Application of ICP-MS to analysis of nuclear fuel debris and radioactive wastes

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The Tohoku Earthquake and the tsunami that followed occurred in March 2011. The surge from the tsunami caused loss of cooling system in Tokyo Electric Power Company Holdings Fukushima Daiichi Nuclear Power Station (1F). The loss of cooling system allowed the fuel in reactor units 1-3 at least partially meltdown and caused hydrogen explosions in unites1 and 3. As the results of the explosions, a large amount of radioactive materials were released into the environment and contaminated a vast area containing the 1F site. Japan Atomic Energy Agency, JAEA, currently sets up an “Okuma Analysis and Research Center” next to the 1F site, which aims at characterizing radioactive wastes and fuel debris generated in the 1F site.

Radioactive waste samples taken in the 1F site are planned to be analysed by mainly conventional radiometric methods. Gamma spectrometry of HPGe detector is used to identify gamma emitters. Beta emitters with negligible or no gamma-ray emission are planned to be determined from measurement of beta activity, which is measured by a liquid scintillation counter or a low background gas flow counter. These measurements require complicated and time-consuming process including chemical separation and purification in advance. To avoid the chemical separation, Inductively Coupled Plasma-Quadrupole Mass Spectrometry, ICP-QMS, which has an advantage of sensitivity over radiometric analysis for long-lived radionuclides, was applied. Isobaric interference is the major task to be solved for the mass spectrometric analysis.

The procedure of the mass-based analytical method for radionuclides and the detailed results for an example case for Zr-93 are described in this presentation.

Analytical methods

Conventional radioactivity measurement. Radiation counting method has been used many years. Gamma spectrometry of HPGe detector is used measuring gamma rays to determine the gamma emission radionuclides after just simple preparation. Beta decay isotopes with very low, or no gamma emission, were planned to be measured its activities by beta counting methods, such as a liquid scintillation counter and a low background gas flow counter. It requires chemical isolation of element before the measurement, because beta counter has poor energy resolution. Alpha decay radionuclides emit close energy alpha particles. Chemical purification is also required, even if alpha spectrometry has some energy resolution. Electron capture radionuclides would be measured low energy X-rays (eg. Low Energy Ge Detectors). Purification process is necessary to avoid increasing background signals by Compton scatter of gamma rays. From the results, almost radionuclides should be purified before counting its radio activities.

Analytical instruments are planned to employ radiometric analysis, namely liquid scintillation counter, low background gas flow counter, alpha spectrometer and gamma spectrometer. All these instruments based on radiometric analysis are very reliable, as they have been used for many years.

ICP-QMS spectrometry. ICP-QMS has been a powerful analytical instrument to measure very low concentration isotopes. Ohtsuka compared detection limit of radiation counting method with ICP-QMS (Ohtsuka, 2006). ICP-QMS has an advantage in long half-life, approximately more than 1,000 years, radionuclides measurements.

As long as using ICP-QMS of single quadrupole mass spectrometer, isobaric interference could not be ignored. Zr-93 is one of the most difficult radionuclides to be analysed by mass spectrometer. When Zr-93(half -life 1.5×10^5Y) is measured by ICP-MS, Nb-93(stable) and Mo-93(half-life 4.0×10^3Y) will interfere, because the same mass number. Triple quadrupole mass ICP-MS (QQQ-ICP-MS: Agilent 8900) is selected to analyse Zr-93. Two quadrupole mass separators (QMS) are tandemly arranged, and octupole-based collision reaction cell is set between them, as shown in figure 1. Sample solutions are heated and ionized in the Ar plasma. These ions are led to the first QMS, that is used as a mass filter to pass through only ions of M/Z= 93, such as $[Zr\text{-}93]^+$, $[Nb\text{-}93]^+$ and $[Mo\text{-}93]^+$. Then these ions are reacted with reaction gas to make different molecule ions, whose mass number will also be different. The second QMS separated ions to be measured and collected by electron multiplier detector.

We studied possibility of Zr separation from Nb and Mo with QQQ-ICP -MS using reaction cell, introducing reaction gas, oxygen or ammonium gas. In the measurement, elemental standards were used pure elemental solutions and concentration was adjusted to 1ppb.The first Q-mass was used as a mass filter, M/z was 93, and the second Q-mass was varied its M/z from 93 to 275.

Figure P36 shows ion production rate detected through the second Q-mass of using two reaction gases. The left figure is for the ion production rate without any gases, “no gas” mode. Right upper figure is for using oxygen and right lower figure is for ammonium gas as reaction gas. Mass shift, difference of M/z, was plotted on the abscissa and ionic intensity on the ordinate. Nb and Mo isobaric interference to Zr were not removed with “no gas” mode, because mass shift has not been observed Zr, Nb and Mo measurement. Small amount of NbO^+ and MoO^+ were found with O_2 mode. Almost Nb and Mo were formed di-oxide ion, but Zr was mono-oxide, this estimate reducing isobaric interference, when the Zr concentration is much higher than those of Nb and Mo.

When using NH_3 as reaction gas, Nb, Mo and Zr, forms different ions, $Nb(NH_4)(NH_2)_4^+$, Mo^+ and $Zr(NH_3)_6^+$, respectively. These elements were separated by QQQ-ICP-MS just adding NH_3 gas as reaction cell. From the result, QQQ-ICP-MS can make possible to measure several nuclides, simultaneously, without any chemical pre-treatment before delivering sample solution to the instrument. Therefore, separation process can be simplified just introducing mixed solutions into the instrument.

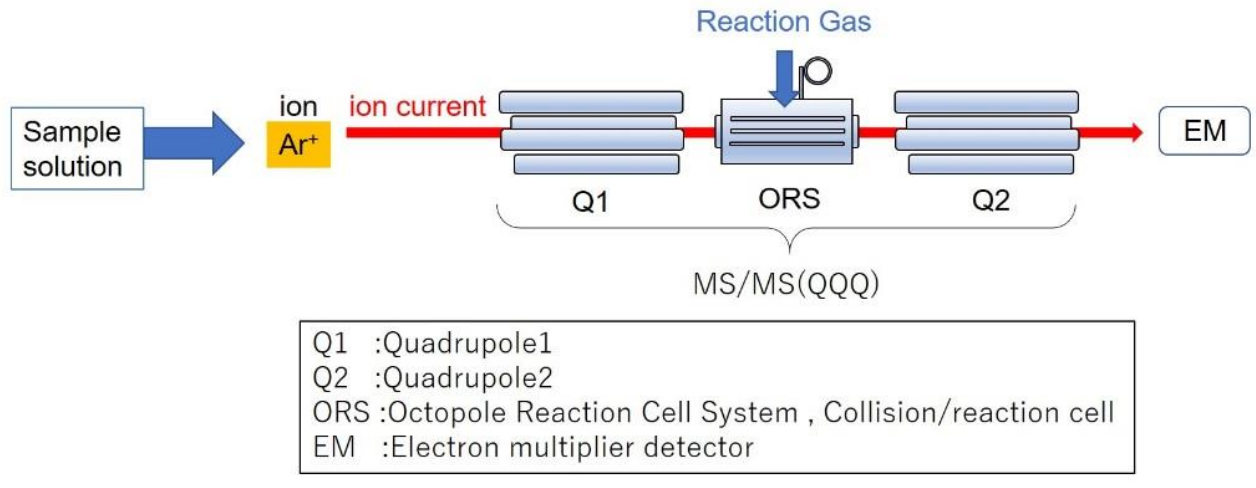

Figure P35: Schematic diagram of ICP-QQQ-MS

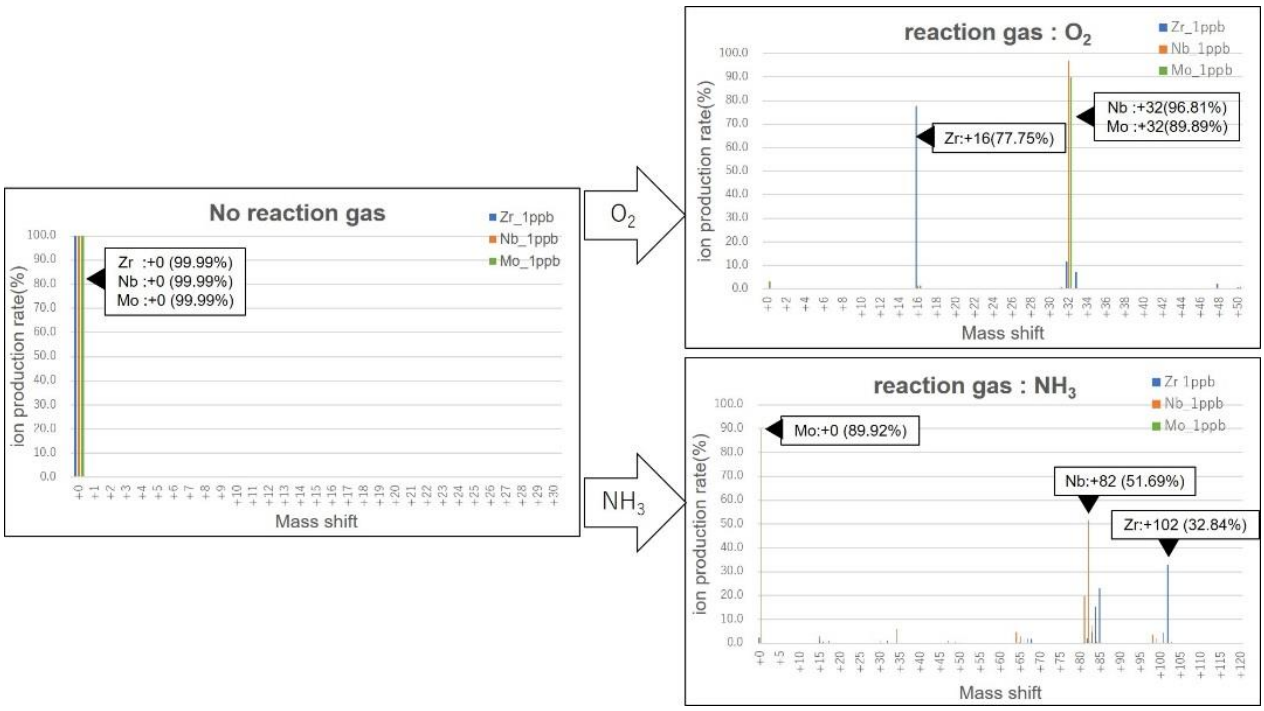

Figure 36: Ion production rate (Mass spectra) of QQQ- ICP -MS

Conclusions

In the QQQ-ICP-MS using O2 and NH3 as a reaction gas, separation condition of Zr from Nb and Mo, was found without chemical purification. QQQ-ICP-MS could measure several nuclides at one time. In this manner, pre-treatment process could be simplified and separation time could be shortened. This can make possible to increase the number of analysis samples.

Acknowledgement

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Reference

Ohtsuka, Y. (2006). Present status and prospects of ultralow level radioactivity measurements (7). Current status of analysis of radionuclides in environmental samples by using a mass spectrometer. *Radioisotopes (Tokyo)*, *55*(10), 651-664.