APPLICATION NOTE

ICP – Mass Spectrometry

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Uranium Isotope Ratio Measurements with the NexION ICP-MS

Introduction

One of the beneficial features of inductively coupled mass spectrometry (ICP-MS) is its ability to measure multiple isotopes of the same element. This ability is useful in many analyses, primarily as confirmation of a correct answer (i.e. if two isotopes of the same element give the same result, the result is most likely correct) or the ability to select another analytical isotope, if an interference exists on the desired isotope.

However, ICP-MS instrumentation can also precisely measure isotope ratios. This type of measurement is important for elements whose isotopic ratios change over time due to natural decay or vary by geography. As a result, isotope ratio measurements have been used for numerous purposes, including dating, provenance of food, and monitoring the metabolism of an enriched species, among many others.

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In order to obtain the most precise isotope ratio results, ions of all isotopes of an element should be detected simultaneously. Because quadrupole-based ICP-MS is a sequential technique (although extremely fast), the ions from different isotopes are detected at different times, which could lead to mass bias and lack of precision. When considering the precision which is sometimes required, quadrupole-based ICP-MS may not be the most appropriate technique for isotope ratio measurements. However, the development of Reaction Cell technology has allowed for more precise measurements of isotope ratios by slowing down the ions so they are detected more closely in time[1,2].

One of the more challenging elements to obtain accurate and precise isotope ratio measurements is uranium (U), due to the wide natural abundances of its isotopes, as shown in Table 1. The wide variation in abundances means that the detector has to rapidly respond to very different signals, which again, could affect the precision of the measurement.

This work demonstrates the ability of PerkinElmer's NexION® 300/350 ICP-MS to precisely measure uranium isotope ratios, with results approaching counting-statistics limit.

Table 1. Natural Abundance of Uranium Isotopes.

Element	U234	U235	U236	U238
% Abundance	0.0055	0.7200	0.0000	99.2745

Experimental

Samples and Sample Preparation

Two certified reference materials (CRMs) of enriched uranium isotopic ratios were used: CRM U005-A and CRM U030-A (U.S. Department of Energy, Washington, DC, USA). The certificate values for both CRMs are shown in Table 2. For analysis, both CRMs were diluted in 2% nitric acid (v/v) to a final concentration of 40 µg/L.

Table 2. Certificate Values for Enriched Uranium Reference Materials .

CRM	Parameter	U234	U235	U236	U238
U005-A	Atom Percent	0.00340 + 0.00007	0.5064 + 0.0003	0.00118 + 0.00001	99.4890 + 0.0003
	Weight Percent	0.00334	0.5000	0.00117	99.4955
U030-A	Atom Percent	0.02778 + 0.00006	3.0404 + 0.0016	0.000599 + 0.000005	96.9312 + 0.0016
	Weight Percent	0.02732	3.0032	0.000594	96.9689

Instrumental Conditions

All analyses were done on a NexION 300S/350S ICP-MS coupled to an ESI SC2 autosampler (Elemental Scientific Inc., Omaha, Nebraska, USA), using the NexION's standard sample introduction system and conditions. The instrumental parameters used are shown in Table 2, and the method parameters appear in Table 3. A low flow of argon was used as the cell gas in order to collisionally damp the ion energies, which improves the precision of the results. All analyses were done in the NexION's Isotope Ratio mode, a check box within the method which allows optimum Universal Cell parameters to be applied to increase the precision of the measurement.

Table 3. NexION 350S ICP-MS Instrumental Parameters

Parameter	Value
Nebulizer	Quartz concentric
Spray Chamber	Quartz cyclonic
Sample Uptake Rate	300 µL/min
Nebulizer Gas Flow	Optimized for 2% CeO/Ce
Injector	2.0 mm id quartz
RF Power	1600W
Cell Gas	Argon

Table 4. Method Parameters.

Parameter	Value
Sweeps/Reading	200
Readings/Replicate	10
Replicates	10
Mode	Isotope Ratio
Internal Standard	U238
Measurement Time per Sample	8 minutes

Isotope	Dwell Time (ms)	Integration Time (sec)	Cell Gas Flow (mL/min)	RPq	RPa
234	8	16	0.2	0.25	0
235	5	10	0.2	0.25	0
236	8	16	0.2	0.25	0
238	1	2	0.2	0.25	0

Results and Discussion

In order to achieve the most precise isotopic ratios, several criteria must be met. One of the most important is that the ions for each isotope should have a very low energy distribution so that they arrive at the detector as close in time as possible. With the NexION, this is accomplished two ways. First, by setting the method to Isotope Ratio mode, the voltages on the Universal Cell are decreased significantly to minimize the energy imparted to the ions in the cell. Secondly, a low flow of argon is introduced into the cell. Since argon is a large gas, it has the effect of collisionally damping the ions so that they lose a significant portion of their energy. As a result, the ions exit the cell with very narrow energy distributions and arrive at the detector at nearly the same time, thus improving the precision and accuracy of the isotope ratios.

One of the challenges of measuring uranium isotopes is that their abundances are so different, as shown in Table 1. The precision of isotope ratio measurements is also dependent on the total number of counts accumulated for each isotope. However, with such a large difference in abundances, the only way to accumulate enough counts is to vary the dwell time (and, ultimately, the integration time) per isotope. However, the result of this action is that the different isotopes are not measured at the same time, which could impact the results.

Results for U isotope ratio measurements are shown in Tables 5-6, where each analysis was done a little bit differently to improve results. In all cases, sample was aspirated continuously with no rinsing in between, and 17 analyses were performed over two hours. Table 6 shows the results for U005-A calibrating with U030-A at the beginning of the run. The results demonstrate excellent accuracy and precision when compared to the certified atom fractions.

Table 5. **Analysis of U005-A (17 samples) with one calibration using U030-A as a standard.** Time from first to last sample: 2 hours (no rinse between samples).

U005-A	2-hour run (17 samples)			
	U234	U235	U236	U238
Cert. Atomic Fraction →	0.0000340	0.005064	0.0000118	0.99489
1	0.0000346	0.0050907	0.0000113	0.9948633
2	0.0000344	0.0050764	0.0000112	0.9948780
3	0.0000351	0.0050803	0.0000114	0.9948733
4	0.0000347	0.0050805	0.0000113	0.9948734
5	0.0000343	0.0050863	0.0000112	0.9948682
6	0.0000345	0.0050924	0.0000111	0.9948620
7	0.0000348	0.0050748	0.0000111	0.9948792
8	0.0000343	0.0050892	0.0000115	0.9948650
9	0.0000343	0.0050783	0.0000116	0.9948758
10	0.0000348	0.0050827	0.0000117	0.9948708
11	0.0000348	0.0050918	0.0000117	0.9948617
12	0.0000347	0.0050876	0.0000114	0.9948664
13	0.0000343	0.0050868	0.0000116	0.9948673
14	0.0000347	0.0050866	0.0000111	0.9948675
15	0.0000343	0.0050743	0.0000111	0.9948804
16	0.0000344	0.0050795	0.0000112	0.9948749
17	0.0000345	0.0050765	0.0000113	0.9948776
Average	0.0000346	0.0050832	0.0000113	0.9948709
Accuracy (%)	1.64	0.38	-3.89	0.00
Ext. Prec. RSD (%)	0.69	0.12	1.87	0.00

Using U030-A as standard

Table 6. **Analysis of U005-A (17 samples) with one calibration using U005-A as a standard.** Time from first to last sample: 2 hours (no rinse between samples).

U005-A	2-hour run (17 samples)			
	U234	U235	U236	U238
Cert. Atomic Fraction →	0.0000340	0.005064	0.0000118	0.99489
1	0.0000338	0.0050542	0.0000117	0.9949003
2	0.0000336	0.0050400	0.0000115	0.9949149
3	0.0000342	0.0050439	0.0000117	0.9949102
4	0.0000338	0.0050441	0.0000117	0.9949104
5	0.0000334	0.0050498	0.0000115	0.9949052
6	0.0000337	0.0050559	0.0000114	0.9948990
7	0.0000340	0.0050384	0.0000114	0.9949162
8	0.0000334	0.0050527	0.0000118	0.9949020
9	0.0000335	0.0050419	0.0000119	0.9949127
10	0.0000339	0.0050463	0.0000120	0.9949077
11	0.0000340	0.0050553	0.0000121	0.9948987
12	0.0000338	0.0050511	0.0000117	0.9949034
13	0.0000334	0.0050504	0.0000119	0.9949043
14	0.0000338	0.0050502	0.0000115	0.9949045
15	0.0000334	0.0050379	0.0000114	0.9949173
16	0.0000335	0.0050430	0.0000116	0.9949119
17	0.0000337	0.0050401	0.0000117	0.9949146
Average	0.0000337	0.0050468	0.0000117	0.9949078
Accuracy (%)	-0.88	-0.34	-1.05	0.00
Ext. Prec. RSD (%)	0.73	0.12	1.83	0.00

Using U005-A as standard

The results in Table 7 comes from the same run as the data in Table 6, with the only difference being that U005-A was used both as a standard and sample. Comparing the results from both tables shows that the accuracy is better when using U005-A as the standard, indicating that more precise results can be obtained when using a standard that has isotopic abundances that more closely match the sample.

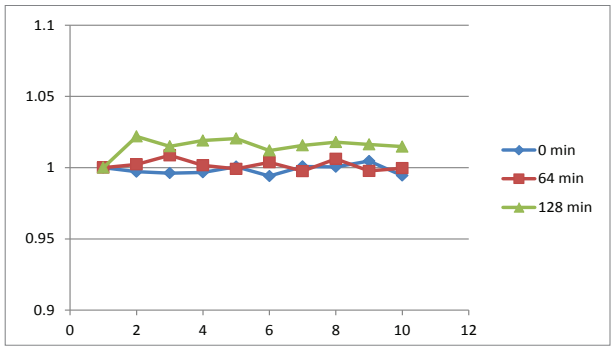
For the most accurate and precise results, it is best to calibrate before every sample. The data in Table 7 were acquired in this way: U005-A was run as a standard then as a sample continuously over two hours, with no rinsing. This manner of analysis provides the ultimate accuracy and precision because each calibration corrects for mass bias.

Table 7. **Analysis of U005-A (9 samples) with nine U005-A standards (in between every sample).** Time from first to last sample: 2 hours (no rinse between samples).

U005-A	2-hour run (9 standards - 9 samples)			
	U234	U235	U236	U238
Cert. Atomic Fraction →	0.0000340	0.005064	0.0000118	0.99489
1	0.0000335	0.0050465	0.0000117	0.9948812
3	0.0000335	0.0050517	0.0000117	0.9948851
5	0.0000335	0.0050531	0.0000117	0.9948856
7	0.0000338	0.0050542	0.0000118	0.9948912
9	0.0000340	0.0050610	0.0000118	0.9948930
11	0.0000340	0.0050632	0.0000119	0.9949003
13	0.0000341	0.0050679	0.0000119	0.9949010
15	0.0000342	0.0050697	0.0000120	0.9949031
17	0.0000345	0.0050730	0.0000120	0.9949074
Average	0.0000339	0.0050600	0.0000118	0.9949074
Accuracy (%)	-0.29	-0.08	0.28	0.00
Ext. Prec. RSD (%)	1.04	0.18	1.03	0.00

Using U005-A alternating as standard and sample

To determine the instrument stability, tests for both short-term and long-term stability were evaluated. Short-term stability was performed by looking at the relative standard deviations from ten replicates of U238 from U005-A that were analyzed one hour apart. Figure 1 shows the plots for each measurement, along with the RSDs for the ten replicates. The highest RSD is 0.60%, indicating exceptional short-term stability over time.



Time	% RSD
0	0.34
1 hour	0.36
2 hours	0.60

Figure 1. Short-term stability and precision for ten replicates of $U238^+$ in three 40 ppb samples of U005-A, analyzed one hour apart. All results normalize to first replicate.

Long-term stability was evaluated by measuring the signal of U238 from 40 ppb U005-A continuously aspirated over two hours. Figure 2 shows the data normalized to the first reading. The overall RSD for the 17 measurements is 1.93%, with a drift of less than 6%, demonstrating excellent instrument stability.

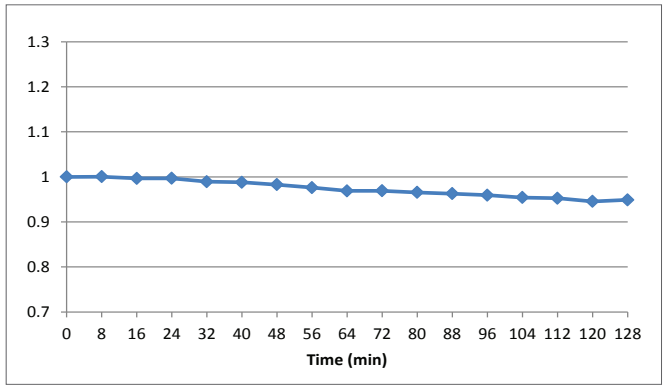


Figure 2. Stability of $U238^+$ over two hours in 40 ppb U005-A. All results normalized to the initial reading.

Conclusion

This work has demonstrated the ability of the NexION 300/350 ICP-MS to accurately measure uranium isotope ratios. Unique characteristics of the Universal Cell allow high precision isotope ratios to be obtained, bordering on the theoretical counting-statistics limit. Other design features of the NexION allow for exceptional signal stability, which is required due to the long measurement times required for high precision isotope ratio measurements.

References

1 Bandura, D.R., Baranov, V.I., Tanner, S.D. J. Anal. At. Spectrom., 15, (2000), 921-928.

2. Bandura, D.R., Tanner, S.D. At. Spectrom. 20, 2, (1999), 69-72.

Consumables Used

Component	Part Number
Sample Uptake Tubing; 0.38 mm id (green/orange), flared, 2-stop	N0777042
Drain Tubing; 1.30 mm id (gray/gray), Santoprene, 2-stop	N0777444
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)

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