

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 ^{136}Xe impurities in the argon plasma gas and possible polyatomic interference from $^{129}\text{I}_2^+$. We showed at WPC 2011 that the isobaric interference from $^{136}\text{Xe}^+$ 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) ($3\sigma, n=10$) for both ^{127}I and ^{129}I were obtained using external calibration, the problem of poor abundance sensitivity of ICP-QMS still remained.

Pu: Plutonium is also 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 $^{239}\text{Pu}/^{240}\text{Pu}/^{241}\text{Pu}/^{242}\text{Pu}$ 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.

The relatively poor abundance sensitivity of conventional ICP-MS is a problem of particular importance for ultra low-level analysis of any 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 (ICP-QQQ) technique using oxygen and ammonia as the reaction cell gases was applied to determine ultratrace levels of these 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

Agilent Technologies has developed a new triple quadrupole ICP-MS (ICP-QQQ). As shown in Fig. 1, it has two quadrupoles, one before and one after the Collision/Reaction Cell. The 1st Quadrupole selects ions entering the cell, providing consistent reaction conditions under changing sample composition. As such, this triple quadrupole configuration solves the biggest problem associated with current single quad reaction cell instruments, allowing analyst to use the reaction cell for more elements/applications, more effectively. The Agilent ICP-QQQ has following features.

- Ultimate collision/reaction cell performance for the removal of polyatomic interferences.
 - Advanced reaction cell overcomes the weaknesses of existing reaction cells due to unique QQQ configuration.
 - Versatile He collision cell. The performance is better than the Agilent 7700 due to the available MS/MS scan function.
- Sensitivity is much higher than Agilent 7700 series ICP-MS. A lab-prototype achieved 810 Mcps/ppm for yttrium with an oxide ratio ($[\text{CeO}^+/\text{Ce}^+]$ of 1.47% using the high matrix x-lens and more than 12 Gcps/ppm with oxide ratio of 2.47% using the high sensitivity s-lens.
- Random background noise is as low as $<0.1\text{cps}$.
- Abundance sensitivity is immeasurably low for both low mass and high mass side; $<10^{-9}$
- Maintains the Agilent 7700 robustness and durability, being applicable to developed Agilent 7700 applications.

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 = $0.982 \times 10^{-6} \pm 0.012 \times 10^{-6}$. 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 unfortunately, radionuclide samples, even if they are reference materials, are still quite 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 ($\text{Xe}^+ + \text{O}_2 \rightarrow \text{Xe} + \text{O}_2^+$, $k_f = 1.1 \times 10^{-10}$). As a result, the isobaric interference from $^{136}\text{Xe}^+$ 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 ICP-QMS still remained as shown in Figure 2b).

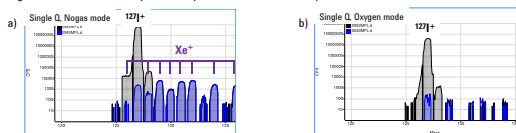


Figure 2 Mass spectra of I and Xe in 8.89mg/L iodine-127 solution. a) conventional no cell gas mode, b) high energy O_2 mode with single QMS.

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.

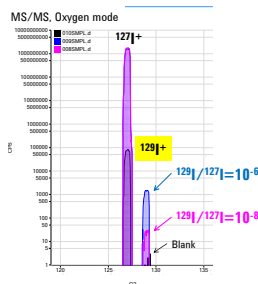


Figure 3 Iodine spectrum for both ^{127}I and ^{129}I by MS/MS mode.

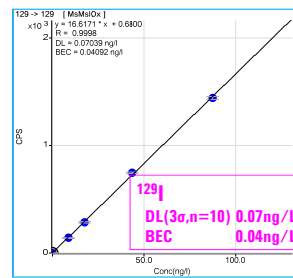


Figure 4 Calibration curve for ^{129}I obtained from diluted NIST 3231 SRM (Level I).

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.

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

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 2. 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^{-6} as reported in the certificate.

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

Sample Name	Standard	127 -> 127 (MuMm Dc)	129 -> 129 (MuMm Dc)	$^{129}\text{I}/^{127}\text{I}$	$^{129}\text{I}/^{127}\text{I}$ (average cert.)	RSD(%)	
NIST3231 10 ⁻⁶	20	387,229,445	2971	7.67E-07	0.947 x 10 ⁻⁶	4.1	
	20	382,389,628	2749	7.19E-07			
	20	382,264,976	312,733,524	1.6	365.6	208.3	3.6
	20	385,488,256	262.9	6.82E-07			
NIST3231 10 ⁻⁶	10	384,270,668	965.9	2.51E-06			
	10	382,822,576	937.4	2.45E-06			
	10	382,988,722	102,626,129	1.3	587.6	588.4	1.8
	10	383,381,442	988.5	2.58E-06			
NIST3231 10 ⁻⁶	10	382,829,884	988.9	2.58E-06			
	10	388,270,948	14.7	3.79E-08			
	10	388,262,342	14.6	3.76E-08			
	10	382,822,610	14.6	3.76E-08			
NIST3231 10 ⁻⁶	10	383,051,762	102,740,409	1.3	114.5	114.5	2.2
	10	382,920,882	142.0	3.70E-07	1.82 x 10 ⁻⁶	7.2	

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 NH_3

Since an appropriate SRM for Pu is not available due to Japanese government regulations, we investigated the behavior of UH^+ and Bi^+ by MS/MS with NH_3 , assuming that the behavior of Pu^+ is similar to Bi^+ . As shown Figure 5, the abundance of UH^+ interference ions was reduced by over five orders of magnitude via reaction with $\text{NH}_3(\text{+He})$ 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.

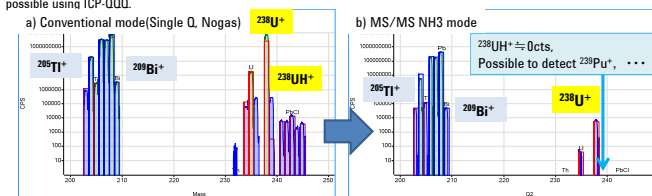


Figure 5 Mass spectra of sample solution including U, Pb (20mg/L) and Tl, Bi (10µg/L) in 2% HCl/1% HNO₃. Mass spectra obtained using a) conventional mode (single quadrupole, No gas mode) and b) MS/MS mode using NH_3 gas as reaction gas.

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.

- $^{136}\text{Xe}^+$ 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 $^{129}\text{I}/^{127}\text{I} = 0.982 \times 10^{-6}$).
- 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 ($3\sigma, n = 10$) for ^{127}I and ^{129}I are 9.6ng/L and 0.07ng/L, respectively.
- Showed the possibility to analyze plutonium (and some other Actinide elements) in high concentration Pb, U matrix samples (HCl solution) by reducing UH^+ ions.

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 triple quadrupole ICP-MS.

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