

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.

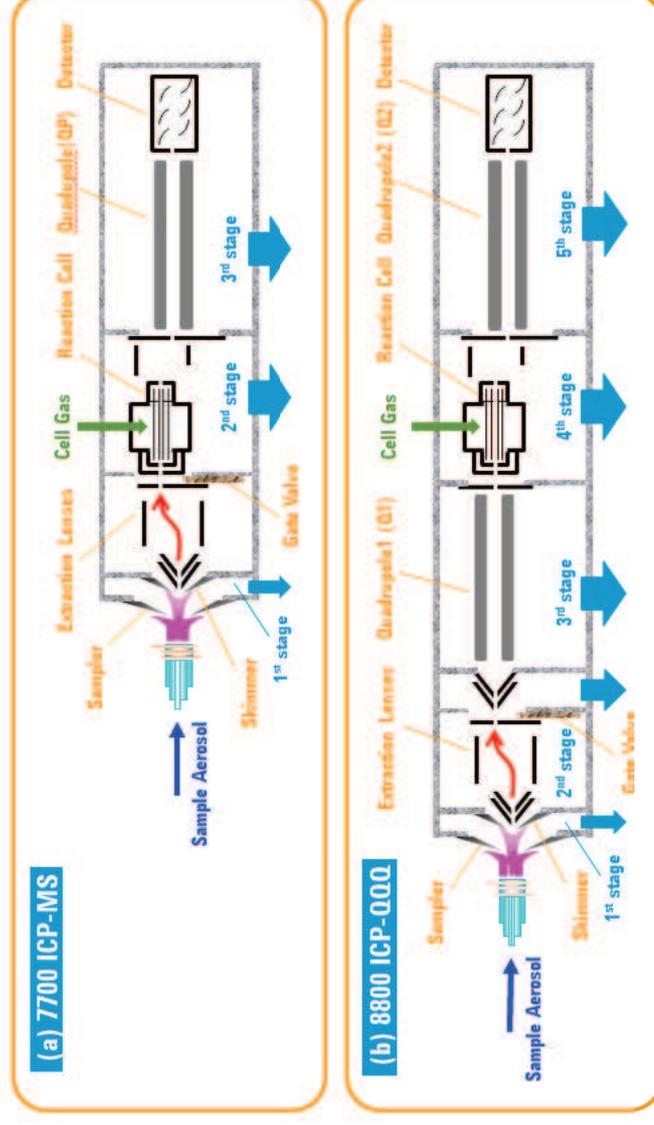


Figure 1. Comparison of hardware configuration between the conventional cell-based ICP-MS(a) and the proposed ICP-QQQ(b).

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 | | | | |
|---|--------------------|----------------------|--------------------|--------------------|
| Interface chamber | Pressure [Pa] | Mean free path [m] | Pressure [Pa] | Mean free path [m] |
| 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.

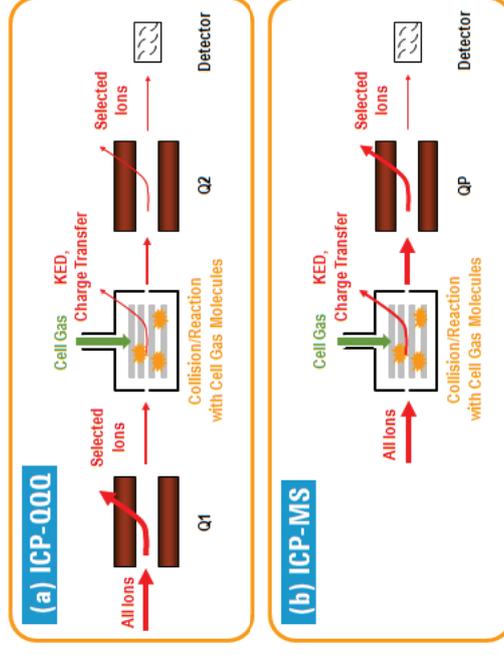


Figure 2. Comparison of principle of operation between the new ICP-QQQ (a) and the conventional cell-based ICP-MS (b).

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

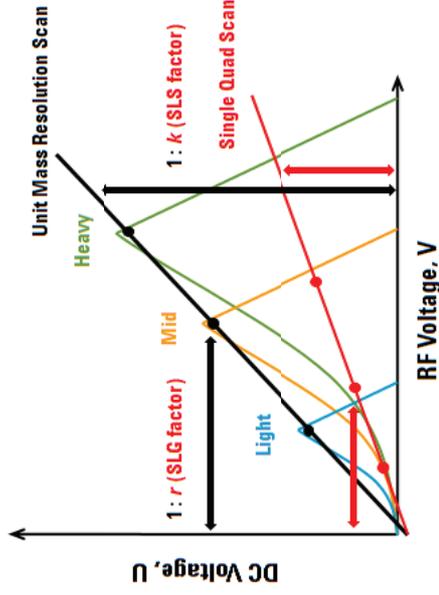
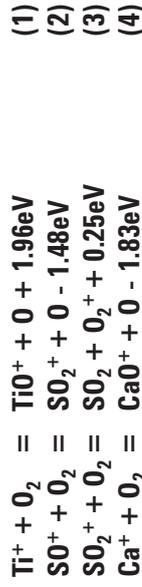


Figure 3. Scan line and stability diagram of quadrupole. Black line: scan line for unit mass resolution scan Red line: scan line of Q1 for single quad scan

Experimental

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:



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

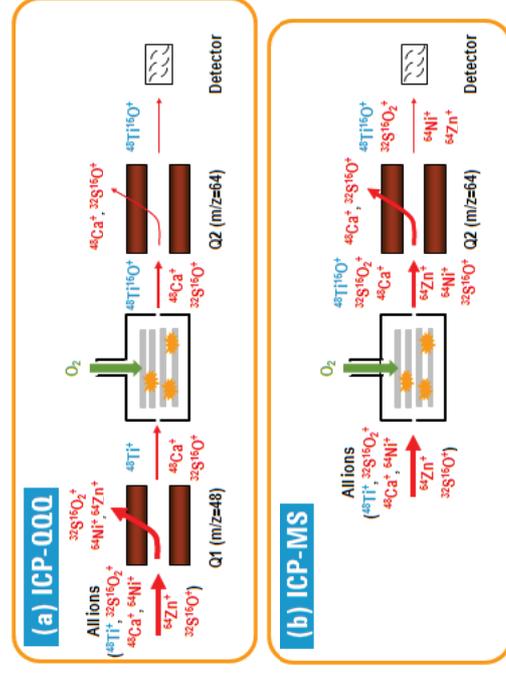


Figure 4. Principle of operation to detect 48Ti by O₂ mode.

Experimental

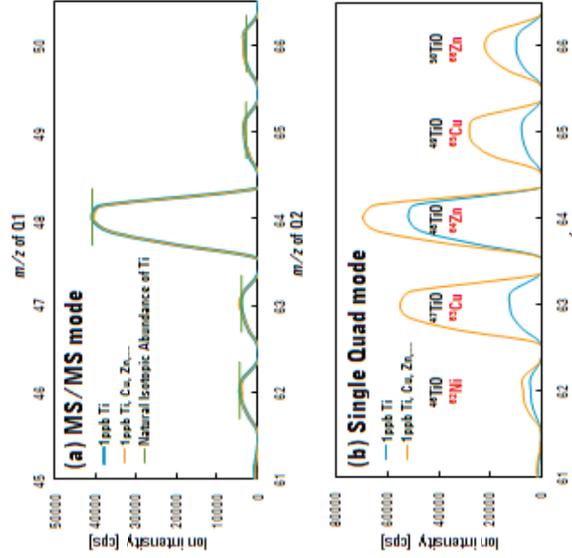


Figure 5. Spectra to measure Ti.
Blue line: 1ppb Ti in 1% HNO₃
Orange line: 1ppb Ti, Cu, Zn, ... in 1% HNO₃
(a) MS/MS mode, (b) Single Quad mode

In general exothermic reactions are promoted in the cell while endothermic reactions are not. So Ti⁺ reacts with O₂ cell gas to form TiO⁺ rapidly (1) while SO⁺ does not react (2). Once SO₂⁺ 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 O₂ 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 ⁴⁸Ti. O₂ and He cell gases were swept while monitoring signal intensity of the standard (10ppb Ti in 10% H₂SO₄) and the blank (10% H₂SO₄). Minute O₂ gas flow less than 0.1mL/min was sufficient to react Ti⁺ with O₂ to form TiO⁺. Interestingly, He gas contributed to the reduction of background originating from sulfur-based interference (SO₂⁺), 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 SO₂⁺ through the reaction (2). He gas also promotes the reaction (1) at a minute O₂ gas flow rate. Optimized O₂ and He cell gas flow rates were 0.07mL/min and 12mL/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% H₂SO₄ 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 (SO₂⁺) 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 ⁴⁸Ti respectively, which indicates strict linearity over very wide dynamic range (50ppt~10ppb).

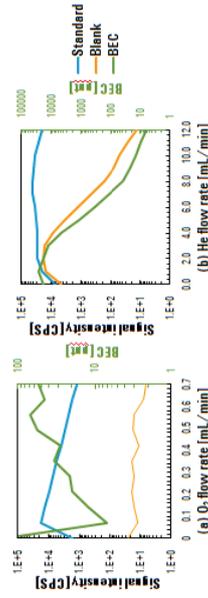


Figure 6. Cell gas flow rate vs. BEC and signal intensity of standard (10ppb Ti in 10% H₂SO₄) and blank(10% H₂SO₄) solution.

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

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

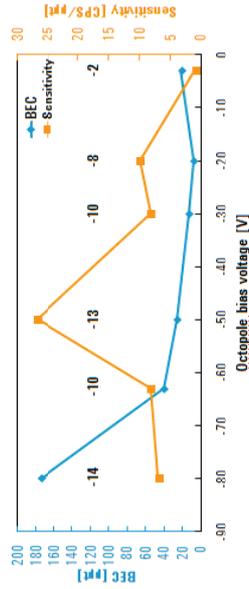


Figure 7. Octopole bias vs. BEC and sensitivity of Ti. Numbers described on each point are optimized energy discrimination. [V]

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 |
| Q1 bias [V] | -5 |
| Octopole bias [V] | -20 |
| Energy discrimination [V] | -8 |
| O₂ flow [mL/min] | 0.07 |
| He flow [mL/min] | 12.0 |

Experimental

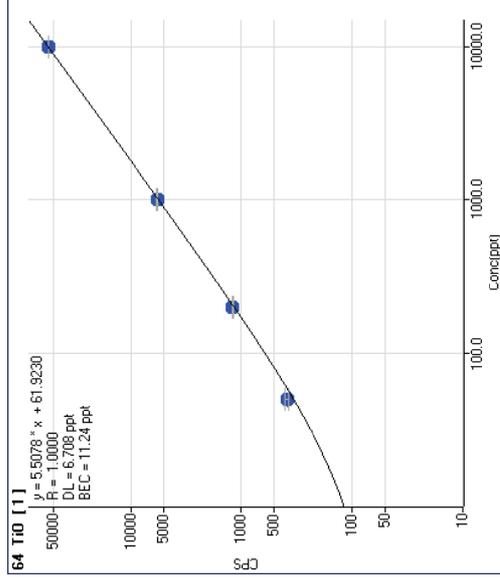


Figure 8. Calibration curve for Ti in 10% H₂SO₄

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/ppm 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.

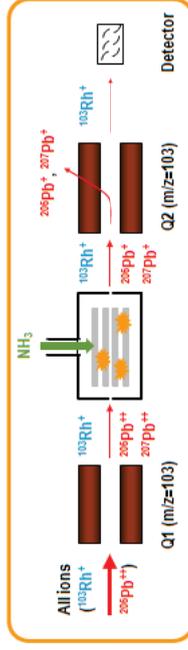


Figure 9. Principle of operation to detect Rh in Pb matrix by NH₃ mode.

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

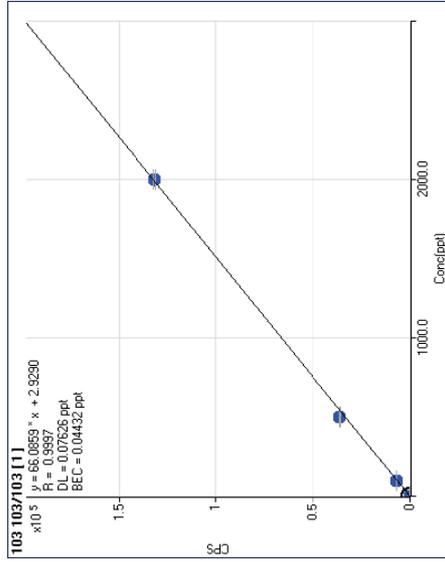


Figure 10. Calibration curve for Rh in 100 ppm Pb

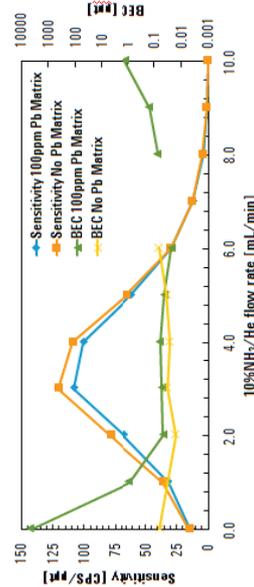


Figure 11. Cell gas flow rate vs. sensitivity and BEC of Rh for the comparison between 100 ppm and no Pb matrix

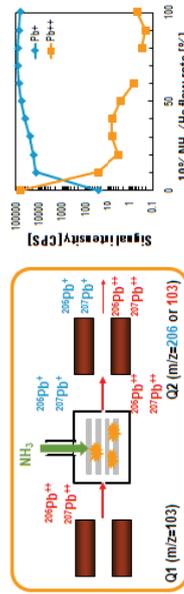


Figure 12. Monitoring of Pb⁺ formation in the cell as a result of charge transfer reaction(1)

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.

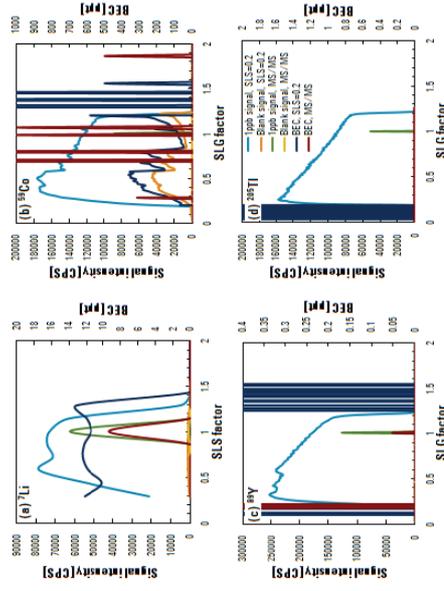


Figure 13. Comparison of signal intensity and BEC between Single Quad mode with various SLG factors and MS/MS mode. (a) ⁷Li, (b) ⁸⁹Y, (c) ⁵⁹Co, (d) ²⁰⁵Tl

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.