Reaction Cell Frontier: Analysis of Radionuclides in Environmental Samples using an Innovative Reaction Cell ICP-MS

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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 $^{127}IH_2^+$. We showed at the Winter Plasma Conference (WPC) 2011 that the isobaric interference from ^{129}Xe$^+$ could be significantly reduced, resulting in a measured ratio for $^{129}I/^{127}I$ 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 $T_{1/2}$ = 24,100y 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 $^{238}Pu/^{239}Pu/^{240}Pu/^{242}Pu$ 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 $^{238}UH^+$, $^{238}UH_2^+$, which interfere with ^{239}Pu and ^{240}Pu, and by the peak tailing of an abundant $^{238}U^+$ ion.

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 $^{129}I/^{127}I$ and lower the detection limit for ^{129}I without loss of abundance sensitivity.

Experimental

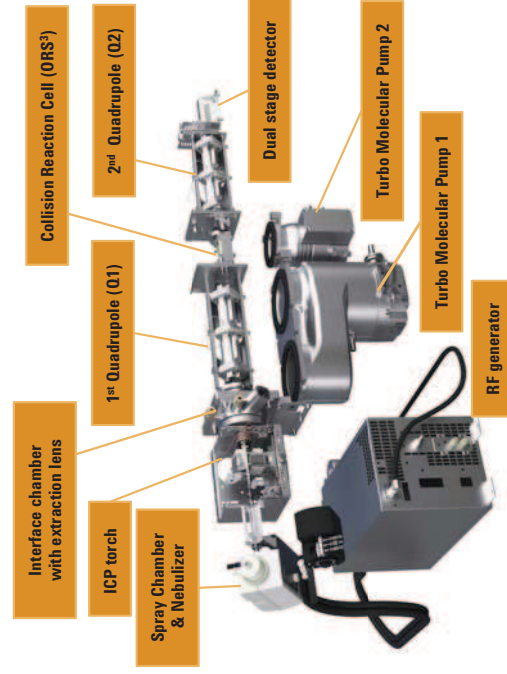Agilent Technologies has developed a new triple quadrupole ICP-MS (ICP-QQQ). As shown in Figure 1, it has two quadrupoles, one before and one after the collision/reaction cell. The first quadrupole selects ions entering the cell, providing **consistent reaction conditions** during changing sample composition. 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

Experimental

Collision Reaction Cell (ORS³)

2nd Quadrupole (Q2)

Dual stage detector

Turbo Molecular Pump 2

Turbo Molecular Pump 1

1st Quadrupole (Q1)

RF generator

Interface chamber with extraction lens

ICP torch

Spray Chamber & Nebulizer

Figure 1. Configuration of Agilent ICP-QQQ

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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 $^{129}I/^{127}I$ = $0.981 \times 10^{-6} \pm 0.012 \times 10^{-6}$, 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 difficult to obtain in Japan due to strict government controls.

Results and Discussion

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

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 (Xe$^+$ + O$_2$ → Xe + O$_2^+$, kr = 1.1 e^{-10}). As a result, the isobaric interference from ^{129}Xe$^+$ is significantly reduced to the level of the instrument background, resulting in a measured ratio for $^{129}I/^{127}I$ 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 I single quad mode still remained as shown in Figure 2b.
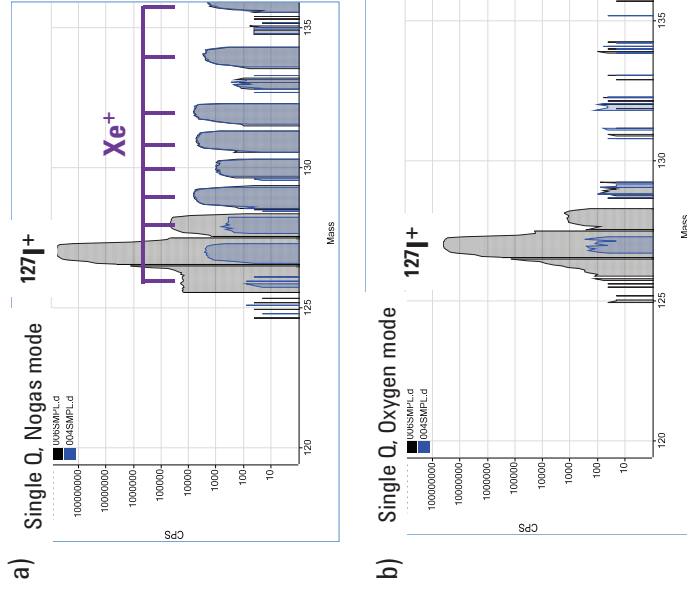
Results and Discussion

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 (3σ, n=10) for ^{129}I was 0.07ng/L.
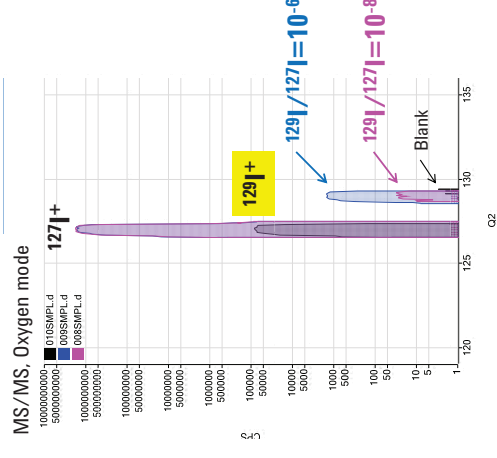

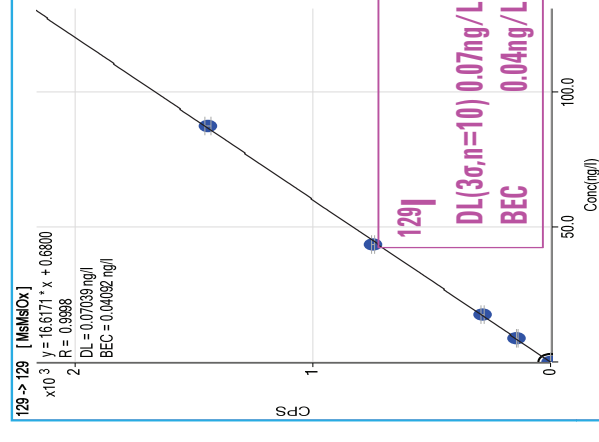Figure 3. Iodine spectrum for both ^{127}I and ^{129}I by MS/MS mode.

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

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Results and Discussion

Analysis of NIST 3231 SRM Level I ($^{129}I/^{127}I$ = 0.981x10^{-6}) and Level II ($^{129}I/^{127}I$ = 0.982x10^{-8})

The $^{129}I/^{127}I$ 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 $^{129}I/^{127}I$ ratio of NIST 3231 SRM corresponded well with the certified value of 0.981x10^{-6} and 0.982x10^{-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]			$^{129}I/^{127}I$	$^{129}I/^{127}I$ (average,n=5)	RSD(%)
		CPS	CPS average	CPS RSD	CPS	CPS average	CPS RSD			
NIST3231 10^{-6} ($^{129}I/^{127}I$ = 0.981 x 10^{-6})	20	301,734,441	302,731,524	0.6	297.1	290.5	3.6	9.72E-07	0.947 x 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		
NIST3231 10^{-8} ($^{129}I/^{127}I$ = 0.982 x 10^{-8})	10	594,277,896	592,626,739	0.3	585.6	589.4	0.8	9.71E-07	0.981 x 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} ($^{129}I/^{127}I$ = 0.982 x 10^{-8})	10	608,737,949	605,248,499	0.5	15.1	14.5	3.3	1.12E-08	1.02 x 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 NH$_3$, 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 NH$_3$(+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:

- $^{129}Xe^+$ background ions were significantly reduced by oxygen reaction

- Achieved analysis of $^{129}I/^{127}I$ ratio of c.a. 1 x10^{-6} and 1x10^{-8} ratio in NIST 3231 SRM Level I (certified value of $^{129}I/^{127}I$ = 0.981x10^{-6}). and Level II (certified value of $^{129}I/^{127}I$ = 0.982x10^{-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
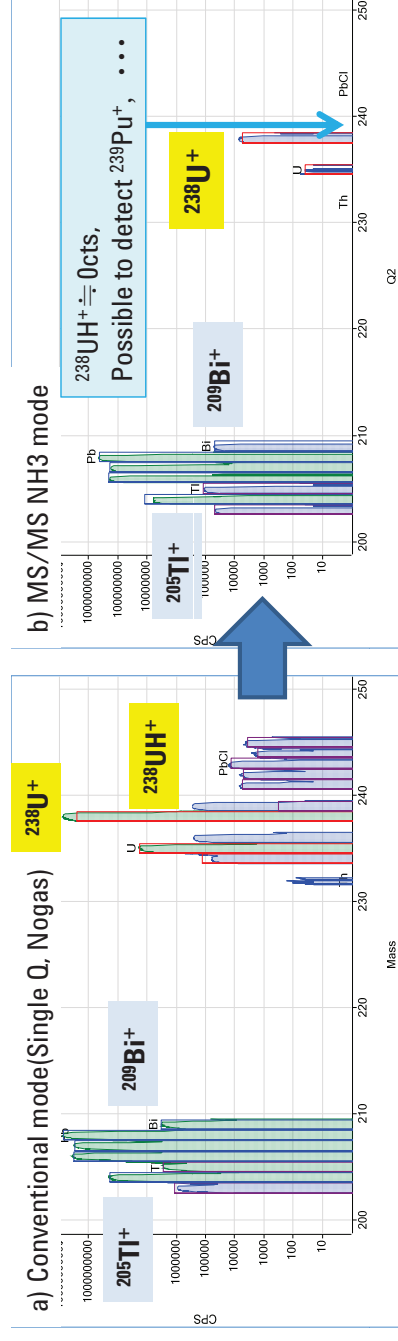

Figure 5. Mass spectra of sample solution including U, Pb (20mg/L) and Tl, Bi (10µg/L) in 2%HCl/1%HNO3. Mass spectra obtained using a) conventional mode (single quadrupole, No gas mode) and b) MS/MS mode using NH$_3$ gas as reaction gas.

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Conclusion

We succeeded in significantly improving the measurable ratio of $^{129}I/^{127}I$ 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.