TECHNICAL NOTE

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A new milestone for ultra-low ^{236}U/^{238}U isotope ratio measurements by ICP-MS/MS†

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Uranium isotope composition in environmental samples allows to trace its origin. Therefore, the analytical community has been working for several years to reduce the detection limit of the ^{236}U/^{238}U isotopic ratio using mass spectrometry, and in particular the ICP-MS/MS technology. The latest generation of ICP-MS/MS, recently commercialized, has improved performance, including better ion transmissions and an extended dynamic range of mass detection. These improvements, the coupling with an efficient desolvating module and the addition of oxygen in the collision/reaction cell permitted to remove the interferences of ^{236}U$^+$ ion measurements (abundance sensitivity of the major isotopes and polyatomic interferences, notably ^{235}UH$^+$ ions). For the first time a precise determination of the ^{236}U/^{238}U isotopic ratio up to 10^{-11} was demonstrated, validated by the analysis of certified reference materials and environmental samples previously measured by AMS. This new limit is a new milestone in the determination of ultra-low ^{236}U/^{238}U isotope ratios and opens the way to various geochemical applications.

Introduction

Uranium isotope measurements are of increasing interest for environmental sciences, nuclear safeguards and nuclear forensics.[1,2] Due to the small natural variations and to an important anthropogenic U dilution by the natural U in the environment, the use of ^{235}U/^{238}U isotope ratios is sometimes irrelevant. Recently, several studies have focused on the minor isotopes of uranium in the environment.[3–5] In fact, a minor isotope like ^{236}U is of prime interest for the determination of the origin of uranium thanks to the variability of its isotope ratios depending on their origin.[6]

The ^{236}U concentration in the environment (not contaminated by nuclear activities) is a few tens of fg per g[7] and their ^{236}U/^{238}U isotope ratios are typically about 10^{-14}–10^{-13}.[6] In U ore, high uranium concentration and neutron flux increase the ^{236}U formation rate and the isotope ratio varies between 10^{-12} and 10^{-10}. Anthropogenic ^{236}U, formed in enriched uranium, was spread in the environment. Global fallout from nuclear weapon tests released uranium thus leading to characteristic ^{236}U/^{238}U isotope ratios of 10^{-9}–10^{-6} and $>10^{-6}$ for sediment and soils impacted by nuclear accidents or releases from nuclear reprocessing plants.

However, the detection of ^{236}U in environmental samples is quite challenging due to its low abundance and requires

therefore instruments with high sensitivity and high resolution. The most efficient technique is the Accelerator Mass Spectrometry (AMS), in which ions are accelerated before the separation of isotopes. Its high resolution allows the detection of very low concentrations of ^{236}U ions and therefore very low ^{236}U/^{238}U isotope ratios of about 10^{-14}.[8] The second most efficient method is the Thermal Ionisation Mass Spectrometry (TIMS), with a detection limit of about 10^{-10}.[6,9] Inductively Coupled Plasma Mass Spectrometry (ICP-MS) techniques were until recently less performant for the determination of ^{236}U/^{238}U isotope ratios.[10–15] Some spectral interferences limit the determination of very low isotope ratios, which are mainly the uranium hydride species (^{235}U^{1}H$^+$), and the abundance sensitivity of most abundant isotopes ^{235}U and ^{238}U. Recent works have focused on the determination of very low isotope ratios by ICP-MS/MS[7,16–18] by improving the hydride formation, the peak tailing *etc.* In a recent work, the lowest isotope ratios measured using the ICP-MS/MS technology in UO$^+$ mode was about 1×10^{-10}.

The present study was motivated by the possibility to experiment with the new model of ICP-MS/MS, the Agilent 8900. The objective of this work is to determine the performances of this new generation of ICP-MS/MS in terms of hydride formation rate and the lowest ^{236}U/^{238}U isotope ratio achievable in UO$_2$$^+$ mode. To this end, measurements of certified references materials and environmental samples were performed.

Experimental

Reagents

High purity nitric acid (VWR Chemicals, Normapur 68%), hydrochloric acid (Merck, Emsure 37%), hydrofluoric acid

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(MERCK, Normapur) and perchloric acid (Prolabo, Suprapur) were used in this work (sample digestion, uranium separation from sample matrix, etc.). Acid dilutions were performed with deionized water (18.2 MΩ cm Milli Q system, Millipore). Sample solutions, instrumental blanks and washing procedures were performed with 2% HNO_3. Moreover, for an efficient instrument washing, 0.05 mol L^{-1} (M) HEDPA and a solution with HF/HNO_3/HCl were used to decrease the uranium background before sample measurements.

Care was taken to avoid the cross-contamination of samples. In addition to high purity reagents, samples were prepared in laminar flow cabinet (ISO 3–ISO 4) to minimise laboratory background. Procedural blanks ($n = 12$) were prepared in the same conditions as samples and analysed by AMS. No contamination was highlighted. Moreover, blank solutions ($n = 32$) were regularly measured between samples to ensure the non-contamination of the instrument (see Calculation procedures section below).

Standards and samples for method validation

As previously,[7] several samples characterised by decreasing $^{236}U/^{238}U$ isotope ratios were measured for method validation. First, a standard from the Joint Research Centre (Geel, Belgium) IRMM-075/6 was analysed. The uranium concentration in the measured solution was 5 µg g^{-1}, and its certified $^{236}U/^{238}U$ isotope ratio is $(1.09 \pm 0.01) \times 10^{-9}$. The second standard is an in-house AMS standard of uranyl nitrate processed before 1918, called KkU, provided by the University of Physics in Vienna.[19] Its isotopic ratio is well-known $(6.98 \pm 0.32) \times 10^{-11}$. Finally, two environmental samples, called MBN and MTG, were analysed. These samples are uranium ores found in the vicinity of former uranium mines in France. They were previously characterised by AMS at VERA Laboratory (Vienna, Austria) and the $^{236}U/^{238}U$ isotope ratios were respectively $(1.04 \pm 0.18) \times 10^{-10}$ for MBN and $(1.13 \pm 0.17) \times 10^{-11}$ for MTG. Uranium concentrations in these samples were approximately 100 µg g^{-1} for MBN and 1300 µg g^{-1} for MTG. Finally, mass fractionation was corrected using a certified standard from the Joint Research Centre (Geel, Belgium) IRMM-184. The uranium concentrations in the measured solutions were respectively about 0.04 µg g^{-1}, 5 µg g^{-1}, 15 µg g^{-1}, 14 µg g^{-1} and 12 µg g^{-1} for IRMM-184, IRMM-075/6, KkU, MBN and MTG respectively.

Sample preparation

Environmental samples were collected in wetlands downstream from former U-mines in France. All samples contain high U concentrations (~3000–4000 µg g^{-1}) and were prepared using the method described in a previous publication.[7] In brief, about 100 mg of samples were dissolved in Savillex® PFA Teflon® vials using concentrated HNO_3 and concentrated HF. Samples were heated to 90 °C overnight with closed lids before adding concentrated $HClO_4$. Samples were heated to 90 °C with open lids for 3 h to evaporate the nitric and hydrofluoric acids. Temperature was increased to 160 °C to evaporate the perchloric acid. Samples were then purified with UTEVA resin (100–150 µm). Samples were loaded on the column in 3 M HNO_3

media and matrix elements were discarded using 6 mL 3 M HNO_3. Th was then eluted using 6 mL 3 M HCl, and finally U was eluted using 6 mL 0.1 M HCl. U fractions were evaporated to dryness and recovered with 0.05 M HNO_3 for ICP-MS measurement.

Instrumentation

To achieve a very low hydride formation rate, a desolvating instrument was used before the introduction of the sample in the ICP-MS. In this work, we used APEX Ω from Elemental Scientific (Nebraska, USA). It allows us to decrease the hydride formation rate in the plasma and to increase the uranium sensitivity. Desolvating instrument gas (nebuliser gas, N_2 gas and Ar gas) and ICP-MS parameters were daily optimized using a 1 ng g^{-1} uranium solution (Table 1). Argon and nitrogen gas quality is "premier". Nitrous oxide (N_2O) or dioxygen (O_2) were used in the CRC. Gas qualities were "technique" for N_2O and "ultrapure" for O_2. All gases are from AirProducts (Aubervilliers, France).

Calculation procedures

Precautions were taken regarding the $^{236}U/^{238}U$ isotope ratio calculation procedure. Indeed, ^{236}U and ^{238}U signals cannot be directly used for the determination of ratios because they are not measured using the same detection mode (pulse counting or analogue). To ensure that isotopes are measured in pulse

Table 1 ICP-MS/MS parameters: desolvating instrument parameters, ICP-MS/MS and acquisition parameters

Parameter	Value
Desolvating system	APEX Ω
Apex Ω spray chamber temperature	140 °C
Apex Ω Peltier cooler temperature	3 °C
Apex Ω desolvator temperature	155 °C
Nebulizer	PFA micro-concentric (ESI)
Nebulizer gas	100 µL min^{-1}
N_2 gas (desolvating system)	2.37 L min^{-1}
Ar gas (desolvating system)	3.35 L min^{-1}
Torch	One-piece (quartz)
Sample gas	0.88 L min^{-1}
Sample uptake	~300 µL min^{-1}
RF power	1500 W
Sampling depth	6 mm
Cell gas (O_2) flow rate	0.435 mL min^{-1}
Extract 1 and 2	−11.2, −186 V
Deflect	10.6 V
Q1 and Q2 mass gain	132, 136
Q1 and Q2 mass offset	126, 124
Q1 and Q2 axis offset	−0.15, −0.08
Octopole bias	−1.0 V
Energy discrimination	−10.0 V
Peak shape	1 point
Integration time of $^{234,235,236}U^{16}O_2^+$, $^{238}U^1H^{16}O_2^+$	1, 0.1, 8, 2 s
Number of sweeps per replicate	100
Number of replicates per sample	10
Sensitivity on $^{238}UO_2^+$	4.3×10^6 cps ppb^{-1}

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counting mode (and to avoid detector overrange due to an extremely high ^{238}U ions flux), the $^{236}U/^{238}U$ isotope ratio was deduced from the $^{236}U/^{234}U$ isotope ratio, as explained in our previous work.[7] All isotopes were measured in mass-shift mode, reacting with oxygen in the CRC. However, for an easy reading, all isotopes will be noted $^{23X}U^+$, instead of $^{23X}U^{16}O_2^+$ and isotope ratios will be expressed as $^{23X}U^+/^{23X}U^+$ and $^{23X}UH^+/^{23X}U^+$ instead of $^{23X}U^{16}O_2^+/^{23X}U^{16}O_2^+$ and $^{23X}U^{16}O_2H^+/^{23X}U^{16}O_2^+$.

For the determination of $^{236}U^+/^{234}U^+$, all signals (10 replicates for each isotope) were corrected for the blank signal. For the blank correction, several ($n = 32$) 0.05 M HNO_3 samples were regularly measured during the analysis sequence. The $^{236}U^+$ signals in these blank solutions were a mean of 0.7 ± 0.5 cps ($k = 2$). The same level of ^{236}U signal was found in the procedural blanks, which demonstrates the non-contamination from the lab or the reagents.

Then, the isotope ratios were corrected for outliers and for hydride formation rate and mass fractionation. After the blank correction, the $^{236}U^+/^{234}U^+$ and $^{238}UH^+/^{234}U^+$ isotope ratios were simply calculated. Outliers were rejected with a 2-sigma test. Then, the $^{236}U^+/^{234}U^+$ isotope ratios were corrected for the hydride formation interferences using eqn (1). More details can be found in ESI.†

$$\left(\frac{^{236}U^+}{^{234}U^+}\right)_{corr} = \left(\frac{^{236}U^+}{^{234}U^+}\right)_{meas} - \left(\frac{^{238}UH^+}{^{234}U^+}\right)_{meas} \times \frac{1}{137.88} \quad (1)$$

where, $\left(\frac{^{236}U^+}{^{234}U^+}\right)_{corr}$ correspond to the isotope ratio corrected for the hydride formation rate, $\left(\frac{^{236}U^+}{^{234}U^+}\right)_{meas}$ correspond to the measured isotope ratio, and $\left(\frac{^{238}UH^+}{^{234}U^+}\right)_{meas}$ is the hydride formation rate measured in the sample. Note that 137.88 is the natural $^{238}U/^{235}U$ isotope ratio value recommended by the IGC subcommision on geochronology. Mass fractionation was considered for $^{236}U^+/^{234}U^+$ and $^{238}UH^+/^{234}U^+$ isotope ratios using the $^{235}U/^{238}U$ ratio measured in the certified standard IRMM-184 in standard bracketing mode. Finally, $^{236}U/^{238}U$ isotope ratios were deduced using the corrected $^{236}U/^{234}U$ and the $^{234}U/^{238}U$ isotope ratios measured in diluted solutions of the samples.

All signal corrections were performed before the mass fractionation correction which was applied to each replicate of measurement. Uncertainties with an extended coverage factor of 2 were determined using eqn (2).

$$u\left(\frac{^{23X}U^+}{^{23X}U^+}\right) = 2 \times \frac{\sigma\left(\frac{^{23X}U^+}{^{23X}U^+}\right)}{\sqrt{N}} \quad (2)$$

where $u\left(\frac{^{23X}U^+}{^{23X}U^+}\right)$ is the uncertainty of measured isotope ratio, $\sigma\left(\frac{^{23X}U^+}{^{23X}U^+}\right)$ is the standard deviation of the replicates (N) of the measured isotope ratios. For the mass fraction correction and the following corrections, uncertainties are propagated during each step.

Means of the N replicates are also presented in the result section; uncertainties of these mean values are based on the propagation of the uncertainties of the N replicates.

The method validation was quantified by the determination of trueness and repeatability for each sample. The trueness (%) of certified values was determined using eqn (3).

$$\text{Trueness}(\%) = \left(\frac{\left(\frac{^{236}U^+}{^{238}U^+}\right)_{meas}}{\left(\frac{^{236}U^+}{^{238}U^+}\right)_{cert}} - 1\right) \times 100 \quad (3)$$

where $\left(\frac{^{236}U^+}{^{238}U^+}\right)_{meas}$ is the measured isotope ratio and $\left(\frac{^{236}U^+}{^{238}U^+}\right)_{cert}$ is the certified isotope ratio.

Repeatabilities (%) were determined with an extended coverage factor of 2, following eqn (4).

$$\text{Repeatability}(\%) = 2 \times \frac{\sigma\left(\frac{^{236}U^+}{^{238}U^+}\right)_n}{\left(\frac{^{236}U^+}{^{238}U^+}\right)_{mean}} \times 100 \quad (4)$$

where $\sigma\left(\frac{^{236}U^+}{^{238}U^+}\right)_n$ is the standard deviation of n repetitions of measurement and $\left(\frac{^{236}U^+}{^{238}U^+}\right)_{mean}$ is the mean of these n repetitions.

Result and discussion

Uranium sensitivity with Agilent ICP-MS/MS

The new generation of Agilent ICP-MS/MS, the 8900, has new capabilities which greatly improve the performances of the ICP-MS/MS technology, compared with the first generation of Agilent 8800. The main differences are better interface cones, lenses and vacuum pump to enhance sensitivity. The major improvement is the widening of the dynamic range of mass filters, which allows now the measurement of isotopes up to a mass to charge ratio of 280. In our study this is a great improvement, as U ions could now be measured as UO_2^+ rather than UO^+. As previously mentioned, all uranium isotopes were measured in mass shift mode: for example, for the ^{238}U determination, Q1 is fixed at $m/z = 238$, uranium isotopes are oxidised in the CRC with reaction gas, then Q2 is fixed at $m/z = 238 + 32 = 270$.
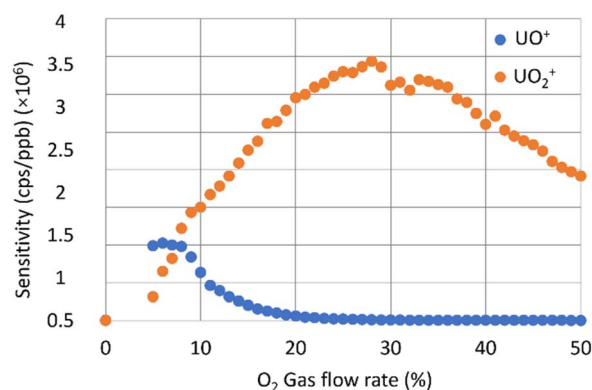

Fig. 1 Uranium oxide sensitivities using oxygen in the CRC, measured as UO^+ (blue) or UO_2^+ (orange).

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Sensitivities obtained with UO^+ and UO_2^+ were compared (Fig. 1). O_2 was injected in the CRC with an increasing flow rate. Sensitivities at $m/z = 254$ and 270 were observed. As in our previous study, a maximum of sensitivity is observed for a O_2 flow rate of 0.04 mL min^{-1} (8%). However, the maximum sensitivity is now about 1×10^6 cps ppb^{-1}, which is an improvement by a factor of 2 compared with the 8800 ICP-MS/MS.[7,20] Regarding the UO_2^+ signal, the maximum of sensitivity is found for 0.435 mL min^{-1} (29%) at a level of 3.5×10^6 cps ppb^{-1}. This improvement of the sensitivity using UO_2^+ is required to decrease the limit of detection of the $^{236}U^+$ ions.

Reaction gas optimisation

In our previous work,[7] efforts were made on the reduction of the hydride formation rate, which is the main interference during ^{236}U measurements using an Agilent 8800 ICP-MS/MS. For this purpose, several reaction gases in CRC, desolvating module and molarity of the nitric acid of the measured solution were tested. The optimal combination consisted in the use of N_2O in CRC, APEX Ω and 0.05 M HNO_3 and allowed us to obtain a sensitivity of 5×10^5 cps ppb^{-1} and a hydride formation rate of 6.40×10^{-9}.

In this work, we compared the performance of Agilent 8800 and Agilent 8900 in terms of sensitivity and hydride formation rate (Fig. 2). As previously mentioned, we observed an increase in sensitivity from 5×10^5 cps ppb^{-1} with Agilent 8800 to a value of 4×10^6 cps ppb^{-1} with Agilent 8900. This increase in sensitivity is mainly due to the improvement of the ion beam transport between the extraction lenses and the detector and to measuring uranium in the UO_2^+ form (a more abundant species than UO^+).

Moreover, results show a decrease of the uranium hydride formation rate UH^+/U^+ to a value of 0.72×10^{-9} with the Agilent 8900 and O_2 as a reaction gas, which is an order of magnitude below the value published in our previous work (6.40×10^{-9}).[7]

This extremely low interference rate brings new limits of detection and the capacities to determine ultra-low $^{236}U/^{238}U$ isotope ratios. To this end, it is possible to quantify the theoretically lowest measurable $^{236}U/^{238}U$ isotope ratio, using eqn (5). Details on this equation can be found in ESI.†

$$\left(\frac{^{236}U^+}{^{238}U^+}\right) = \frac{UH^+/U^+}{^{235}UH^+/^{236}U^+} \times \frac{1}{137.88} \tag{5}$$

with a hydride formation rate of 7.2×10^{-10} and an interference to signal ratio of 1, the new lowest measurable $^{236}U/^{238}U$ isotope ratio is 5×10^{-12}. Consequently, the developed method is now sufficiently effective for the quantification of $^{236}U/^{238}U$ isotope ratios in uranium ore, hence the discrimination between anthropogenic uranium (from global fallout or nuclear industry releases) and natural uranium (from uranium ore).

Nitrous oxide was also tested with the Agilent 8900 ICP-MS/MS. In our previous work, using N_2O in the CRC allows us to greatly decrease the hydride formation rate. Surprisingly, in this work, our results show a decrease of the sensitivity from 4.3×10^6 cps ppb^{-1} with O_2 to 2.4×10^6 cps ppb^{-1} using N_2O, and also a decline of the hydride formation rate to 1.01×10^{-9}. This result is consistent with recent published research using N_2O in Agilent 8900 ICP-MS/MS.[21] Authors put forward the bigger size of the N_2O molecule and the loss of analyte by collision. Accordingly, we used O_2 as a reaction gas and the APEX Ω desolvating module to quantify the $^{236}U/^{238}U$ isotope ratios in a certified reference solution and environmental samples.

Validation of the method with certified reference materials

The developed method was validated through the measurement of a certified reference solution, IRMM 075/6 (Fig. 3), and an in-house AMS standard of uranyl nitrate, KkU (Fig. 4).

The IRMM standard is certified for a $^{236}U/^{238}U$ isotope ratio of 1.0885 (63) $\times 10^{-9}$. This is the lowest certified material commercially available for uranium ratios. The mean of 8 replicates shows a value of 1.098 (30) $\times 10^{-9}$ ($k = 2$) (Fig. 3). The relative uncertainty is 2.7%. It is worth mentioning that this value is lower by a factor of 2 compared with previous results on
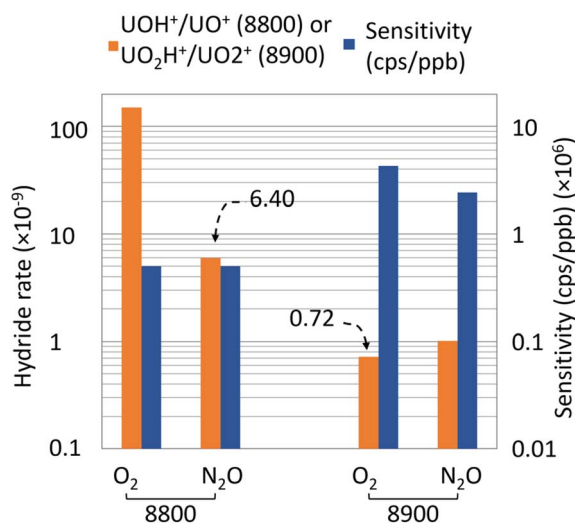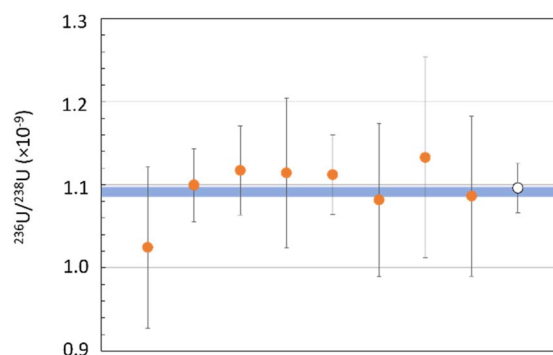

Fig. 2 Comparison of the hydride formation rate and sensitivity with Agilent 8800 ICP-MS/MS (left) from Jaegler et al. (2020) and Agilent 8900 ICP-MS/MS (right) using O_2 or N_2O as a reaction gas in the CRC.

Fig. 3 Measurement of $^{236}U/^{238}U$ isotope ratios in IRMM 075/6 certified reference material. The open dot corresponds to the mean of the measurements (red dots). The blue rectangle highlights the certified value uncertainties. Uncertainties are extended with a coverage factor of 2.

Fig. 4 Measurement of $^{236}U/^{238}U$ isotope ratios in KkU reference material. The open dot corresponds to the mean of the measurements (red dots). The blue rectangle highlights the certified value uncertainties. Uncertainties are extended with a coverage factor of 2.
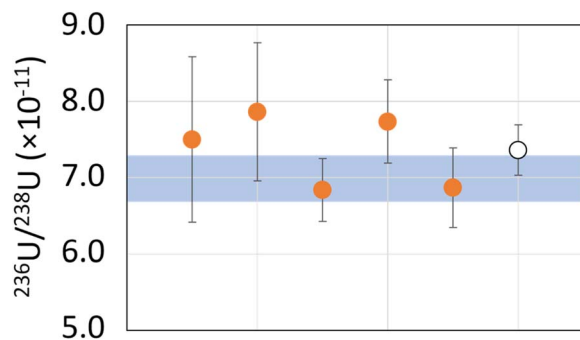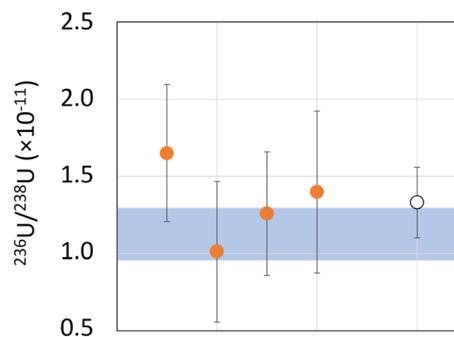
the same certified reference material (4.6%).[7] The trueness equals 0.9%, and the repeatability is 5.9% ($k = 2$).

Regarding the AMS standard, KkU sample, with a usual reference value of 6.98 (32) $\times 10^{-11}$, results on 5 measurement repetitions show a value of 7.36 (33) $\times 10^{-11}$ ($k = 2$). The relative uncertainty is 4.5%, the trueness is 5.5% and the repeatability is 13% ($k = 2$).

These results on reference material IRMM 075/6 and KkU are in good agreement with the certified values, demonstrated by the trueness lower than 1% and 6% respectively. Relative uncertainties better than 5% and repeatabilities better than 15% (using a coverage factor of 2) validated the measurement method to uranium ratios down to 10^{-11}. This is the first time that $^{236}U/^{238}U$ isotope ratios at this level were determined using an ICP-MS/MS. To confirm the capabilities of our method, environmental samples were also analysed.

Validation of the method with environmental samples

The environmental samples are two fraction of uranium ores, MBN and MTG, whose $^{236}U/^{238}U$ isotope ratios were previously determined by AMS. The ICP-MS/MS results were compared to the AMS results to validate the developed method.

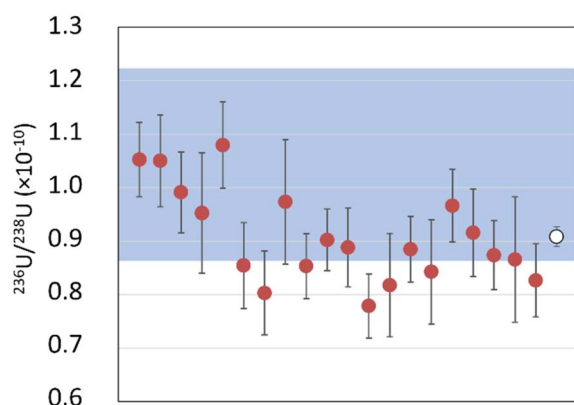Fig. 5 Measurements of $^{236}U/^{238}U$ isotope ratios in MBN sample. The open dot corresponds to the mean of the measurements (red dots). The blue rectangle highlights the certified value uncertainties. Uncertainties are extended with a coverage factor of 2.

Fig. 6 Measurements of $^{236}U/^{238}U$ isotope ratios in MTG sample. The open dot corresponds to the mean of the measurements (red dots). The blue rectangle highlights the certified value uncertainties. Uncertainties are extended with a coverage factor of 2.

$^{236}U/^{238}U$ isotope ratio measurements by AMS on MBN sample showed a value of 1.04 (18) $\times 10^{-10}$ ($k = 2$). The mean value of ICP-MS/MS measurements over 20 repetitions is 9.08 (18) $\times 10^{-11}$ (Fig. 5). The relative uncertainty equals 2.0% ($k = 2$), the trueness is -13%, whereas the repeatability is 19% ($k = 2$).

The uranium ratio in the MTG sample determined by AMS was 1.13 (17) $\times 10^{-11}$ ($k = 2$) (Fig. 6). ICP-MS/MS measurements over 4 repetitions show a mean value of 1.33 (23) $\times 10^{-11}$ ($k = 2$), a trueness of 18% and a repeatability of 40% ($k = 2$).

AMS and ICP-MS/MS measurements are in good agreement even for ultra-low $^{236}U/^{238}U$ isotope ratios at level 10^{-11} with trueness values below 20% for both samples. These results confirmed the capabilities of the developed method to reach a new milestone in the determination of ultra-low levels of $^{236}U/^{238}U$ isotope ratios in environmental samples.

Conclusions

The capabilities of a new generation of ICP-MS/MS were tested to reach a new limit of detection for the $^{236}U/^{238}U$ isotope ratio of 10^{-11}. This is one order of magnitude lower than the previously published limit of detection of 10^{-10}.[7] Earlier on, this level was a clear boundary in the capabilities of the method, as interferences were too significant to reach an accurate determination of the $^{236}U/^{238}U$ isotope ratio below 10^{-10}. With the new performance of the last generation of ICP-MS/MS and their capabilities to remove or reduce the measurement interferences, an accurate detection down to 10^{-11} is now possible.

This new limit is now very close to the theoretical lowest achievable $^{236}U/^{238}U$ isotope ratio (5×10^{-12}). However, there are still some drawbacks that are difficult to subvert: high sample volumes for samples with natural U concentration (~10 g of sample, considering 3 µg g^{-1} for the Earth crust[22]) and instrumental memory effects requiring long washout time to ensure that uranium contamination is completely removed. With great care of the blank level, accurate detection of $^{236}U/^{238}U$ isotope ratios below 10^{-11} could be achievable. This

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method can be performed for example to discriminate uranium ore and natural uranium in environmental samples.

Author contributions

HJ, AG performed the ICP-MS/MS investigations. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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