Improved abundance sensitivity in MC-ICP-MS for determination of $^{236}U/^{238}U$ isotope ratios in the 10^{-7} to 10^{-8} range

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A multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS)—Nu Plasma HR—equipped with an ion deceleration filter ('high abundance sensitivity channel') was optimized for the determination of extremely low uranium isotope ratios and applied for the first time for the analysis of $^{236}U/^{238}U$ isotope ratios in the 10^{-8} to 10^{-7} range in isotopic reference material IRMM-184, as well as in two unknown samples obtained in the frame of a round-robin exercise. The application of the ion deceleration lens system in the Nu Plasma ICP-MS allowed a reduction of peak tailing from $^{238}U^+$ ions at $m/z = 236$ down to 3×10^{-9}, whereas the absolute sensitivity for uranium was reduced by only about 30%. Thus, abundance sensitivity was improved by almost two orders of magnitude and the minimum determinable $^{236}U/^{238}U$ ratio was improved by more than one order of magnitude compared with conventional sector-field ICP-MS or TIMS. However, interference by $^{235}U^1H^+$ ions deteriorated the accuracy and increased the measurement uncertainty up to 48%, in particular in the case of samples enriched in ^{235}U. Deviation of the measured value from the certified ones varied from −24% to 17.7% but was within the measurement uncertainty.

Introduction

The determination of ^{236}U is challenging, because extremely low ^{236}U quantities have to be measured in the presence of a large excess of ^{238}U and ^{235}U. Both isotopes represent severe sources of interference in mass spectrometric and radiometric determinations of ^{236}U. Because of the presence of interfering peaks from the α-decay of ^{235}U the determination of the $^{236}U/^{238}U$ isotopic ratio by α-spectrometry is limited to 3×10^{-5}.[1,2] Typical abundance sensitivity for the uranium isotopic ratio measurements with conventional thermal ionization mass spectrometers (TIMS) is about 10^{-7}.[3,4] By the use of a special lens deceleration system for TIMS an upper limit for $^{236}U/^{238}U$ of 6×10^{-10} was achieved.[5] Accelerator mass spectrometry (AMS) is well established for uranium isotope ratio measurements and reaches typically abundance sensitivities for ^{236}U in the range of 10^{-11} [6–8] to 10^{-12}.[9]

Compared with these mentioned methods inductively coupled plasma mass spectrometry (ICP-MS) has the advantage of a much simpler sample preparation and much shorter measurement times. Thus, ICP-MS has been widely used for routine ^{236}U determination in environmental samples.[10,11] However, up to now the limited abundance sensitivity provided by common ICP-MS instruments as well as interference by $^{235}U^1H^+$ ions has hampered the determination of $^{236}U/^{238}U$ isotope ratios in the 10^{-7} range and below.[10–13] Thus, several groups reported recently the minimal $^{236}U/^{238}U$ ratio detectable by sector-field ICP-MS as low as $\sim 2 \times 10^{-7}$ [10,11] and $(3–5) \times 10^{-7}$.[13]

The present work describes the application of a multicollector ICP-MS, NU Plasma, with improved abundance sensitivity for rapid and ultra-sensitive measurement of $^{236}U/^{238}U$ isotope ratios in the low 10^{-7} and 10^{-8} range.

Experimental

Standards, reagents and samples

Isotope standard reference material U-500 (NIST, Gaithersburg, MD, USA) and uranium solution with natural isotopic composition were used for the determination of mass bias and ion counter gain in MC-ICP-MS and for the determination of uranium hydride UH^+/U^+ ratio, respectively. Isotope ratios of uranium were measured in an isotopic standard solution of uranium IRMM 184 (IRMM, Geel, Belgium) and in two unknown samples obtained in the frame of a round robin exercise. The solutions were diluted, with deionized water (18 MΩ) obtained from a Millipore Milli-Q-Plus water purifier, to about 20 ng ml^{-1} and acidified to 1% (v/v) HNO_3 by using sub-boiled HNO_3.

ICP-MS instrumentation and measurement procedure

A high-resolution sector field MC-ICP-MS with a Nier–Johnson geometry (Nu Instruments, Wrexham, UK) equipped with a standard ion collector block was coupled to a high efficiency solution introduction system (APEX IR, Elemental Scientific, Inc., Omaha, NE). The intensities of $^{235}U^+$ and $^{238}U^+$ ions were measured with two Faraday detectors whereas the $^{236}U^+$ intensity was monitored with an ion counter placed behind a

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Table 1 Operational parameters of the MC-ICP-MS

Rf power/W	1300
Cooling gas flow rate/L min^{-1}	13
Auxiliary gas flow rate/L min^{-1}	0.71
Nebulizer gas pressure/psi	35
Mass resolution	300
Detector arrangement	
^{238}U	L1 (Faraday cup)
^{236}U	IC0 (Ion counter)
^{235}U	L3 (Faraday cup)
Ion counter gain/V	1900
Retard voltage/V	4005
Lens voltage/V	3910
Number of cycles	10
Number of blocks	8
Analysis time/min	10

special ion deceleration filter ('retardation filter')[14] for high abundance sensitivity using the conditions listed in Table 1. The measured ^{236}U/^{238}U ratios were corrected taking account of instrumental background, dead time of the ion counter, peak tailing from ^{238}U$^+$ and ^{235}U^{1}H$^+$ intensity on $m/z = 236$. The average value and its combined uncertainty were calculated by using GUM Workbench Pro Version 2.3.2.33 software (Danish Technological Institute).

Comparative isotopic measurements were performed with a sector-field ICP-MS (ELEMENT 2, ThermoFinnigan, Bremen, Germany) and with a TIMS (Finnigan MAT 262, ThermoElectron Bremen, Germany). Further details of those systems are described elsewhere.[11,15]

Results and discussion

Optimization of MC-ICP-MS

Experimental parameters of MC-ICP-MS, including nebulizer gas, rf power and ion transfer lens potentials, were optimized with respect to the maximum ion intensity of ^{238}U$^+$ using a uranium solution of natural composition. The peak tailing originating from ^{238}U in the vicinity of m/z = 236 was analyzed by using uranium solution with a ^{236}U/^{238}U ratio of about 10^{-6}, prepared by mixing natural uranium and U-500. The ^{236}U/^{238}U ratio was chosen in such a way that the ^{236}U$^+$ peak could still be distinguished on the low mass tail of ^{238}U$^+$ (Fig. 1a). The potentials on the retard filter installed in the front of the ion counter IC0 were tuned in respect of (i) the lowest peak tailing and (ii) the minimal loss of the ^{236}U$^+$ intensity. Thus, applying the retardation filter resulted in improved abundance sensitivity by more than two orders of magnitude, with a relatively small loss of intensity for ^{236}U$^+$ of about 30% (Fig. 1b).

In sector-field mass spectrometers peak tailing on the lower mass side results mainly from ions losing energy by collision with residual gas molecules or by scattering on ion lenses, *etc.*, in the analyzer. In particular for ICP-MS, where the ion source works under atmospheric pressure, the abundance sensitivity for the ^{236}U/^{238}U isotope ratio is limited by a relatively high pressure of the residue gases in the mass analyzer. Thus, a typical abundance sensitivity ratio at m/z = 236, resulting from ^{238}U$^+$, is about 5×10^{-6} for a sector-field ICP-MS (Table 2). On the other hand, using higher mass resolution in a conventional sector-field ICP-MS also results in reduced peak tailing, as was reported by Ketterer *et al.*[10] with an example of using the ICP-MS Axiom. Also, application of a sector-field ICP-MS ELEMENT 2 at a mass resolution $m/\Delta m$ = 4000 allows abundance sensitivity for ^{236}U/^{238}U as low as 3×10^{-7}.[11] It should be mentioned, however, that application of higher mass resolution reduces the absolute sensitivity by at least 10-fold, which represents a significant shortage when analyzing such ultra-low abundant isotopes.

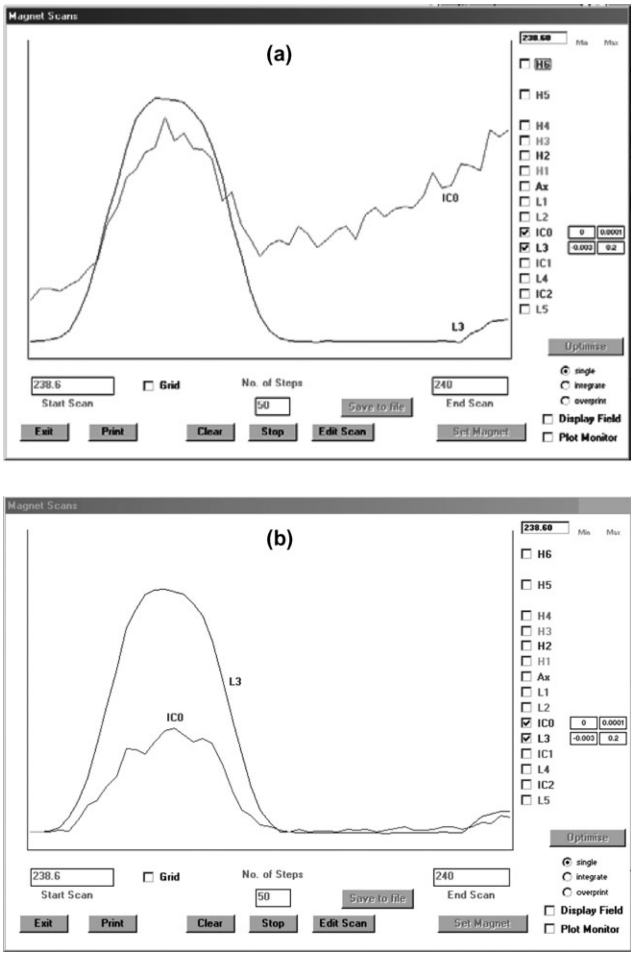

Fig. 1 Illustration of reducing peak tailing from ^{238}U at in the m/z = 236 region; the figure presents ion peaks of ^{235}U measured with Faraday L3 and ^{236}U measured with ion counter IC0 with optimized retardation filter voltages switched off (a) and on (b). The measurements were performed by using a uranium solution with ^{236}U/^{238}U ratio of about 10^{-6} prepared by mixing natural uranium and U-500 standard.

Table 2 summarizes the figures of merit of MC-ICP-MS for ^{236}U/^{238}U ratio measurements in comparison with single collector sector-field ICP-MS (with an example of ICP-MS ELEMENT 2) and TIMS. The ELEMENT 2 (at $m/\Delta m$ = 300) coupled with APEX provided the highest sensitivity of about 5 counts per attogram, which corresponds to $\sim 2 \times 10^{-3}$ counts per atom for uranium isotopes: however, this high absolute sensitivity is coupled with poor abundance sensitivity. Application of a higher mass resolution reduces

Table 2 Figures of merit of different ICP-MS (connected with Apex)

ICP-MS	Absolute sensitivity for ^{236}U/counts ag^{-1}	Abundance sensitivity for ^{236}U/^{238}U ratio	UH$^+$/U$^+$ ratio	Minimum detectable ^{236}U/^{238}U isotope ratio	RSD of ^{236}U/^{238}U ratio of 10^{-7} (%)
MC-ICP-MS Nu without retard lens	3.8	1.5×10^{-6}	4.7×10^{-6}	1×10^{-6}	—
MC-ICP-MS Nu with retard lens	2.6	3×10^{-9}	4.7×10^{-6}	1×10^{-8}	4.7[a]
ICP-MS Element 2 at $m/\Delta m = 300$	5.0	5×10^{-6}	1.6×10^{-5}	2×10^{-6}	—
ICP-MS Element 2 at $m/\Delta m = 4000$	0.5	3×10^{-7}	1.6×10^{-5}	1.2×10^{-7}	4.5[b]
TIMS 262	~8.0	1–2 × 10^{-6}	—	2×10^{-6}	—

[a] Isotope ratio was measured in 20 ng g^{-1} uranium solution, measurement time of 10 min, $n = 8$. [b] Isotope ratio was measured in 100 ng g^{-1} uranium solution, measurement time of 10 min, $n = 8$.

both the peak tailing effect at $m/z = 236$ and the absolute sensitivity for uranium by about one order of magnitude, and therefore, it is difficult to compromise the experimental conditions of conventional ICP-MS for ultra-trace ^{236}U determination.

Contrary to higher mass resolution, using the ion deceleration filter in MC-ICP-MS reduces the absolute sensitivity by about only 30%, and in combination with very good abundance sensitivity it strongly enhances its capability for determination of extremely low ^{236}U/^{238}U isotope ratios. Although TIMS has slightly better absolute sensitivity in comparison with MC-ICP-MS, it normally requires a longer analysis time (in this work the measurement block took three hours).

However, ^{236}U analysis by ICP-MS is limited by several factors, including the high-mass peak tailing from ^{235}U and interference by ^{235}U^{1}H$^+$ at $m = 236$ u. In this work the minimum determinable ^{236}U/^{238}U isotope ratios by different mass spectrometric methods were evaluated from 6 repetitive analyses of natural uranium solution (*i.e.*, containing no detectable ^{236}U) by using 3σ criteria (Table 2), *i.e.*, three-fold standard deviation of a superposition of contributions from the low-mass peak tail of ^{238}U, high-mass peak tail of ^{235}U and ^{235}U^{1}H$^+$. In the case of MC-ICP-MS with retard lens, despite the the abundance sensitivity of 3×10^{-9}, the minimum determinable ^{236}U/^{238}U isotope ratio was only 1×10^{-8} as a result of the contribution by the UH$^+$/U$^+$ rate variation. This value is by more than one order of magnitude better than the corresponding limit for ^{236}U/^{238}U of 2×10^{-7} obtained recently by Ketterer *et al.*[10] using an Axiom ICP-MS and by Boulyga and Heumann by using an ICP-MS ELEMENT 2.[11] It should be mentioned also that the minimum determinable ^{236}U/^{238}U isotope ratio depends on the enrichment with ^{235}U, *i.e.*, it will be higher in the case of enriched uranium and lower in the case of depleted uranium.

Aerosol desolvation within the sample introduction system or application of heavy water for sample dissolution[13] are further approaches to reducing the UH$^+$/U$^+$ ratio. The lowest uranium hydride rate (UH$^+$/U$^+$ = 1.1×10^{-6}) has been achieved up to date by using APEX with a Peltier cooled Nafion® membrane desolvator ACM in combination with the Element 2.[11] Application of a membrane desolvator can also be useful for improving the MC-ICP-MS performance.

Isotopic analysis of uranium containing solutions

When analyzing uranium isotope ratios in the 10^{-7} range, the precision of both MC-ICP-MS and ICP-MS with a single ion detector was similar and mainly limited by poor counting statistics (Table 2).

In order to evaluate the accuracy of measured ^{236}U/^{238}U isotope ratios two samples with unknown isotope abundances as well as uranium isotopic standard IRMM-184 were analyzed in a round-robin exercise. The results are given in Fig. 2 and Table 3 together with the certified values. Also the results obtained by using ICP-MS Element 2 are given for comparison. The applied TIMS 262 had a significantly worse abundance sensitivity of 1–2 × 10^{-6} and therefore it could not be applied for determination of the ^{236}U/^{238}U ratio in these samples.

Deviation of the MC-ICP-MS results from the certified values was 17.7% and −24% in the case of two unknown samples and 0.1% in the case of IRMM-184. The large measurement uncertainties of up to 48% were significantly higher than the corresponding RSDs and they were mainly due to the uncertainty of ^{235}U^{1}H$^+$ and peak tailing contribution (Fig. 3), particularly in the case of sample 2 enriched with ^{235}U by about 2.4%.

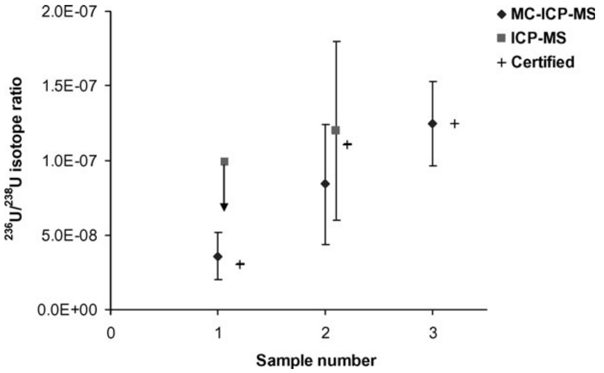

Fig. 2 Measured and certified ^{236}U/^{238}U isotopic ratios in two samples of round robin-exercise (samples 1 and 2) and in isotopic standard solution of uranium IRMM-184 (sample 3): average values are given with combined measurement uncertainties with a coverage factor of 2.

Table 3 $^{236}U/^{238}U$ isotope ratios measured by using ICP-MS

Sample	$^{236}U/^{238}U$ isotope ratio MC-ICP-MS	ICP-MS	Certified
1	$(3.6 \pm 1.6) \times 10^{-8}$	$< 10^{-7}$	$(3.0579 \pm 0.0083) \times 10^{-8}$
2	$(8.4 \pm 4.0) \times 10^{-8}$	$(1.2 \pm 0.6) \times 10^{-7}$	$(1.1054 \pm 0.0029) \times 10^{-7}$
IRMM 184	$(1.25 \pm 0.28) \times 10^{-7}$		$(1.2446 \pm 0.0017) \times 10^{-7}$

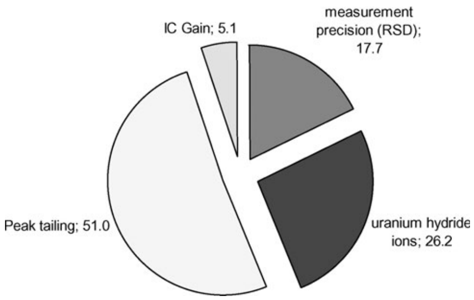

Fig. 3 Relative contribution of main uncertainty sources (%) for $^{236}U/^{238}U$ isotope ratio measured in sample 2 by using MC-ICP-MS; mass bias was compensated by calibration of ion counter (IC) gain against the corresponding ratio of U-500 isotope standard.

In general, MC-ICP-MS with the high-efficiency solution introduction systems offers high sensitivity for the determination of ^{236}U and for an extremely low $^{236}U/^{238}U$ isotope ratio of about 10^{-8}, which is better by more than one order of magnitude compared with conventional sector-field ICP-MS. The MC-ICP-MS increasingly becomes competitive with such sophisticated techniques as AMS or resonance ionization mass spectrometry in the field of extremely low-abundant isotope analysis, whereas the precision of $^{236}U/^{238}U$ isotope ratio measurement using MC-ICP-MS is better than that of AMS or RIMS. MC-ICP-MS is competitive with other techniques with respect to its better time-effectiveness and lower labour expenses. Moreover, MC-ICP-MS is also a promising method for ultra-trace analysis of other long-lived radionuclides, in particular for environmental monitoring of radioactive contamination.

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