ion species. In the cell pressurized by NH₃ gas interference ion Pb⁺⁺ extracted from Q1 receives an electron from NH₃ to form Pb⁺ by charge transfer reaction(1). While analyte ion Rh⁺ keeps its positive charge due to exothermic reaction(2) and does not react with NH₃ cell gas to form a product ion. Both Q1 and Q2 mass setting(m/z) is 103 but the proposed configuration has the advantage over the conventional ICP-MS in terms of simple reaction in the cell because Q1 can preselect the ion species that enter the cell, and reject the ions that may react with NH₃ to form new interfering products at m/z=103.

In order to simplify the experiment, 100ppm Pb matrix sample diluted in 1% nitric acid(HNO₃) was prepared and the performance of the proposed system was evaluated. Table 3 and Figure 10 show the experimental condition and the calibration line of Rh in 100ppm Pb matrix respectively. Even in high(100ppm) Pb matrix, the proposed system achieved 66cps/ppt in sensitivity and 44ppq in BEC, which is equivalent to 440pg/g Rh contained in Pb button assuming that 0.1mg Pb button is digested into 1g solution(100ppm Pb) without any condensation sample preparation.

In order to check the degree of matrix interference and suppression vs. cell gas flow rate, 100ppm and no Pb matrix sample were prepared and analyzed by the proposed system as indicated in Figure 11. When the cell gas flow is more than 2mL/min, most of interference ions are removed. Furthermore the sensitivity suppression caused by high Pb matrix is not so significant.

In order to monitor the charge transfer reaction of Pb⁺⁺ in the cell(1), 100 ppm Pb matrix sample was introduced to the proposed system whose Q1 mass setting is 103(fixed) to allow only Pb⁺⁺ to enter the cell and Q2 mass setting is 103 and 206 to monitor the signal of Pb⁺⁺ and Pb⁺ as indicated in Figure 12. As the increase of NH₃ flow rate, charge transfer reaction was promoted and the signal intensity of Pb⁺ increased while the interference ion Pb⁺⁺ which overlaps Rh⁺ decreased.

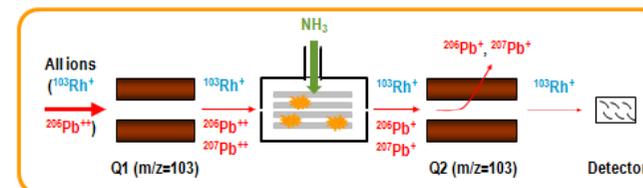


Figure 9. Principle of operation to detect Rh in Pb matrix by NH₃ mode.

Table 3. Experimental conditions

Instrument	Agilent8800 Lab. Proto.
Nebulizer	MicroMist
Extraction lenses	x-model lens
RF power [W]	1550
Carrier gas flow [L/min]	1.03
Makeup gas flow [L/min]	0
Sampling depth [mm]	8.0
QP1 bias [V]	0
Octopole bias [V]	-30
Energy discrimination [V]	-12
10% NH₃/He flow [mL/min]	5.0

Experimental

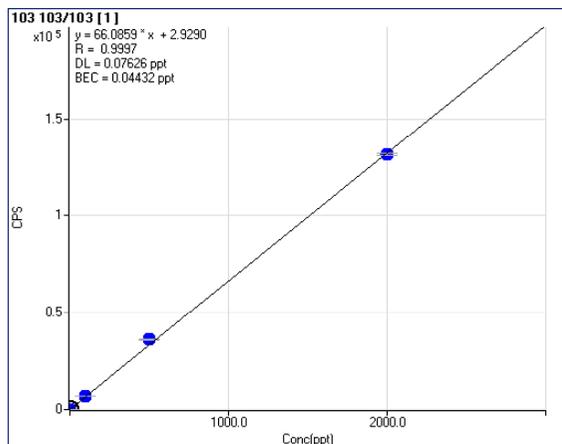


Figure 10. Calibration curve for Rh in 100 ppm Pb

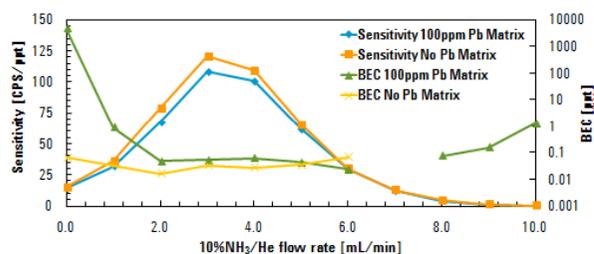


Figure 11. Cell gas flow rate vs. sensitivity and BEC of Rh for the comparison between 100 ppm and no Pb matrix

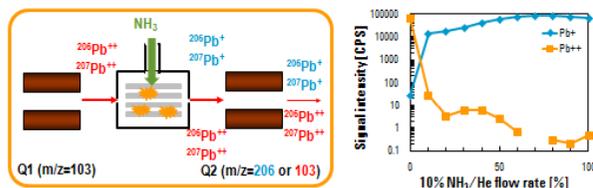


Figure 12. Monitoring of Pb⁺ formation in the cell as a result of charge transfer reaction(1)

Single Quad Mode

Single Quad mode in which Q1 is driven as an ion guide was evaluated by monitoring the sensitivity and BEC with varying SLG factor as indicated in Figure 12. The SLS factor was fixed to be 0.2 to check the performance of Single Quad mode and its performance was compared with that of MS/MS mode.

The heavier the monitored mass, the more sensitivity improvement at Single Quad mode over MS/MS mode was observed. This is because higher mass resolution is required at unit mass resolution scan when heavier masses are set. So, the ion transmission efficiency of heavier masses at Q1 is inferior to that of lighter mass in MS/MS mode. Single Quad mode can drive Q1 as a lower resolution ion guide than MS/MS mode and improve the ion transmission efficiency. More than twice the sensitivity can be expected at heavy mass elements. Another point is that the BEC is suddenly aggravated at SLG factors lower than 0.85 as indicated in Figure 12 (b). This is because intense ion current originated by Ar⁺, O₂⁺ and N₂⁺ are introduced to the cell under this condition some residual gas molecules such as water and hydrocarbons are ionized. Once such residual gas molecules whose mass is the same as the analyte's are ionized, they become interference ions and increase the background. So it is important to check not only the signal intensity of a standard sample but also the background when optimizing the tuning parameters in Single Quad mode.

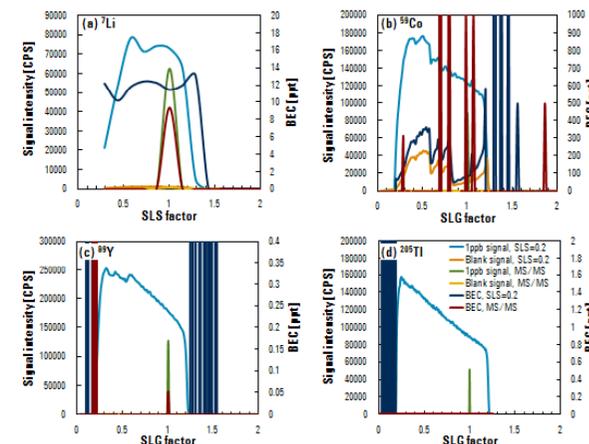


Figure 13. Comparison of signal intensity and BEC between Single Quad mode with various SLG factors and MS/MS mode.

(a) ⁷Li, (b) ⁵⁹Co, (c) ⁸⁹Y, (d) ²⁰⁵Tl

Conclusions

- A Triple quadrupole ICP-MS system has been developed, and the principles of operation and advantages of the proposed system with an additional quadrupole before the cell are explained.
- As an example, Ti detection which is exposed to Cu, Zn interferences were studied using O₂ cell gas and the advantages of the new system were explained by comparing the experimental results of MS/MS mode and Single Quad mode.
- Ti detection as a trace impurity in sulfuric acid was studied using O₂ cell gas. By adding He gas to the cell gas, sulfur-based interferences were dramatically reduced.
- As another example, Rh detection in Pb matrix which is exposed to doubly charged Pb interference was studied using NH₃ as the cell gas.
- Single Quad mode which is a compatible operation mode with the conventional cell-based ICP-MS system is explained. Its advantages (superior sensitivity for heavy mass elements) over MS/MS mode was studied and a caution which requires attention (sudden BEC increase) was explained.

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Introduction

ICP-MS equipped with collision/reaction cell is now the standard analytical technique for metallic impurities of materials including environmental samples, food, rocks, drinking water and chemicals. However, spectral interferences still create problems when determining several elements. Dilution or use of the minor isotope was the best choice to avoid such problems, however semiconductor industries in particular require higher detectability of elements in complex but highly pure chemicals. For example, on determination of Ti in H_2SO_4 , ^{47}Ti is chosen and ^{46}Ti is used for the analysis of H_3PO_4 ; what isotope of Ti should be used for analyzing the mixture of H_2SO_4 and H_3PO_4 ? In the example of phosphorus, P has only one isotope of ^{31}P which is susceptible to common HNO_3 spectral interference. Until now, the use of high resolution ICP-MS was the solution. This poster demonstrates how the new ICP Triple Quadrupole MS (ICP-QQQ) from Agilent can solve these issues.

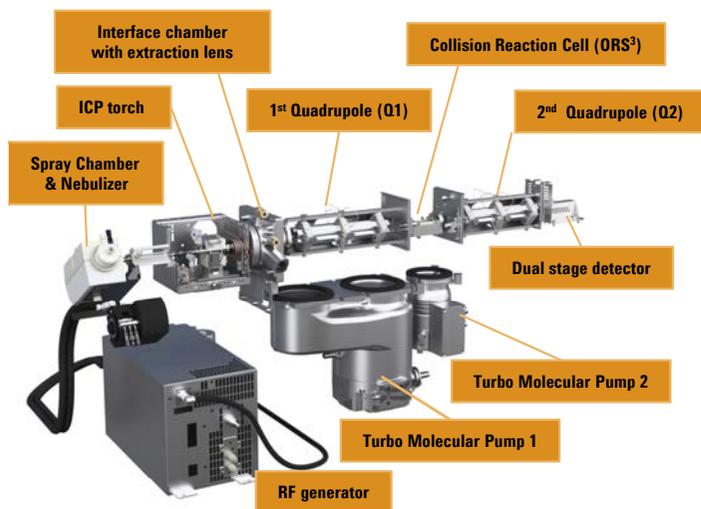


Figure 1. Configuration of Agilent ICP-QQQ

Experimental

Instrument

The Agilent ICP-QQQ as illustrated in Figure 1 was used, with hydrogen, oxygen and ammonia gases chosen as the reaction cell gas. PFA nebulizer, 2.5 mm injector (quartz or platinum) torch and spray chamber (quartz or PFA) were the sample introduction devices. The sample solution was introduced by self aspiration of the nebulizer. The sampling cone and skimmer cone were made of platinum with nickel. Metallic impurities of all the chemicals used for analysis were guaranteed to be less than 10 ppb by manufacturers.

Operating Conditions

- RF power: 1600 W
- Sampling depth: 8 mm
- Carrier gas flow rate: 0.8 L/min (Uptake is approx. 200mL/min)
- Makeup gas flow rate: 0.4 L/min
- ORS gas: 100% H_2 , 10% NH_3 balanced with He and 100% O_2
- Purity of ORS gases was higher than 99.995%.

Table 1. BEC of Phosphorus in UPW (0.8% HNO_3), ppb

	H_2	NH_3 with H_2	O_2
$^{31}P / ^{31}PH_3$	0.07	$^{31}P / ^{31}P^{14}NH_3$ 0.12	$^{31}P / ^{31}P^{16}O$ 0.10
$^{31}P / ^{31}PH_4$	0.08	$^{31}P / ^{31}P(NH_3)_2$ 0.10	$^{31}P / ^{31}P^{16}O^{16}O$ 0.20
H_2 flow rate	10 scc/min	NH_3 flow rate 0.5 scc/min H_2 flow rate 10 scc/min	O_2 flow rate 5 scc/min

Q1 was set at mass 31 to introduce ^{31}P and isobaric polyatomic ions, and Q2 was set at different masses to pass only product ions. Addition of hydrogen to the ammonia reaction cell enhanced the production of PNH_3 and $P(NH_3)_2$ ions.

Results and Discussion

Spectral interference by nitric acid, which is the major problem hampering P detection by conventional ICP-MS, was completely eliminated, as shown in Figure 2.

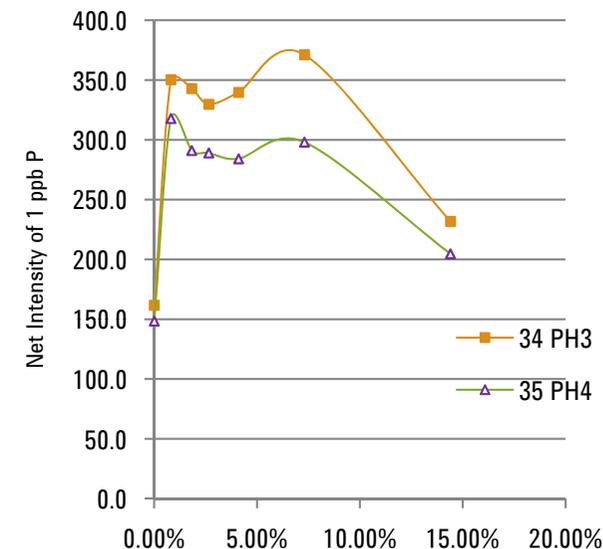


Figure 2. Effect of HNO_3 concentration on P signal

20% Hydrochloric Acid

The major spectral interferences found in Cl-matrices solution are $^{35}Cl^{16}O$ on ^{51}V , $^{35}Cl^{16}OH$ on ^{52}Cr , $^{37}Cl^{37}Cl$ on ^{74}Ge and $^{40}Ar^{35}Cl$ on ^{75}As . BECs and DLs of these elements shown below were obtained from 20% HCl.

	V	Cr	Ge	As
ORS Gas	NH_3	NH_3	O_2	O_2
Q1 / Q2	$^{51}V / ^{51}V$	$^{52}Cr / ^{52}Cr(NH_3)_2$	$^{74}Ge / ^{74}Ge^{16}O$	$^{74}Ge / ^{74}GeO_2$ / $^{75}As / ^{75}As^{16}O$
BEC, ppt	0.4	13	4	3
DL, ppt	0.4	8	1.5	2.5

Results and Discussion

10x Diluted Sulfuric Acid (9.8%)

BEC of phosphorus obtained from 9.8% H₂SO₄ by ICP-QQQ reaction mode was compared with that of conventional He collision mode. NH₃, H₂ and O₂ reaction gases provided similar BECs.

Mode	NH ₃		H ₂	O ₂
Q1 / Q2	³¹ P / ³¹ PNH ₃	³¹ P / ³¹ P(NH ₃) ₂	³¹ P / ³¹ PH ₄	³¹ P / ³¹ P ¹⁶ O
BEC, ppb	0.16	0.15	0.16	0.14
7700s He	20 ppb			

H₂SO₄ is well known to create troublesome polyatomic ions which make it difficult to determine some elements at ppt levels. Spectral interferences of ³²S¹⁶O on ⁴⁸Ti and of ³⁴S¹⁶OH on ⁵¹V could be avoided by using NH₃ gas reaction for determination. However, appropriate reactions were not found to create product ions of Cr and Zn. For determination of these elements, He collision is still the best choice to avoid spectral interferences of ³⁶S¹⁶O and S₂ ions.

	⁴⁸ Ti	⁵¹ V	⁵² Cr	⁶⁸ Zn		
Mode	QQQ reaction	QQQ reaction	QQQ reaction	He collision	QQQ reaction	He collision
Product ion	TiNH ₃	V	CrNH ₃	Cr	ZnNH ₃	Zn
BEC, ppt	2	0.1	50	6	1.5	1
7700s He	60	3	8		1	

Results and Discussion

2000ppm Si matrix

Most manufacturers of semiconductor devices routinely analyze Si VPD samples which sometimes contain high Si matrix. Si matrix as high as 2000 ppm produces polyatomic ions of Si that interfere with P and Ti. Elimination of these interferences is shown below. A low uptake nebulizer (50 mL/min) and robust plasma conditions were applied. Si solution was made from Si wafer, but the solution may have been contaminated.

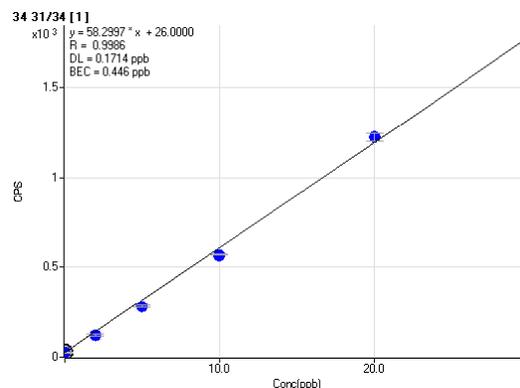


Figure 3. Calibration Curve of Phosphorus

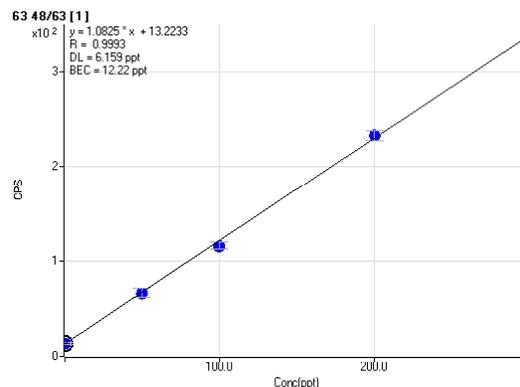


Figure 4. Calibration curve of Titanium

Conclusions

ICP-QQQ works very well to avoid spectral interferences which could not be solved by conventional collision/reaction technology. It makes it possible to determine ultra trace impurities even in complex mixtures of high purity chemicals such as HF, HNO₃, H₂SO₄ and H₃PO₄.

Introduction

Long-lived radionuclides have been released continuously into the environment as a result of human nuclear activities such as nuclear weapons tests, accidents at nuclear power plants, and by emissions from spent nuclear fuel reprocessing plants. Inductively coupled plasma mass spectrometry (ICP-MS) is often used for the analysis of these radionuclides.

I-129: Iodine-129 is a long-lived radionuclide (half life $T_{1/2} = 15.7$ My). The determination of iodine-129 in environmental samples is very difficult by ICP-MS due to its relatively low sensitivity, high background caused by ^{129}Xe impurities in the argon plasma gas, and possible polyatomic interference from $^{127}\text{IH}_2^+$. We showed at the Winter Plasma Conference (WPC) 2011 that the isobaric interference from $^{129}\text{Xe}^+$ could be significantly reduced, resulting in a measured ratio for $^{129}\text{I}/^{127}\text{I}$ of 10^{-7} in NIST 3231 SRM Level I. Although good linearity, low background equivalent concentrations (BEC) and detection limits (DL) (3σ , $n=10$) for both ^{127}I and ^{129}I were obtained using external calibration, the problem of poor abundance sensitivity of ICP-MS still remained.

Pu: Plutonium is also a long-lived radionuclide (half life $T_{1/2} = 24,100\text{y}$ for Pu-239, 6,563y for Pu-240). Analysis of plutonium in environmental samples is needed for dosimetric reasons, especially in the case of nuclear accidents. Because of the good sensitivity, short analysis time and $^{238}\text{Pu}/^{239}\text{Pu}/^{240}\text{Pu}/^{242}\text{Pu}$ isotopic information, ICP-MS has become a plausible alternative and complement to alpha spectroscopy. However, the accurate determination of plutonium by ICP-MS is hampered by severe spectral interferences from polyatomic molecules in the plasma such as $^{238}\text{UH}^+$, $^{238}\text{UH}_2^+$, which interfere with ^{239}Pu and ^{240}Pu . and by the peak tailing of an abundant $^{238}\text{U}^+$ ion.

Introduction

The relatively poor abundance sensitivity of conventional ICP-MS is a problem of particular importance for ultra low-level analysis of elements such as radionuclide elements which are adjacent in mass to elements of much higher natural abundance.

In this study, in order to overcome the challenges due to the relatively poor abundance sensitivity of conventional ICP-single quadrupole MS, a newly developed triple quadrupole ICP-MS technique using oxygen and ammonia as the reaction cell gases was applied to determine ultra-trace levels of those elements in aqueous samples. We aimed to improve the measurable ratio of $^{129}\text{I}/^{127}\text{I}$ and lower the detection limit for ^{129}I without loss of abundance sensitivity.

Experimental



Figure 1. Configuration of Agilent ICP-QQQ

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 $<0.2\text{cps}$
- Abundance sensitivity is immeasurably low: $<10^{-9}$
- Maintains Agilent 7700 compatible robustness and durability, being applicable to developed Agilent 7700 applications

Experimental

Reference Materials and Calibration Standards

For the analysis of Iodine, NIST (National Institute of Standards & Technology, Gaithersburg MD, USA) Standard Reference Material 3231, Iodine-129 Isotopic Standards, Level I and II, were used as calibration standards by diluting with de-ionized Milli-Q water and 0.5% TMAH. Level I Certified Value for $^{129}\text{I}/^{127}\text{I} = 0.981 \times 10^{-6} \pm 0.012 \times 10^{-6}$, Level II = $0.982 \times 10^{-8} \pm 0.012 \times 10^{-8}$. These reference materials were used to check the linearity of the Iodine isotopes and to validate the isotopic ratio of Iodine-129 and Iodine-127.

In order to demonstrate the analysis of plutonium, Tl and Bi were monitored as surrogates for plutonium because radionuclide samples, even if they are reference materials, are difficult to obtain in Japan due to strict government controls.

Results and Discussion

a) Analysis of ratio of $^{129}\text{I}/^{127}\text{I}$

Xe^+ Background Removal by Reaction with O_2

Figure 2 compares the plasma background spectrum in no gas mode versus high energy oxygen mode using single quad mode on the ICP-QQQ. Oxygen reacts with xenon ions via charge transfer ($\text{Xe}^+ + \text{O}_2 \rightarrow \text{Xe} + \text{O}_2^+$, $k_r = 1.1 \text{ e}^{-10}$). As a result, the isobaric interference from $^{129}\text{Xe}^+$ is significantly reduced to the level of the instrument background, resulting in a measured ratio for $^{129}\text{I}/^{127}\text{I}$ of 10^{-7} in NIST 3231 SRM Level I. Although good linearity, low background equivalent concentrations (BEC) and detection limits (DL) ($3\sigma, n=10$) for both ^{127}I and ^{129}I were obtained using external calibration, the problem of poor abundance sensitivity of I single quad mode still remained as shown in Figure 2b.

Results and Discussion

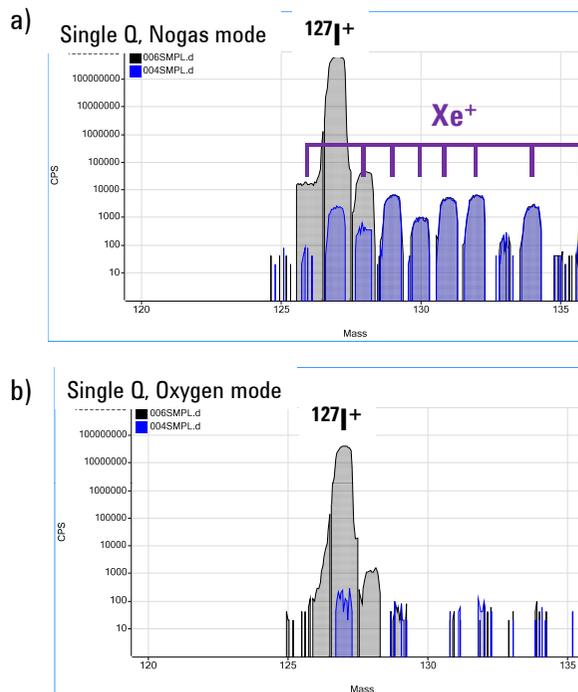


Figure 2. Mass spectra of I and Xe in 8.89mg/L Iodine-127 solution. a) conventional no cell gas mode, b) high energy O_2 mode with single quad MS.

Abundance sensitivity

Iodine spectra from NIST 3231 and a blank solution for both ^{127}I and ^{129}I are shown in Figure 3. As shown, superior abundance sensitivity (no tailing) is obtained using MS/MS mode without sensitivity loss or interference from the adjacent peak.

Calibration Curves for ^{127}I and ^{129}I

In order to check the linearity of both isotopes, diluted NIST 3231 SRM in different concentrations in 0.5% TMAH alkaline solutions were analyzed as calibration standards. Calibration curves are shown in Figure 4. From Figure 4, the BEC for ^{129}I was 0.04ng/L and the detection limit ($3\sigma, n=10$) for ^{129}I was 0.07ng/L.

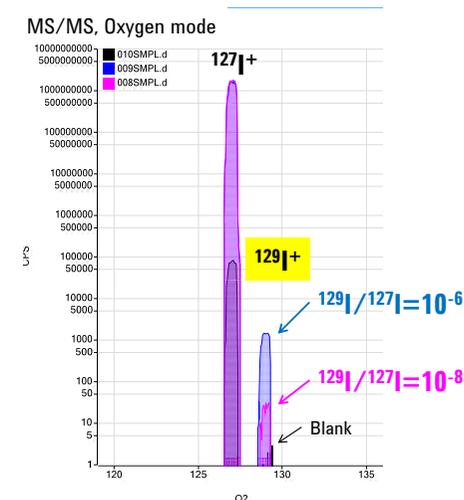


Figure 3. Iodine spectrum for both ^{127}I and ^{129}I by MS/MS mode.

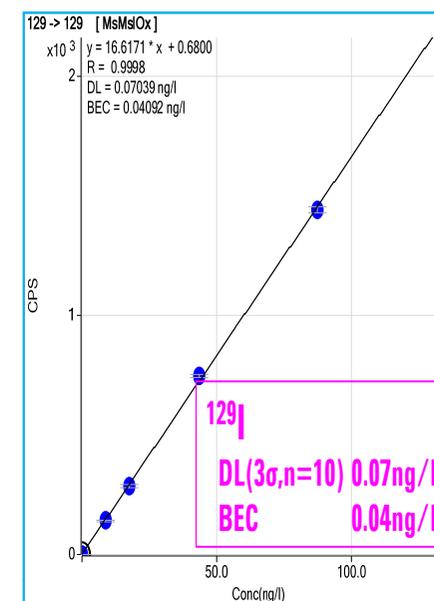


Figure 4. Calibration curve for ^{129}I obtained from diluted NIST 3231 SRM (Level I).

Results and Discussion

Analysis of NIST 3231 SRM Level I ($^{129}\text{I}/^{127}\text{I} = 0.981 \times 10^{-6}$) and Level II ($^{129}\text{I}/^{127}\text{I} = 0.982 \times 10^{-8}$)

The $^{129}\text{I}/^{127}\text{I}$ ratio of diluted NIST 3231 SRM at different concentrations was analyzed using ICP-QQQ. The results are summarized in Table 1. After subtracting the ^{129}I blank, the measured $^{129}\text{I}/^{127}\text{I}$ ratio of NIST 3231 SRM corresponded well with the certified value of 0.981×10^{-6} and 0.982×10^{-8} as reported in the certificate.

Table 1. Analytical results of NIST 3231 Level I and Level II

Sample Name	Dilution Factor	127 -> 127 [MsMs Ox]			129 -> 129 [MsMs Ox]			$^{129}\text{I}/^{127}\text{I}$	$^{129}\text{I}/^{127}\text{I}$ (average, n=5)	RSD(%)
		CPS	CPS average	CPS RSD	CPS	CPS average	CPS RSD			
NIST3231 10^{-6} ($^{129}\text{I}/^{127}\text{I} = 0.981 \times 10^{-6}$)	20	301,734,441	302,731,524	0.6	297.1	290.5	3.6	9.72E-07	0.947×10^{-6}	4.1
		303,368,628			274.8			8.93E-07		
		300,284,575			300.5			9.88E-07		
		305,488,255			285.9			9.23E-07		
		302,781,721			294.4			9.60E-07		
	10	594,277,896	592,626,739	0.3	585.6	589.4	0.8	9.71E-07	0.981×10^{-6}	0.8
592,633,576	597.4	9.94E-07								
590,000,723	586.5	9.80E-07								
593,387,443	588.5	9.78E-07								
592,834,056	588.9	9.79E-07								
NIST3231 10^{-8} ($^{129}\text{I}/^{127}\text{I} = 0.982 \times 10^{-8}$)	10	608,737,949	605,248,499	0.5	15.1	14.5	3.3	1.12E-08	1.02×10^{-8}	7.2
		608,536,242			14.8			1.07E-08		
		602,626,536			14.2			9.79E-09		
		603,091,763			13.9			9.29E-09		
		603,250,003			14.5			1.03E-08		

b) Possibility of MS/MS for Analysis of Pu, Am, ... in U, Pb (HCl) matrix solution

Reduction of UH⁺ interference for Pu analysis by reaction with NH₃

Since an appropriate SRM for Pu was not available due to Japanese government regulations, we investigated the behavior of UH⁺ and Bi⁺ by MS/MS with NH₃, assuming that the behavior of Pu⁺ is similar to Bi⁺.

Results and Discussion

As shown Figure 5, the abundance of UH⁺ interference ions was reduced by over five orders of magnitude via reaction with NH₃(+He) gas, while the Bi⁺ (also Tl⁺) intensity was reduced about one order. Good abundance sensitivity gave us no effect on m/z = 239 from m/z = 238. As a result, it is thought that the analysis of several radioactive isotopes of Pu and Am which are affected by high concentrations of U may be possible using ICP-QQQ.

Conclusions

Using the newly developed triple quadrupole ICP-MS (ICP-QQQ), we demonstrated good analytical performance for radionuclide analysis using the highly selective MS/MS mode with the collision/reaction cell which resulted in superior abundance sensitivity:

- $^{129}\text{Xe}^+$ background ions were significantly reduced by oxygen reaction
- Achieved analysis of $^{129}\text{I}/^{127}\text{I}$ ratio of c.a. 1×10^{-6} and 1×10^{-8} ratio in NIST 3231 SRM Level I (certified value of $^{129}\text{I}/^{127}\text{I} = 0.981 \times 10^{-6}$). and Level II (certified value of $^{129}\text{I}/^{127}\text{I} = 0.982 \times 10^{-8}$)
- Calibration curves for ^{127}I , and ^{129}I show excellent linearity. This means that external calibration can be routinely applied to the analysis of ^{127}I and ^{129}I
- Detection limits (3σ , n = 10) for ^{127}I and ^{129}I were 9.6ng/L, and 0.07ng/L, respectively.
- Demonstrated the possibility of analyzing plutonium (and other Actinide elements) in high concentration Pb, U matrix samples (HCl solution) by reducing UH⁺ ions

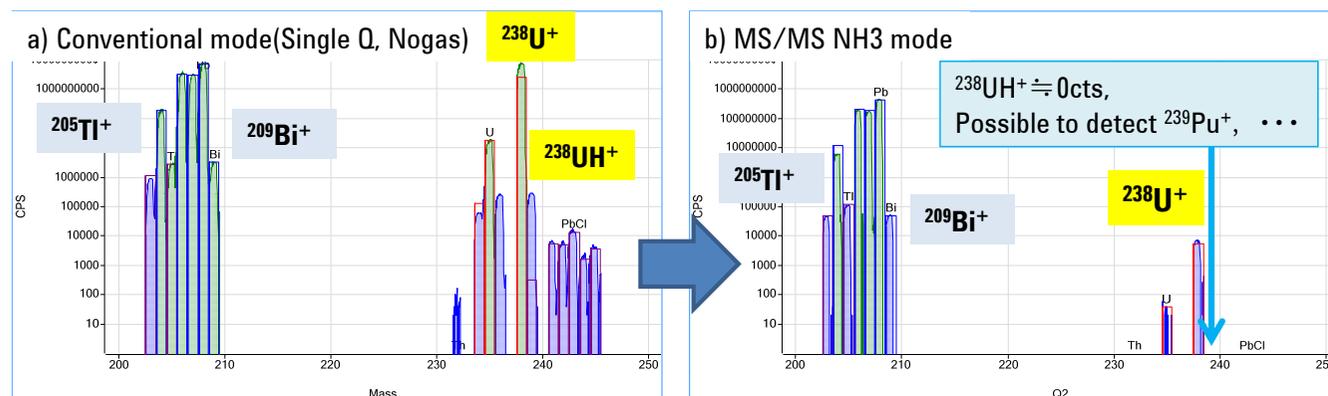


Figure 5. Mass spectra of sample solution including U, Pb (20mg/L) and Tl, Bi (10µg/L) in 2%HCl/1%HNO₃. Mass spectra obtained using a) conventional mode (single quadrupole, No gas mode) and b) MS/MS mode using NH₃ gas as reaction gas.

Conclusion

We succeeded in significantly improving the measurable ratio of $^{129}\text{I}/^{127}\text{I}$ and lowering detection limit for ^{129}I without a loss of abundance sensitivity in aqueous environmental samples using the Agilent 8800 ICP-QQQ

For future work, we are planning to investigate the performance for radionuclide CRMs and real samples.

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.

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 ⁺⁺	

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

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

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, H₂ and NH₃+H₂ modes, they were detected as SeO⁺ in O₂+H₂ mode. In this mode, Se⁺ reacts with O₂, 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 O₂ is endothermic ($\Delta H_r=0.769$ eV), however, the reaction was promoted through the application of an octopole bias of -18 V, effectively forming SeO⁺. Addition of small amount of H₂ into the cell was found to be effective at further reducing the BEC.

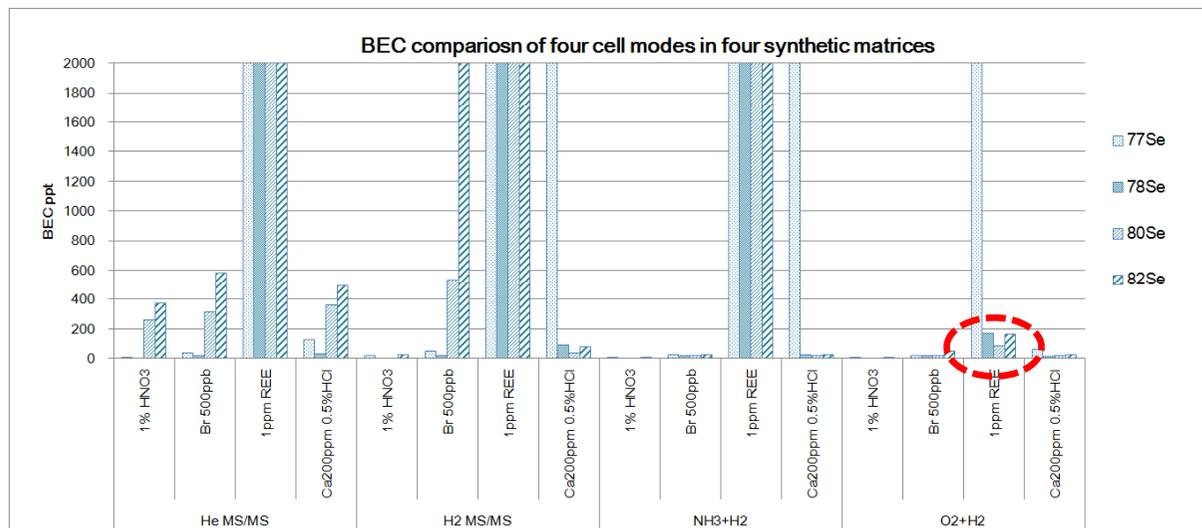


Figure 2. Result of interference removal capability study

From Figure 2, we can see O₂+H₂ mass shift method gives the best interference removal capability, allowing for the measurement of three Se isotopes, ⁷⁸Se, ⁸⁰Se and ⁸²Se nearly free from interference. O₂ 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.

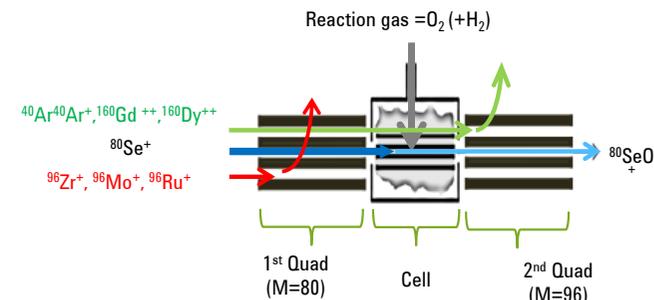


Figure 3. Illustration of O₂ mass shift method of ICP-QQQ

Selenium Online Isotope Dilution Analysis (OIDA)

A ⁸²Se enriched standard (⁸²Se 97.43%, ⁸⁰Se 1.65% and ⁷⁸Se 0.51%) was purchased from Oak Ridge National Laboratory. The standard was dissolved in ultrapure HNO₃, 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.

$$C_x = C_r \left(\frac{r_{R_m} - R_s}{R_m - R_s} \right) \left(\frac{R_s - R_m}{R_x - r_{R_m}} \right) \quad [1]$$

R_m : measured isotope ratio of mixed reference standard and spike solution
 r_{R_m} : measured isotope ratio of mixed unknown sample and spike solution
 C_x : concentration of unknown sample
 C_r : concentration of natural reference standard
 R_s : natural isotope ratio
 R_x : isotope ratio of spike

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 $C_x \approx C_r$ is met². Theoretically the error = 0 when $C_x = C_r$ 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 $C_x \ll C_r$ or $C_x \gg C_r$. 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 ⁸²Se/⁷⁸Se suffers from a severe mass bias effect, there was a larger uncertainty in the determined concentration.

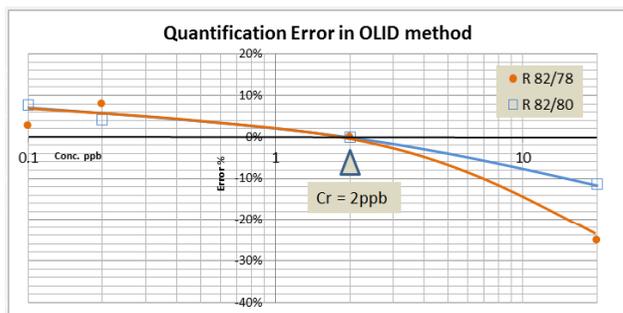


Figure 4. Quantification error of ID method

Se analysis by OIDA using O₂+H₂ 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 HNO₃, HCl and H₂O₂. 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.

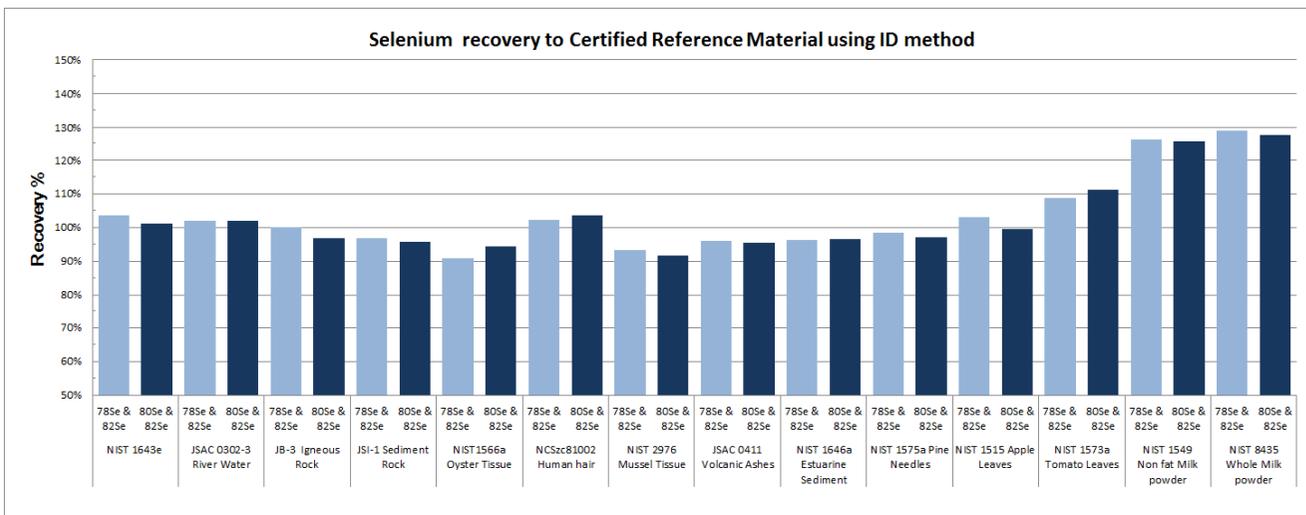


Figure 5. Results of Se analysis in CRMs by OIDA using O₂+ H₂ mass shift method of ICP-QQQ

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

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