Using ICP-QQQ for UO_2^+ product ion measurement to reduce uranium hydride ion interference and enable trace ^{236}U isotopic analysis

Application note
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Introduction

Uranium 236 is a long-lived radionuclide which is created from the naturally occurring trace isotope ^{235}U (0.72% abundance) by thermal neutron capture. This process leads to a natural abundance of ^{236}U in the range from 10^{-14}—10^{-13} relative to the major ^{238}U isotope ($^{236}U/^{238}U$). ^{236}U is also created during the process of uranium enrichment for nuclear fuel or weapons, and as a waste product from the consumption of enriched uranium fuel in nuclear reactors. The $^{236}U/^{238}U$ ratio is increased up to 10^{-3} in spent nuclear fuel, with background levels in the environment increased up to around 10^{-7}—10^{-8} as a result of global fallout [1]. The $^{236}U/^{238}U$ isotope ratio can therefore be used as a sensitive method to trace the accidental release of enriched uranium fuel, spent fuel and nuclear waste, and to investigate the effects of nuclear technology on the environment and human health. Consequently, instrumentation used in the accurate study of global fallout needs to perform $^{236}U/^{238}U$ isotopic ratio analysis at the $<10^{-9}$ level.

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Acceleration Mass Spectrometry (AMS) is often used for U isotope studies, as its high sensitivity provides a detection limit for $^{236}U/^{238}U$ of 10^{-13} [2]. Since ICP-MS is more widely available than AMS and sample preparation is much simpler, a number of analysts have investigated ICP-MS for the analysis of $^{236}U/^{238}U$ [3, 4, 5]. The main challenges for ICP-MS for this application are the interference on $^{236}U^+$ by the hydride ion $^{235}UH^+$, and the contribution at m/z 236 from tailing of the $^{235}U^+$ and $^{238}U^+$ peaks. Hydride overlap and peak tailing are more problematic in samples that have been enriched, as these contain a higher proportion of ^{235}U.

Tanimizu et al demonstrated that the $^{235}UH^+$ interference could be effectively avoided using O_2 cell gas on an Agilent 8800 ICP-QQQ, in combination with sample introduction via a membrane desolvator [6]. The O_2 reaction gas reacts less readily with UH^+ than with U^+, so the UOH^+ product ion forms to a lesser degree than UO^+, allowing ^{236}U to be measured as $^{236}UO^+$, without a significant contribution from $^{235}UOH^+$.

The problem of peak tailing can also be alleviated with ICP-QQQ, as MS/MS operation dramatically improves abundance sensitivity (AS) performance. AS is a measure of the contribution that the adjacent peaks (at M − 1 and M + 1) make to the target analyte mass. The AS of the Agilent ICP-QQQ's tandem MS configuration is the product of the abundance sensitivities of the two quadrupoles (Q1 AS x Q2 AS), so overall AS in MS/MS mode is $<<10^{-10}$. This is several orders of magnitude better than the AS that can be achieved on conventional quadrupole ICP-MS or sector field ICP-MS, and the reduced contribution from peak tailing permits measurement of the $^{236}U/^{238}U$ ratio at the 10^{-10} level [6].

Agilent's second generation ICP-QQQ, the Agilent 8900 Triple Quadrupole ICP-MS, was used for the analysis, as it offers high sensitivity and an extended mass range to allow the measurement of uranium as the oxide (UO^+) and dioxide (UO_2^+) reaction product ions. In this work, uranium was measured via its dioxide ion, UO_2^+, due to the efficient conversion (almost 100%) of U^+ to UO_2^+ with O_2 cell gas. For this approach to be successful, ICP-QQQ with MS/MS capability is necessary to give control of the reaction processes and product ions formed. The application is beyond the scope of conventional quadrupole ICP-MS (ICP-QMS), which lacks a mass selection step prior to the collision/reaction cell (CRC). For instance, when ^{236}U is the analyte of interest, $^{236}U^{16}O^{16}O^+$ (at m/z 268) will suffer a severe overlap from $^{235}U^{17}O^{16}O^+$, as ICP-QMS has no way to reject $^{235}U^+$ before

it enters the CRC. With ICP-QQQ, the first quadrupole (Q1) controls the ions that can enter the cell, so inter-isotope product ion overlaps cannot occur. This makes the approach of using UO^+ or UO_2^+ for isotopic analysis measurements both controllable and consistent.

Experimental

Instrumentation
An Agilent 8900 ICP-QQQ (#100, Advanced Applications Configuration) was used for all measurements. The instrument was fitted with a standard quartz torch with 2.5 mm injector, and the standard x-lens was used. A self-aspirating PFA nebulizer (part number G3139-65100) was used for sample delivery, to provide better washout compared to the standard glass concentric nebulizer and peristaltic pump. Plasma conditions were optimized for maximum sensitivity, leading to a slightly higher than normal total carrier gas flow rate and a CeO^+/Ce^+ of 1.8%. These plasma conditions did not significantly increase the level of UH^+, as hydride ion formation is not dependent on carrier gas flow rate. Instrument operating conditions are given in Table 1.

Table 1. ICP-QQQ operating conditions

Parameter	Unit	Value
RF power	W	1550
Sampling depth	mm	8.0
Carrier gas flow rate	L/min	0.8
Makeup gas flow rate	L/min	0.30
Extraction 1 lens	V	-15
Extraction 2 lens	V	-250
Omega lens	V	12
Omega bias lens	V	-180
Octp Bias	V	0
KED	V	-10
Acquisition mode		MS/MS
Wait time offset	ms	10

Reagents
Uranium solutions were prepared at suitable concentrations by diluting SPEX multi element standard XSTC-331 (SPEX CertiPrep, Metuchen, NJ, USA) with de-ionized water. All sample, blank, and rinse solutions were spiked with high purity TAMAPURE 100 HNO_3 (Tama Kagaku, Saitama, Japan) to a concentration of 1%.

Results and discussion

UO$^+$ and UO$_2^+$ formation as a function of O$_2$ cell gas flow rate

The rate of formation of UO$^+$ and UO$_2^+$ was studied as a function of O$_2$ cell gas flow rate. A solution containing 10 ppb uranium (1000x dilution of XSTC-331) was introduced into the ICP-QQQ. The signals of ^{238}U$^+$, ^{238}U^{16}O$^+$, and ^{238}U^{16}O^{16}O$^+$ were measured via three mass pairs (Q1→Q2) = (238→238), (238→254) and (238→270), and plotted against the O$_2$ cell gas flow rate. The octopole bias (Octp Bias) voltage was optimized to give the maximum UO$_2^+$ signal (0 V).
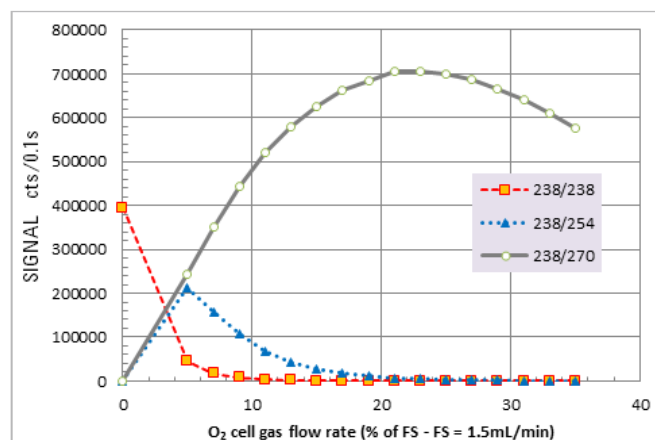

Figure 1. U$^+$ (238 → 238), UO$^+$ (238 → 254), and UO$_2^+$ (238 → 270) as a function of O$_2$ cell gas flow rate

Figure 1 shows that UO$^+$ formation reaches a maximum at an O$_2$ flow rate of 5% of full scale (equivalent to 0.074 mL/min as O$_2$), which is in good agreement with Tanimizu [6]. Above 0.075 mL/min flow rate, the formation of UO$^+$ decreased, while the formation of UO$_2^+$ increased, reaching a maximum at an O$_2$ flow of 22% of full scale (0.33 mL/min). This indicates the conversion of UO$^+$ to UO$_2^+$ via a chain reaction. The highest count of UO$_2^+$ at 22% flow rate far exceeded the counts of U$^+$ at a flow rate of 0% (i.e. no gas mode). The 8900 was optimized for highest sensitivity for the UO$_2^+$ product ion, which may explain the apparent increase in sensitivity for UO$_2^+$ compared to U$^+$.

Effect of product ion selection on hydride ion formation rate

The hydride ratio was measured at the optimal O$_2$ flow rate for U$^+$ and each of the U-oxide product ions: ^{238}UH$^+$/^{238}U$^+$, ^{238}UOH$^+$/^{238}UO$^+$, and ^{238}UO$_2$H$^+$/^{238}UO$_2^+$.

A sample containing 50 ppb U (200x diluted XSTC-331) was introduced as the test solution for the measurement of the hydride formation ratio. Ten replicate measurements were made, with integration times of 1s and 10s for the analyte and hydride ions respectively. The results, summarized in Table 2, show that measuring UO$^+$ decreases the hydride ratio by a factor of ~20, while measuring UO$_2^+$ leads to more than a three orders of magnitude improvement, reducing the hydride ratio to 10^{-8}. The findings suggest the interference of ^{235}U hydride on ^{236}U could also be reduced by around three orders of magnitude by measuring ^{236}U as the ^{236}UO$_2^+$ product ion.

Uranium detection limit

The detection limit (DL) of U was estimated using the UO$_2^+$ method. A blank solution was introduced and the signal of the three mass pairs (236→268; 238→270 and 239→271) corresponding to ^{236}U$^+$→^{236}UO$_2^+$; ^{238}U$^+$→^{238}UO$_2^+$; and ^{238}UH$^+$→^{238}UO$_2$H$^+$ were measured using an integration time of 10 s. The results in Table 3 are based on 10 replicate measurements. As shown, very low background counts were obtained for each of the mass pairs of interest. The DL for U was calculated from the concentration equivalent to three times the standard deviation of the background, using the sensitivity of ^{238}UO$_2^+$ given in Table 2 and the background for mass pair 238→270 in Table 3. The DL for uranium was calculated to be 0.34 ppq (fg/g).

Table 2. UH$^+$/U$^+$ ratios obtained by measuring uranium as U$^+$, UO$^+$ and UO$_2^+$

		U$^+$ analysis			UH$^+$ analysis			UH$^+$/U$^+$
	O$_2$ cell gas flow	Mass pair for U$^+$	Count	RSD	Mass pair for UH$^+$	Count	RSD	
	%	Q1/Q2	cps	%	Q1/Q2	cps	%	
as U$^+$	0	238/238	24168974	2.8	239/239	1578.5	0.6	6.53E-05
as UO$^+$	5	238/254	14152816	4.2	239/255	48.9	4.3	3.46E-06
as UOO$^+$	22	238/270	40527770	2.0	239/271	2.3	20.8	5.68E-08

Table 3. Blank signal and SD for mass pairs used for $^{236}U/^{238}U$ analysis using UO_2^+ method with an O_2 cell gas flow rate of 0.33 mL/min, n = 10

236→268		238→270		239→271	
Count-cps	SD cps	Count-cps	SD cps	Count-cps	SD cps
0.15	0.14	0.18	0.09	0.09	0.09

Conclusions

The Agilent 8900 ICP-QQQ operating in MS/MS mode with O_2 cell gas has been shown to be suitable for the measurement of U as its reaction product ion UO_2^+. This approach was successful in reducing the contribution from the hydride ion (i.e. ^{235}UH overlap on ^{236}U), the formation of which was decreased by three orders of magnitude compared to direct, on-mass measurement of U^+. MS/MS mode with O_2 cell gas gave a UO_2H^+/UO_2^+ ratio in the 10^{-8} range, without the use of a desolvation system, suggesting that the approach could be successful in reducing the interference of $^{235}UH^+$ on $^{236}U^+$, even in samples containing enriched U. This has the potential to allow rapid trace-level measurement of $^{236}U/^{238}U$ isotopic ratios, providing valuable information on global fallout following accidental release of nuclear material into the environment.

Considering that the typical $^{235}U/^{238}U$ ratio is 7×10^{-3}, our results suggest that the ^{235}UH interference on ^{236}U can be reduced sufficiently to allow $^{236}U/^{238}U$ measurement in the 10^{-10} range to be achieved using this method. The ultra-low instrumental background noise level and high sensitivity of the 8900 ICP-QQQ meant that a DL of uranium of 0.34 fg/g was achieved.

Based on previous studies, it is anticipated that a lower DL for U, and $^{236}U/^{238}U$ measurements with lower ^{236}U abundance, could be achieved by combining the Agilent 8900 ICP-QQQ with sample introduction using a membrane desolvation system.

References

1. A. Sakaguchi, K. Kawai, P. Steiner, F. Quinto, et al, *Science of the Total Environment*, 2009, 407, 4238

2. F. Quinto, P. Steier, G. Wallner, A. Wallner et al, *Applied Radiation and Isotopes*, 2009, 67, 1775

3. S. F. Boulyga and J. S. Becker, Fresenius *J. Anal. Chem.*, 2001, 370, 612

4. S. F. Boulyga, U. Klötzli and T. Prohaska, *J. Anal. At. Spectrom.*, 2006, 21, 1427

5. J. G. Arnason, C. N. Pellegri and P. J. Parsons, *J. Anal. At. Spectrom.*, 2015, 30, 126

6. M. Tanimizu, N. Sugiyama, E. Ponzevera and G. Bayon, J. *Anal. At. Spectrom*., 2013, 28, 1372

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