New Reaction Cell ICP-MS with Improved Ion Optics Arrangement and Vacuum System

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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 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 proposed configuration can dramatically reduce the spectroscopic interferences as well as background noise.

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

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

Hardware Configuration

Ion Optics Arrangement

Fig. 1 shows the comparison of hardware configuration 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 proposed system has a first quadrupole termed as "Quadrupole1 (Q1)" and related electrostatic ion lenses at the entrance and the exit of Q1, and they are located between the ion extraction lenses and the collision/reaction cell(ORS). The quadrupole downstream of the cell is termed as "Quadrupole2(Q2)", whose design is the same as that of 7700's quadrupole. All the ion lenses including off-axis ion extraction lenses and collision reaction cell which are used in 7700 are also used in the proposed system, so that the tuning parameters of the proposed system except for Q1 are almost compatible with those of 7700.

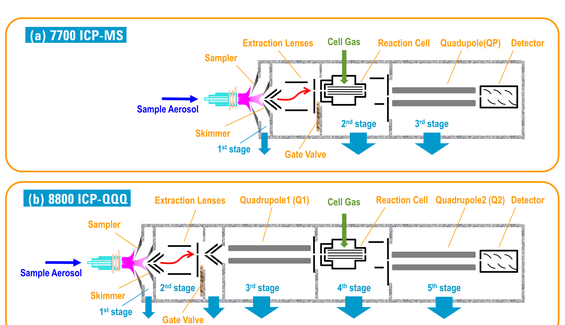

Fig. 1 Comparison of hardware configuration between the conventional cell-based ICP-MS(a) and the proposed ICP-QQQ(b).

Vacuum System

The ion source of ICP-MS is inductively coupled plasma (ICP) in atmospheric pressure. The ICP including analyte ions are required to be sampled and extracted through the interface region from the atmospheric pressure 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 is proposed. Usually a rotary oil pump is adopted to evacuate the interface region roughly down to hundreds Pascal order, and turbo molecular pump (TMP) evacuates subsequent vacuum stages at the pressures in the orders of 10^{-2}~10^{-5} Pa. Another point is that various collision/reaction gases are introduced into the cell which are located at the intermediate vacuum stage in differential pumping system. Especially in ICP-MS, relatively high flow rate (~15mL/min) and low-molecular-weight gases such as H_2 or He which TMP doesn't work well to pump down are often used as collision/reaction gases. 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 proposed system was considered to be tailored to ICP-QQQ configuration, and a 5 stage vacuum system has been adopted while that of 7700 is a 3 stage as indicated in Fig. 1. In the proposed system the chambers where extraction lenses and Q1 are installed are divided and pumped down independently as 2nd and 3rd stages on the proposed system while extraction lenses and cell are installed in the same vacuum stage on 7700.

Table 1 shows the comparison of pressure and mean free path of Ar ion colliding with Ar gas molecule at each vacuum region. Compared to the cell, quadrupole requires 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 Q1 chamber if a 4 stage vacuum system is adopted. By dividing the chamber for extraction lenses and Q1, Ar gas flow into 3rd stage can be dramatically reduced because most of Ar gas entering into the 2nd stage through the skimmer orifice is evacuated by the pump attached to 2nd stage, so that the pressure in 3rd stage can be approximately 5×10^{-4} Pa which is about 40 times lower pressure 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

Fig. 2 shows the comparison of principle of operation between the proposed system and the conventional cell-based ICP-MS. On conventional ICP-MS all ions generated in the ion source enter the cell pressurized by various cell gases, and some of interference ions can be removed. On the other hand the proposed system equips 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. 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.

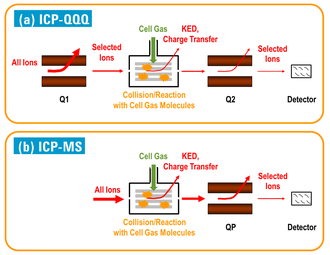

Fig. 2 Comparison of principle of operation between the proposed ICP-QQQ(a) and the conventional cell-based ICP-MS(b).

Single Quad Mode

Not all analytes suffer from spectral interferences that need to be remove by MS/MS operation. However, their sensitivity must be compromised in MS/MS mode compared with the conventional ICP-MS due to decrease of 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 mass filter improves ion transmission efficiency at Q1 and works as a conventional ICP-MS without sacrificing sensitivity of the analytes which does not suffer spectral interferences.

Fig. 3 shows the scan line of Q1 working in Single Quad mode and the stability diagram of quadrupole. 2 parameters, termed as "Scan Line Slope(SLS) factor" and "Scan Line Gain(SLG) factor", determine the operating condition of Q1 in Single Quad mode. SLS factor, setting U voltage relative to that for unit mass resolution, governs the degree of bandpass mass width. In general the lower SLS factor is set, the broader bandpass mass width is realized. If SLS factor is set to be 0, Q1 is driven as an RF only quadrupole, that is, a high pass filter with low mass cut-off. SLG factor, setting V voltage relative to that for unit mass resolution, governs the position of bandpass window. The lower SLG factor is set, the lower mass band pass window moves toward. If Q1 is driven as RF only quadrupole, the lower SLG factor, the lower the cut-off mass of this high pass filter.

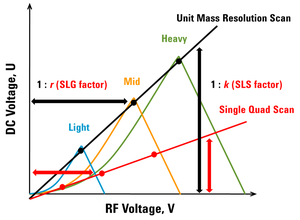

Fig. 3 Scan line and stability diagram of quadrupole.
Black line; scan line for unit mass resolution scan
Red line; scan line of Q1 for single quad scan

Experimental

Titanium(Ti) Detection by O_2 Gas Mode

Fig. 5 shows the principle of detection for ^{48}Ti by the proposed system and a conventional ICP-MS using O_2 as cell gas.

One of the challenges to detect Ti as TiO is to measure the sample in which zinc(Zn) or nickel(Ni) coexist with Ti. Ti whose major isotope is 48u is detected as its oxide(TiO) whose mass is 64u. However, Zn and Ni also have isotopes whose mass is 64u and overlap analyte(TiO^+) spectrum as atomic interferences on a conventional ICP-MS. On the proposed system Q1 whose mass setting(m/z) is 48 ensures their elimination, so it can measure Ti as TiO^+ without suffering from the interferences originated from Zn and Ni. In order to check the benefit of MS/MS capability, 1ppb Ti sample ,and 1ppb Ti with 1ppb Cu and Zn sample were prepared and acquired their mass spectra on MS/MS mode(a) and Single Quad mode(b) by the proposed system. On Single Quad mode(b) emulating the conventional ICP-MS Cu and Zn interferences overlap on the all isotopes of Ti spectrum. On the other hand, MS/MS mode removes such interferences by Q1 and the spectrum agrees with the natural isotopic abundance of Ti.

Another challenge is to measure Ti containing as a trace impurity in sulfuric acid(H_2SO_4) because Ti^+ is exposed to intense sulfur-based interference ions(SO^+). But on the proposed system the ion-molecule reactions in the cell are predictable to an extent as Q1 can control the ion species entering the cell. The following is the thermochemical equations of reaction between relevant ions and O_2 cell gas;

$$Ti^+ + O_2 = TiO^+ + O + 1.96eV \quad (1)$$
$$SO^+ + O_2 = SO_2^+ + O - 1.48eV \quad (2)$$
$$SO_2^+ + O_2 = SO_3 + O_2^+ + 0.25eV \quad (3)$$
$$Ca^+ + O_2 = CaO^+ + O - 1.83eV \quad (4)$$

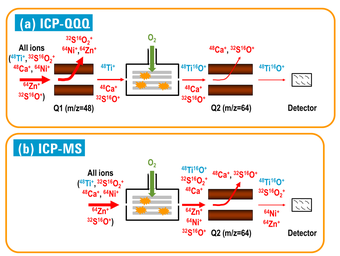

Fig. 4 Principle of operation to detect ^{48}Ti by O_2 mode.

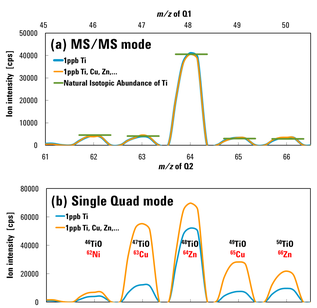

Fig. 5 Spectra to measure Ti.
Blue line; 1ppb Ti in 1% HNO_3
Orange line; 1ppb Ti, Cu, Zn, ... in 1% HNO_3
(a)MS/MS mode, (b)Single Quad mode

In general exoothermic 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^+ are formed in the plasma, it is difficult to remove them in the cell(3), but the proposed system ensures their 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).

Fig. 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 0.1mL/min was sufficient to react Ti^+ with O_2 to form TiO^+. Interestingly, He gas contributed to the reduction of background originated from sulfur-based interference(SO_2^+) dramatically, maintaining the Ti sensitivity. The higher He flow was set, the lower 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 0.07mL/min and 12mL/min respectively. Octopole bias voltage is also the important parameter to optimize the analytical condition, and Fig. 7 shows the BEC and sensitivity of Ti in 10% H_2SO_4 under the various octopole bias condition. Energy discrimination(voltage difference between octopole bias and Q2 bias) and deflect lens voltage are optimized to minimize the BEC at the octopole bias condition. As a result lowest BEC(~10ppt) was acquired at c.a. -20V octopole bias. At octopole bias voltage lower than -20V, the lower voltage was applied, the higher background count rate was originated, which aggravated BEC. This may be because interference ions(SO_2^+) were not sufficiently thermalized at the octopole bias condition lower than -20V. At octopole bias voltage higher than -20V, the signal intensity of TiO^+ decreased significantly, which aggravated BEC. Table 2 and Fig. 8 show the experimental condition and the calibration curve of ^{48}Ti respectively, which indicates strict linearity in very wide dynamic range(50ppt~10ppb).

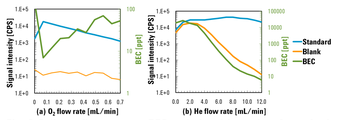

Fig. 6 Cell gas flow rate vs. BEC and signal intensity of standard (10ppb Ti in 10% H_2SO_4) and blank(10% H_2SO_4) solution.
(a)O_2 flow sweep, He flow rate is 12mL/min(fixed)
(b)He flow sweep, O_2 flow rate is 0.07mL/min(fixed)

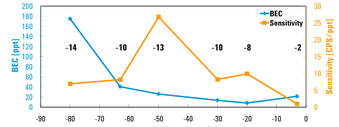

Fig. 7 Octopole bias vs. BEC and sensitivity of Ti. Numbers described on each point are optimized energy discrimination. [V]

Table 2 Experimental condition.

Instrument	Agilent8800 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
OP1 bias [V]	-5
Octopole bias [V]	-20
Energy discrimination [V]	-8
O2 flow [mL/min]	0.07
He flow [mL/min]	12.0

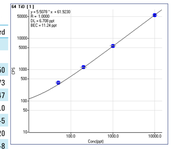

Fig. 8 Calibration curve for Ti in 10% H_2SO_4.

Rhodium(Rh) Detection in Lead(Pb) matrix by NH_3 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($^{206}Pb^{++}$) overlaps analyte Rh ion($^{103}Rh^+$). Fig. 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 NH_3 cell gas;

$$Pb^{++} + NH_3 = Pb^+ + NH_3^+ + 4.96eV \quad (1)$$
$$Rh^+ + NH_3 = Rh + NH_3^+ - 2.61eV \quad (2)$$

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 NH_3 gas interference ion Pb^{++} extracted from Q1 receives an electron from NH_3 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 NH_3 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 NH_3 to form new interfering products at m/z=103.

In order to simplify the experiment, 100ppm Pb matrix sample diluted in 1% nitric acid(HNO_3) was prepared and the performance of the proposed system was evaluated. Table 3 and Fig. 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 Fig. 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), 100ppm 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 Fig. 12. As the increase of NH_3 flow rate, charge transfer reaction was promoted and the signal intensity of Pb^+ increased while the interference ion Pb^{++} which overlaps Rh^+ decreased.

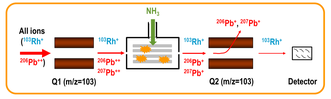

Fig. 9 Principle of operation to detect Rh in Pb matrix by NH_3 mode.

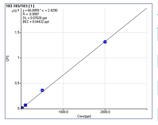

Fig. 10 Calibration curve for Rh in 100ppm Pb matrix.

Table 3 Experimental condition.

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
OP1 bias [V]	0
Octopole bias [V]	-30
Energy discrimination [V]	-12
10% NH_3/He flow [mL/min]	5.0

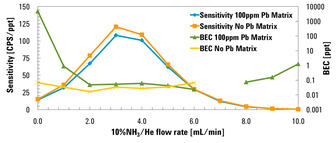

Fig. 11 Cell gas flow rate vs. sensitivity and BEC of Rh for the comparison between 100ppm and no Pb matrix.

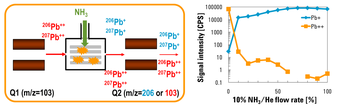

Fig. 11 Monitoring of Pb^+ formation in the cell as a result of charge transfer reaction(1).

Single Quad Mode

Single Quad mode in which Q1 is driven as an ion guide was evaluated by monitoring the sensitivity and BEC with sweeping SLG factor as indicated in Fig. 12. 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 mass is monitored, the more sensitivity improvement at Single Quad mode over MS/MS mode was observed. This is because the higher mass resolution is required at unit mass resolution scan when the heavier mass is set. So ion transmission efficiency of heavier mass 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 and more than twice the sensitivity can be expected at heavy mass element. Another point is that the BEC is suddenly aggravated at the SLG factor lower than 0.85 as indicated in Fig. 12 (b). This is because intense ion current originated by Ar^+, O_2^+ and N_2^+ are introduced to the cell at this condition and ionized some residual gas molecules such as water and hydrocarbons. Once such residual gas molecules whose mass is the same as analyte's are ionized, they become interference ions and increase the background. So it is important to check not only the signal intensity of standard sample but also the background when optimizing the tuning parameter concerning the Single Quad mode.

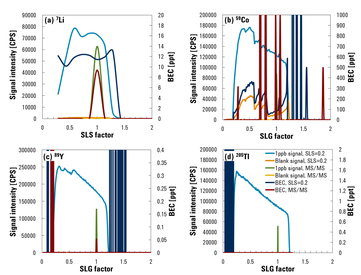

Fig. 9 Comparison of signal intensity and BEC between Single Quad mode with various SLG factor and MS/MS mode.
(a) ^{7}Li, (b) ^{59}Co, (c) ^{89}Y, (d) ^{205}Tl

Conclusion

- Triple quadrupole ICP-MS system was newly developed, and the principle of operation and the advantage of the proposed system which has an additional quadrupole before the cell are explained.
- As an example, Ti detection which is exposed to Cu, Zn interferences are studied using O_2 cell gas and the advantage of the proposed system are explained by comparing the experimental result of MS/MS mode and Single Quad mode.
- Ti detection as a trace impurity in sulfuric acid is studied using O_2 cell gas. By adding He gas to the cell gas, sulfur-based interference was dramatically reduced.
- As another example, Rh detection in Pb matrix which is exposed to doubly charged Pb interference are studied using NH_3 as cell gas.
- Single Quad mode which is a compatible operation mode with the conventional cell-based ICP-MS system are explained. Its advantage(superior sensitivity of heavy mass element) over MS/MS mode are studied and a caution to which should be paid attention(sudden BEC increase) are explained.