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Recent Developments in MC-ICP-MS for Uranium Isotopic Determination from Small Samples

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Abstract

Uranium isotope ratio determination for nuclear forensics, nuclear safeguards and for environmental applications can be challenging due to the large isotopic differences between samples and because of the low abundance of ^{234}U and ^{236}U. For some applications the total uranium quantities can be limited, or it is desirable to run at lower concentrations for radiological protection. Recent developments in inlet systems and detector technologies allow small samples to be analyzed at higher precisions using MC-ICP-MS.

Here we evaluate the combination of Elemental Scientific apex Ω desolvation system and micro*FAST* MC dual loop-loading flow-injection system with the Thermo Scientific NEPTUNE Plus MC-ICP-MS. The inlet systems allow for the efficient handling of small sample volumes with efficient desolvation to minimize the hydride interference on ^{236}U. The highest ICP sampling efficiency is realized using the Thermo Scientific Jet Interface.

Thermo Scientific 10^{13} ohm amplifier technology allows small ion beams to be measured at higher precision, offering the highest signal/noise ratio with a linear and stable response that covers a wide dynamic range (ca. 1 kcps – 30 Mcps).

For nanogram quantities of low enriched and depleted uranium standards the ^{235}U was measured with 10^{13} ohm amplifier technology. The minor isotopes (^{234}U and ^{236}U) were measured by SEM ion counters with RPQ lens filters, which offer the lowest detection limits. For sample amounts ca. 20 ng the minor isotopes can be moved onto 10^{13} ohm amplifiers and the ^{235}U onto standard 10^{11} ohm amplifier. To illustrate the application a set of solutions from environmental particles [1] were analyzed, the use of precise three isotope ratio plots allows for source attribution with increased confidence.

apex Ω

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Methodology

Isotope ratio determination made using a Thermo Scientific NEPTUNE Plus MC-ICP-MS, with Jet Interface and Elemental Scientific apex Ω high-efficiency desolvating nebulizer system. Samples and standards were diluted in 3 wt.% HNO_3 to ca. 25 ng/g uranium concentration. Four 'sample' measurements were bracketed by measurement of the NBS U-010 standard and a blank. Each measurement consisted of two 30-second half-mass off-peak baselines and 7-minutes on-peak acquisition. 10^{13} ohm amplifier technology was used for the quantification of ^{234}U and ^{236}U. Sample measurements were corrected, ratio against ratio, using the NBS U-010 values determined by Richter and Goldberg (2003). Uncertainty was propagated from the isotope ratio measurements and the standard reference values. Sensitivity was ca. 1600 V/ppm at 119 µl/min nebulizer uptake rate, with a UO/U ratio of ca. 1% and negligible hydride. The 3.5 E-07 LoQ for $^{236}U/^{238}U$ was determined from repeat measurement of NBS U-0002. The drift of $^{235}U/^{238}U$ over the standard measurement sequence was ca. 22 ppm/hour (2RSD).

Sample Introduction

The nebulized solution was introduced to the NEPTUNE Plus via an apex Ω desolvating system. The apex Ω integrates heating, condensing, and membrane desolvation with complete software control for high precision remote tuning.

Mass Spectrometry

A Thermo Scientific NEPTUNE Plus MC-ICP-MS with Jet Interface Option was used. The high-sensitivity Jet sample and X-type skimmer cones in combination with the apex Ω provide the highest sensitivity. This combination is recommended for U isotope precision.

Sensitivity

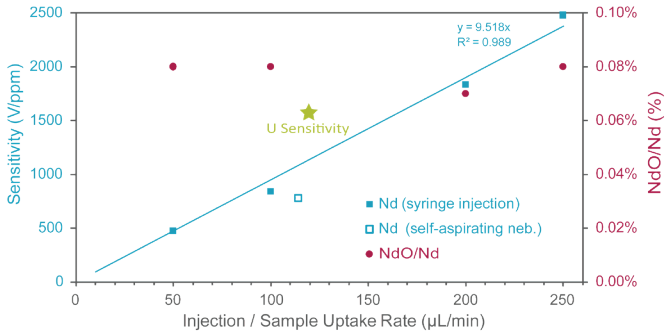

Figure 1. Nd sensitivity and oxides using Thermo Scientific Jet Interface with ESI apex Ω.

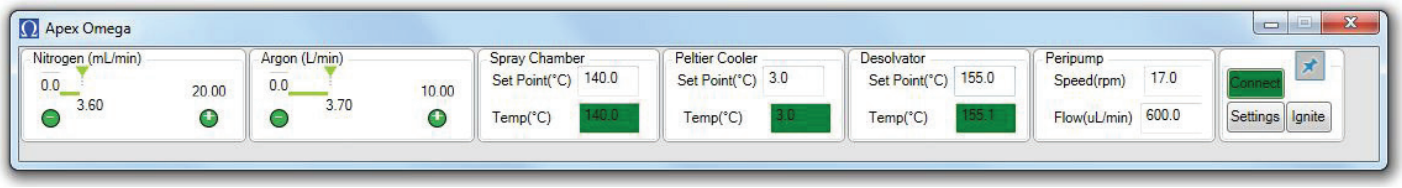

Figure 2. apex Ω screenshot showing software control for precise gas tuning.

Stability

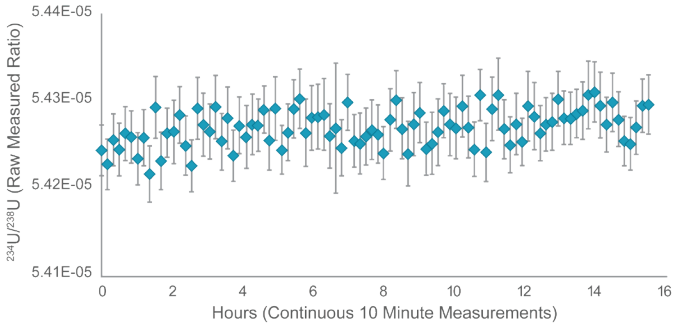

Figure 3. $^{234}U/^{238}U$ measured with 131 kcps (2mV) ^{234}U on 10^{13} Ω amplifier from 25 ng/g NBS U-010
92 x 10-minute runs spanning 15.5 hours
Raw Ratio RSD: 0.04% (external), 2SE error bars (internal)

Washout

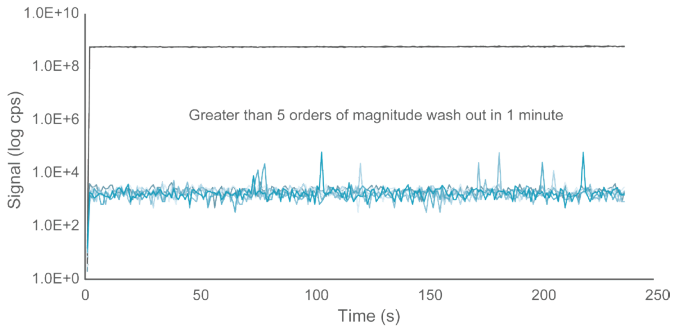

Figure 4. Greater than 5 orders of magnitude wash out obtained within 1 minute of running a 1 ppm uranium sample for 4 minutes.

Table 1. Note that the certified reference values for NBS U-010 would change the mean values and expand the uncertainty significantly for $^{234}U/^{238}U$ and $^{236}U/^{238}U$.

CRM Accuracy and Precision

		$^{243}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$
NBS U-005	Mean	0.000021889	0.00491913	0.000047459
	SD	0.000000032	0.00000024	0.000000038
	RSD	0.15%	0.005%	0.08%
NBS U-0002	Mean	0.000001653	0.00017724	
	SD	0.000000042	0.00000016	
	RSD	2.5%	0.09%	
IRMM-184	Mean	0.000053230	0.00726026	<3.5E-7
	SD	0.000000049	0.00000016	
	RSD	0.09%	0.002%	
IRMM-183	Mean	0.000019824	0.00321731	0.000148529
	SD	0.000000050	0.00000019	0.000000037
	RSD	0.25%	0.006%	0.02%

Results

Solution samples were obtained from the dissolution of uranium oxide grains isolated from soil and dust sample collected in the vicinity of Colonie, NY, USA. The soil and dust samples were contaminated by the combustion of scrap uranium metal at a former National Lead Industries (NLI) plant that operated from 1958 - 1984. The environmental case study is described in detail by Lloyd et al. (2009a). The procedures for the isolation of the 20 - 65 µm diameter grains and the chemical separation of uranium is described in Lloyd et al. (2009b). The isotopic compositions of the individual uranium oxide grains are all from depleted uranium with ^{236}U incorporated from reprocessed uranium. The isotopic composition are compatible with the tails assays from the Paducah Gaseous Diffusion Plant (PGDP) and the mixing of these materials at the former NLI plant at Colonie. Precise minor isotope data and the plots of three isotope ratios increases confidence in source apportionment.

Isotopic Compositions

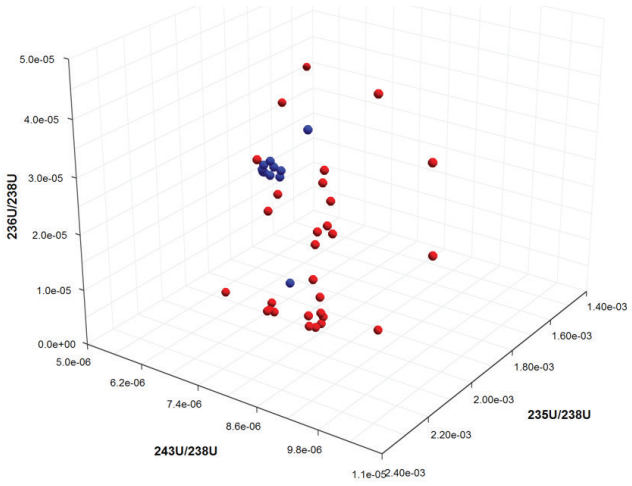

Figure 5. Isotopic Compositions of Colonie UOx Grains (blue) and PGDP tails assays (red).

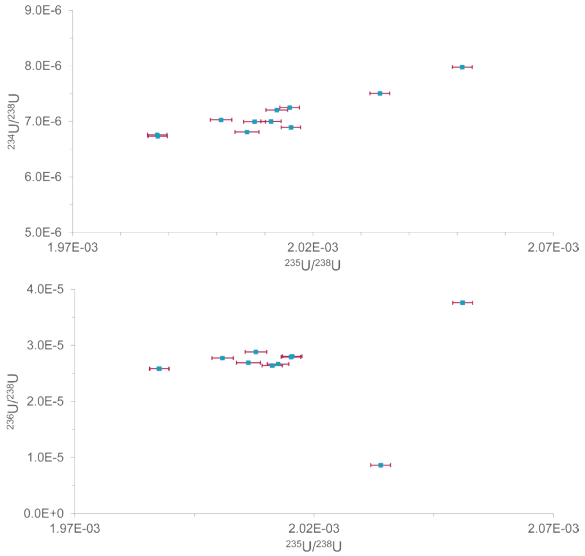

Figure 6. Isotopic Compositions of Individual Uranium Oxide Grains.

Conclusions

- An experimental setup was optimized for precise and accurate determination of uranium isotope ratios from single uranium oxide grains.
- The ESI apex Ω is a new high-efficiency desolvating nebulizer system, offering low-oxides, low hydrides, and highest sensitivity up to 250 µl/min introduction rate.
- The ESI apex Ω is tuned via software for precise optimization. The stability of gas flow regulation is proven by $^{235}U/^{238}U$ mass bias stabilities that are typically better than 60 ppm (1RSD) over analytical sessions of 15+ hours.
- The sensitivity and stability of the inlet system and ICP interface is utilized by ion detection on detectors that have complimentary performance characteristics. The combination with Thermo Scientific 10^{13} ohm amplifier technology allows minor isotopes to be measured more precisely from limited samples.

References

Richter & Goldberg 2003, Int. J. Mass Spectrom., 229, 181–197.

Lloyd et al., 2009a, Sci. Total Environ., 408(2), 397–407.

Lloyd et al., 2009b, J. Anal. At. Spectrom., 24(6), 752–758.