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Pushing limits of ICP-MS/MS for the determination of ultra-low $^{236}\text{U}/^{238}\text{U}$ isotope ratios

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ABSTRACT: Determination of uranium isotope ratios is of great expedience for assessing its origin in environmental samples. In particular, the $^{236}\text{U}/^{238}\text{U}$ isotope ratio provides a powerful tool to discriminate between the different sources of uranium (uranium ore, geochemical background and uranium from anthropogenic activities). However, in the environment, this ratio is typically below 10^{-8} . This low abundance of ^{236}U and the presence in large excess of major isotopes (mainly ^{238}U and ^{235}U) complicates the accurate detection of ^{236}U signal by mass spectrometry and thus highly sensitive analytical instruments providing high abundance sensitivity are required. This work pushes the limits of triple quadrupole-based ICP-MS technology for accurate detection of $^{236}\text{U}/^{238}\text{U}$ isotope ratios down to 10^{-10} , which is so far mainly achievable by AMS. Coupled with an efficient desolvating module, N_2O was used as the reaction gas in the collision reaction cell of the ICP-MS/MS. This configuration allows a significant decrease of the uranium polyatomic interferences ($^{235}\text{UH}^+$ ions) and an accurate determination of low $^{236}\text{U}/^{238}\text{U}$ isotope ratios. This new methodology was successfully validated through measurements of certified reference material from 10^{-7} to 10^{-9} and then through comparisons with AMS measurement results for ratios down to 10^{-10} . This is the first time that $^{236}\text{U}/^{238}\text{U}$ isotope ratios as low as 10^{-10} were determined by ICP-MS/MS. The possibility of measuring low $^{236}\text{U}/^{238}\text{U}$ isotope ratios can offer a large variety of geochemical applications in particular for the determination of uranium sources in the environment.

INTRODUCTION

In the environment, ^{238}U , ^{235}U and ^{234}U isotopes are the main constituents of naturally occurring uranium, whereas other minor isotopes, like ^{236}U , can only be found at ultra-trace concentrations (few tens of fg/g). The main production pathway in nature of this isotope is by neutron capture reaction $^{235}\text{U}(n, \gamma)^{236}\text{U}$ and its abundance depends on uranium concentration and neutron flux. The mean $^{236}\text{U}/^{238}\text{U}$ isotope ratio level in Earth crust is $10^{-14} - 10^{-13}$.¹ However, anthropogenic ^{236}U was globally deposited on Earth surface through atmospheric nuclear weapon tests leading to a characteristic $^{236}\text{U}/^{238}\text{U}$ isotope ratio of $10^{-8} - 10^{-9}$ in most environmental samples.²⁻⁹ In addition, anthropogenic ^{236}U was locally released into the environment in the vicinity of nuclear fuel reprocessing facilities or after nuclear power plant accidents, with $^{236}\text{U}/^{238}\text{U}$ isotope ratio signatures above 10^{-9} .¹⁰⁻¹⁵ In uranium ore, high uranium concentrations associated with high neutron flux lead to a higher production of ^{236}U with $^{236}\text{U}/^{238}\text{U}$ isotope ratios with a typical signature of about 10^{-10} .^{1,16-23} In the case of U-ores the main sources of neutrons are: (i) (α, n) reactions, with light elements and (ii) spontaneous and neutron-induced fission of ^{238}U and ^{235}U respectively.¹⁷ This high isotopic contrast between the sources makes $^{236}\text{U}/^{238}\text{U}$ isotope ratios a relevant

tracer for uranium source identification in the environment.^{1,24} Uranium isotope investigations are therefore of increasing interest for environmental monitoring, nuclear safeguards and nuclear forensics.^{25,26} However, due to the low abundance of ^{236}U in the environment, instruments with high sensitivity and high abundance sensitivity capabilities are required.

For the investigation of $^{236}\text{U}/^{238}\text{U}$ isotope ratios at environmental levels, the reference technique is Accelerator Mass Spectrometer (AMS)^{2,3,5,15,16,27-31} and ratios down to 10^{-10} were also measured by Thermal Ionisation Mass Spectrometer (TIMS).^{1,18} Even if Inductively Coupled Plasma Mass Spectrometer (ICP-MS) has been widely used for the investigation of various radionuclides³²⁻³⁶ its use for the determination of ^{236}U in environmental samples remains challenging due to the presence of spectral interferences: peak tailing (from ^{235}U at $m+1$ and ^{238}U at $m-2$) and $^{235}\text{UH}^+$ hydride ions formations.^{1,37} These interferences limits the detection of $^{236}\text{U}/^{238}\text{U}$ lower than $10^{-5} - 10^{-6}$ range with ICP-MS.³⁸ It should be noted that hydride formation is the major interference contribution at $m/z=236$ compared to the peak tailing: typical values for quadrupole mass spectrometers are about 2×10^{-6} (at $m-1$) and about 3×10^{-5} (without desolvating system) for peak tailing and hydrides respectively.^{1,38-40}

Several authors proposed different methodologies for reducing $^{235}\text{U}^+$ formation during ICP-MS measurement.^{34,41,42} Main improvements include sensitivity increase and reduction of hydride formation rate by using desolvating introduction systems. Recently development of Inductively Coupled Plasma tandem Mass Spectrometer (ICP-MS/MS) offered new possibilities for low $^{236}\text{U}/^{238}\text{U}$ isotope ratio determination.^{1,4,37,43,44} This become possible using the double mass filter with O_2 in the Collision Reaction Cell (CRC) and the measurement of uranium isotopes in mass shift mode (UO^+). The spectral overlapping at $m/z=252$ ($^{236}\text{U}^{16}\text{O}^+$) from minor oxygen isotopes ($^{235}\text{U}^{17}\text{O}$ and $^{234}\text{U}^{18}\text{O}$) is avoided due to the selective introduction of the ions in the CRC thanks to the first mass filter. This configuration also improves significantly the abundance sensitivity (lower than 10^{-10})^{36,45} due to the use of two mass filters and reduces the uranium hydride formation: UOH^+ formation is less favorable compared to that of UH^+ .^{37,43} Typical hydride ratios (UOH^+/UO^+) using O_2 and desolvating modules^{43,44} as the introduction system turns around $10^{-6} - 10^{-8}$ and in a recent work⁴⁵ the authors investigated the use of CO_2/He as the collision reaction gas and obtained a hydride formation rate of 1.2×10^{-8} . However, even if analyzing U^+ in its oxidized state allows achieving low hydride formation rates, further reducing of UOH^+ formation could offer the possibility to measure lower $^{236}\text{U}/^{238}\text{U}$ isotope ratios ($<10^{-9}$).

Nonetheless, to date, the lowest isotope ratios measured by ICP-MS/MS in environmental samples are $(7.2 \pm 0.8) \times 10^{-9}$ in a sediments⁴⁴, $(2.3 \pm 2.8) \times 10^{-9}$ in seawater⁴³ and $(1.5 \pm 0.63) \times 10^{-8}$ in soils³⁷. However, these last two studies suffered from large uncertainties (42-122%) and measurements were not validated with isotopically certified materials ($^{236}\text{U}/^{238}\text{U}$).^{37,43}

The aim of the present study is to establish a new method for reducing hydride formation as far as possible for the investigation of low $^{236}\text{U}/^{238}\text{U}$ isotope ratios by using an ICP-MS/MS Agilent 8800. For this reason, nitrous oxide (N_2O) was used as reaction gas in the CRC. N_2O has already been successfully used for element determination in environmental samples.⁴⁶⁻⁵⁰ In these studies, an improvement of the sensitivity and a decrease of the interferences were observed.^{48,50} However, to our best knowledge, it has never been tested for ^{236}U measurements. The performance of this method was then validated on certified references materials and environmental samples.

EXPERIMENTAL SECTION

REAGENTS. High-purity acids obtained by distillation (Savillex® DST-1000 system) from nitric acid (VWR Chemicals, Normapur 68 %) and hydrochloric acid (Merck, Emsure 37 %) were used in this work for sample digestion and uranium chemical purification. Others acids are hydrofluoric acid (MERCK, Normapur) and perchloric acid (Prolabo, Suprapur) and were used for sample mineralisation. All acid dilutions were performed with deionised water (18.2 M Ω cm Milli Q system, Millipore). 0.05 mol.L⁻¹ (M) HNO_3 acid was used for sample recoveries and 0.5 M HNO_3 acid was used for blank solutions and also for the instrument washing procedure between measurements. Moreover, for a more efficient instrument washing, 0.03 M HEDPA was used to decrease the uranium background level.

STANDARDS AND SAMPLES FOR METHOD VALIDATION. The proposed method was validated by measuring certified reference materials from the Joint Research Centre (Geel, Belgium). Three standards were used, IRMM 184, IRMM-075/05 and IRMM-075/06, with different levels of $^{236}\text{U}/^{238}\text{U}$ certified isotope ratios: $(1.24 \pm 0.01) \times 10^{-7}$, $(1.07 \pm 0.08) \times 10^{-8}$ and $(1.09 \pm 0.01) \times 10^{-9}$ respectively. Uranium concentration in the measured solution of standards are 1 $\mu\text{g.g}^{-1}$ for IRMM 184, 10 $\mu\text{g.g}^{-1}$ for IRMM-075/05 and 30 $\mu\text{g.g}^{-1}$ for IRMM-075/06. As no certified material is available for lower $^{236}\text{U}/^{238}\text{U}$ isotope ratios, three environmental samples previously characterised by the Vienna Environmental Research Accelerator (VERA) using an Accelerator Mass Spectrometer (AMS) were used to validate the method for lower ratios. Two sediment samples C2-5 and C2-30 were collected in a wetland draining a former uranium mine.^{51,52} These samples are highly enriched in uranium with concentrations of about 4500 $\mu\text{g.g}^{-1}$ and about 2500 $\mu\text{g.g}^{-1}$, respectively, and $^{236}\text{U}/^{238}\text{U}$ isotope ratios were determined by AMS measurements to a level of $(3.57 \pm 0.26) \times 10^{-10}$ and $(3.50 \pm 0.19) \times 10^{-10}$, respectively. Uranium concentrations in the measured solution are 50 $\mu\text{g.g}^{-1}$ for C2-5 and 40 $\mu\text{g.g}^{-1}$ for C2-30. A third sample, MBN, an uranium ore, was measured with AMS to $(1.04 \pm 0.17) \times 10^{-10}$. Uranium concentration in the measured solution is 70 $\mu\text{g.g}^{-1}$ for MBN sample. Finally, an in-house standard of uranyl nitrate processed before 1918, called KkU, provided by the University of Physics in Vienna was used to test the method for an isotope ratio of $(6.98 \pm 0.32) \times 10^{-11}$.³ Uranium concentration in this measured solution is about 200 $\mu\text{g.g}^{-1}$. With these standards and samples, the method developed in this work has been tested from $^{236}\text{U}/^{238}\text{U}$ isotope ratio of 1×10^{-7} to 7×10^{-11} .

SAMPLE PREPARATION. Radiochemical process of the environmental samples is adapted from previously published method.⁵³ About 100 mg of samples were placed in Savillex® PFA Teflon® vials. Total sample dissolutions were carried out using concentrated HNO_3 acid (1 ml) and concentrated HF acid (1 mL). Vials with closed lids were heated at 90°C overnight using Evapoclean (Analab) system. HClO_4 acid (300 μL) was then added and samples were heated again at 90°C with open lids during 3 h to evaporate HNO_3 and HF acids. Temperature was then increased to 160°C to enable the perchloric acid evaporation. Samples were recovered with 3M HNO_3 acid and purified on chromatographic columns filled with UTEVA (100 – 150 μm) resin. After loading onto the columns, samples and resin were rinsed with 3 M HNO_3 acid. Th was eliminated with 3 M HCl and U was finally eluted with 0.1 M HCl. Samples were evaporated to dryness and finally recovered with 0.05 M HNO_3 before ICP-MS measurements. Instrumental mass fractionation during measurements was corrected internally using a thallium standard solution. To this end, a diluted solution of Tl from an isotopic reference material (NIST-SRM 997; certified for $^{205}\text{Tl}/^{203}\text{Tl}$ isotope ratio) was prepared and 1 ng.g^{-1} of this solution was added to each measured samples before analysis.

INSTRUMENTATION. In this work, an Apex HF (without desolvating membrane) and APEX Ω (with an included desolvating membrane) from Elemental Scientific (Nebraska, USA) were tested to increase the sensitivity while decreasing the uranium oxide and hydride formation rates in the plasma.

Desolvating instrument gas (nebulizer gas, N₂ and Ar) flow rates were daily optimized to obtain the maximum of uranium signal and signal to background ratio. Measurements were performed on an ICP-MS/MS Agilent 8800. It was daily optimized with a solution containing about 1 ng.g⁻¹ of uranium. The operating parameters allowing the lowest hydride rate are presented in Table 1. Several gas were tested in the CRC. Gas qualities are “Technique” for nitrous oxide, “Ultrapure” for dioxygen and carbon dioxide, “premier” quality for argon, dinitrogen and helium. All gases are from Air Products (Aubervilliers, France). He gas was introduced through the dedicated inlet line, while O₂, CO₂ or N₂O through the 4th gas inlet line. Gas flow rates were adjusted in order to maximize the uranium signal and signal to background ratio.

One key-parameter to perform measurements at these levels of isotope ratios is the blank level and memory effect of the instrument. It is important to ensure that no uranium remains in the desolvating system or in the ICP-MS/MS. It requires long washing times with high purity acids, while controlling the uranium counts rates before measurements of each samples. Moreover 0.03 M HEDPA was used for its complexing proprieties that allow an efficient washing of the desolvating system and the ICP-MS/MS. Between each measurements, uranium background levels were controlled with less than 1 cps for ²³⁵U⁺ signal and 0 cps for ²³⁶U⁺ signal. Hence, no instrumental blank correction was performed. Instrumental mass fractionation was corrected using the exponential mass fractionation law^{54,55} and the measurement of the thallium standard certified for the ²⁰⁵Tl/²⁰³Tl isotope ratio. This analyse allows to correct for the mass fractionation of two uranium ratios during sample measurements: ²³⁴U/²³⁵U and ²³⁶U/²³⁴U isotope ratios.

Table 1: ICP-MS/MS operating conditions: sample introduction system, ICP-MS/MS parameters and acquisitions parameters used during the measurements in order to obtain the lowest hydride formation rate.

Parameter	Value
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)
Desolvating system	APEX Ω
N ₂ gas (desolvating system)	3 L min ⁻¹
Ar gas (desolvating system)	4 L min ⁻¹
Torch	One-piece (Quartz)
Sample gas	0.90 L min ⁻¹
Sample uptake	~300 μL min ⁻¹
RF power	1550 W
Sampling depth	6 mm
Cell gas (N ₂ O) flow rate	0.04 mL min ⁻¹
Extract 1 and 2	-5, -190 V
Deflect	13 V
Q1 and Q2 Mass Gain	157, 131

Q1 and Q2 Mass Offset	125, 126
Q1 and Q2 Axis Offset	0.14, 0.02
Octopole Bias	-8 V
Energy discrimination	0 V
Peak shape	1 point
Integration time of ^{234,235,236} U ¹⁶ O ⁺ , ²³⁸ U ¹⁶ H ¹⁶ O ⁺	2, 1, 8, 2 s
Integration time of ²⁰³ Tl, ²⁰⁵ Tl	1 s
Number of sweeps per replicate	100
Number of replicates per sample	15
Sensitivity on ²³⁸ UO ⁺	500 000 cps/ppb

PROCEDURES. Indeed, in order to ensure the same detection mode (pulse counting) for the analysed U isotopes only ²³⁴U was measured in the same batch with ²³⁶U. Accordingly, ²³⁶U/²³⁴U isotope ratio was characterised in mass shift mode (²³⁶UO⁺/²³⁴UO⁺, however, for easy reading, all uranium ratios will simply be noted ^{23X}U⁺/^{23X}U⁺, as well as ^{23X}UOH⁺/^{23X}UO⁺ will be expressed as ^{23X}UH⁺/^{23X}U⁺). Hydride correction was performed using the next equation (Eq. 1). Details on this equation could be found in Supplementary Information.

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

Where, (²³⁶U⁺/²³⁴U⁺)_{corr} is the hydride corrected ²³⁶U⁺/²³⁴U⁺ isotope ratio, (²³⁶U⁺/²³⁴U⁺)_{meas} is the measured ²³⁶U⁺/²³⁴U⁺ isotope ratio without corrections and (²³⁸UH⁺/²³⁴U⁺)_{meas} is the measured ²³⁸UH⁺/²³⁴U⁺ isotope ratio. The 137.88 value corresponds to the natural ²³⁸U/²³⁵U isotope ratio. It is worth mentioning that recent works^{56,57} estimated the mean terrestrial ²³⁸U/²³⁵U to be ~137.82, however the value of 137.88 remain the ‘official’ value (the one recommended by the IGC Sub-commission on Geochronology) and that almost all geochronological calculations in the literature are based on that value.

The mass fractionation corrected ²³⁶U/²³⁴U and ²³⁴U/²³⁸U isotope ratios were used for the final calculation of ²³⁶U/²³⁸U isotope ratio. The ²³⁴U/²³⁸U isotope ratio was previously determined in a diluted fraction of the samples by measuring the ²³⁴U/²³⁵U isotope ratio in the same experimental settings (UO⁺) and by using Tl isotopes for the instrumental mass fractionation corrections. We considered that processes like uranium mass independent fractionation during uranium-oxygen reaction in the CRC can be considerate as negligible, regarding to ²³⁶U/²³⁸U natural variations. To convert the ²³⁴U/²³⁵U isotope ratio, the natural ²³⁸U/²³⁵U isotope ratio (137.88) has been used.

RESULT AND DISCUSSION

REDUCTION OF THE HYDRIDE FORMATION RATE.

Minimisation of the hydride formation rate (expressed as ²³⁸UH⁺/²³⁸U⁺) is mandatory for the determination of low ²³⁶U/²³⁸U isotope ratios. Typical hydride values without gas in the CRC and by using an APEX-HF were determined at about 25×10⁻⁶ (Figure 1), which is in good agreement with previous

studies.^{34,45,58} Moreover, the N₂ gas in the APEX-HF was tested at different flow rates and, as it can be seen in figure 1, its use has not led to a hydride reduction.

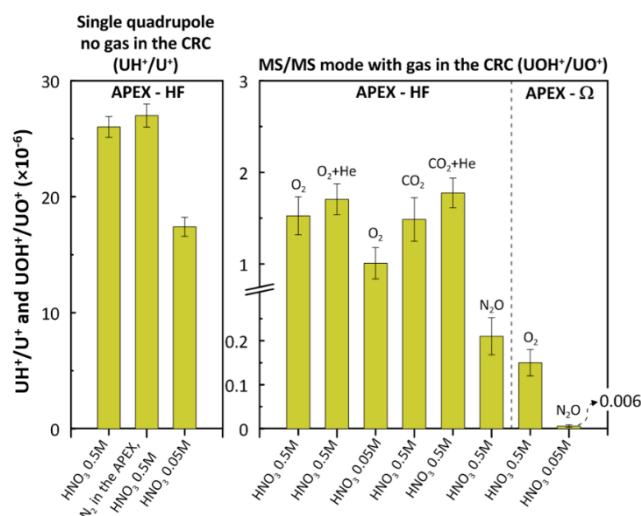


Figure 1: Comparison of uranium hydride formation rate in different configurations: using the APEX HF and the APEX Ω , without gas in on-mass mode or with different gas (O₂, O₂ +He, CO₂, CO₂+He, N₂O) in the CRC in MS/MS mode (mass-shift mode UO⁺) and with different nitric acid molarities. Cell gas flow rates were: O₂ at 0.05 mL.min⁻¹, He at 0.5 mL.min⁻¹, CO₂ at 0.04 mL.min⁻¹ and N₂O at 0.04 mL.min⁻¹.

One parameter that influences the hydride formation rate is the molarity of the nitric acid of the analysed solution. Different acid molarities were tested and a decrease of the hydride formation rate was observed with the decrease of the molarity of the nitric acid, due to the minimisation of the available H⁺ to form uranium hydrides. We also observed that for concentrations lower than 0.05M, no significant improvement of hydride formation was obtained. The use of 0.05 M HNO₃ allowed a hydride reduction by a factor of ~1.5 (Figure 1). Therefore, 0.05 M HNO₃ acid was chosen for the standards and samples analysis as it is a good compromise between an efficient sample recovery and a low hydride formation rate in the ICP-MS/MS.

As previously mentioned, pioneering work of Tanimizu et al.⁴³ showed that analysing uranium isotopes in UO⁺ form drastically reduces the hydride formation (UOH⁺/UO⁺). This is clearly shown in figure 1; in MS/MS mode with O₂ in the CRC (0.05 mL.min⁻¹) hydride rate has fallen against no gas mode by a factor of 17 (~1.5×10⁻⁶). For similar instrumental configuration and settings, Diez-Fernandez et al.⁴⁴ obtained comparable hydride rates. Collisional processes in the CRC by introducing simultaneously O₂ and He (0.05 mL.min⁻¹ and 0.5 mL.min⁻¹, respectively) have led to a signal decrease without a further suppression of the hydride formation (Figure 1).

As for the no gas mode, in the MS/MS mode the acid molarity played an important role in the hydride formation. For 0.05M of HNO₃, a similar decrease (a factor of ~1.5) of the hydride rate has been observed.

In a recent work, Hou et al.⁴⁵ by using CO₂ and He in the CRC obtained a hydride formation rate of 1.2×10⁻⁸. In our case, the use of CO₂ (0.04 mL.min⁻¹) and a mixing of CO₂ and He (0.04 mL.min⁻¹ and 0.5 mL.min⁻¹, respectively) in the CRC

has not resulted in any decrease of the hydride formation (Figure 1). The obtained in this work values (~1.7×10⁻⁶) have been found to be similar with that using O₂ in the CRC and in good agreement with the study of Diez-Fernandez et al.⁴⁴. It should be noted that Hou et al.⁴⁵ used high gas flow rates (1.2 mL.min⁻¹ for CO₂ and 8.0 mL.min⁻¹ for He) and thus their results cannot be directly compared to our study. However, an important decrease of the uranium sensitivity was observed with the increase of CO₂ and He flow rate in the CRC which doesn't meet the need for ultra-low ²³⁶U/²³⁸U isotope characterisation.

To our best knowledge, this is the first time the influence of the N₂O gas on the uranium hydride formation in an ICP-MS/MS mass spectrometer was tested. By using N₂O in the CRC and the APEX-HF as the introduction system, a significant hydride formation decrease compared to that obtained with O₂ was observed (factor of ~8, Figure 1). This decrease could be explained by the competitive hydride formation between UO⁺ and N_x⁺ provided by the N₂O gas (part of the available H⁺ to form UO⁺ is consumed to form N_xH⁺).

Diez-Fernandez et al.⁴⁴ compared the influence of different desolvating systems on hydride formation and showed that the use of the APEX Ω and Aridus provide a significant decrease of the hydride formation compared to the use of the APEX-HF. They found that with the APEX Ω and O₂ in the CRC, the hydride rate has fallen by a factor of 10 (UH⁺/U⁺ = 0.4×10⁻⁶). Their observations are in good agreement with our findings: for similar experimental conditions (APEX Ω and O₂ in the CRC) we obtained a hydride rate in the same order of magnitude, ~0.15×10⁻⁶ (Figure 1). Hou et al.⁴⁵ also observed a significant hydride decrease with the use of the APEX Ω compared to other introduction systems. The hydride decrease with the use of the APEX Ω can be explained by the presence of a helical EPTFE fluoropolymer membrane desolvator, allowing a more efficient removal of solvent and matrix components of a sample than what the APEX-HF is capable of.

Finally, the combination of all the previously tested parameters allowing the decrease of the hydride formation (N₂O in the CRC, APEX Ω and 0.05M HNO₃) has led to a significant decrease of the hydride formation rate. With this new protocol, the lowest hydride formation rate reached a minimum of 0.006×10⁻⁶ (6×10⁻⁹) during measurements of certified standard materials (Figure 1). To our best knowledge, this is the lowest hydride rate value ever obtained with an ICP-MS or ICP-MS/MS technique bringing new possibilities for accurate determination of ultra-low ²³⁶U/²³⁸U isotope ratios. The benefit of this extremely low hydride rate to the determination of ultra-low ²³⁶U/²³⁸U isotope ratios can be quantified using equation 2. Equation 2 states the ²³⁶U⁺/²³⁸U⁺ ratio as a function of the interference to signal ratio ²³⁵UH⁺/²³⁶U⁺ (at m/z = 236) and of the hydride rate formation (UH⁺/U⁺) (see also Supplementary Information).

$$\frac{{}^{236}\text{U}^+}{{}^{238}\text{U}^+} = \frac{\text{UH}^+/\text{U}^+}{{}^{235}\text{UH}^+ / {}^{236}\text{U}^+} \times \frac{1}{137.88} \quad (2)$$

With the help of this equation, using the hydride rate value obtained in this work (6×10^{-9}) and by fixing an interference to signal ratio at 1 (for higher ratios the interference correction is more important than the signal) the theoretical lowest measurable $^{236}\text{U}/^{238}\text{U}$ isotope ratio is about 4×10^{-11} (see Figure S1 in Supplementary Information.) This ratio is almost two orders of magnitude below the lowest isotope ratios measured by ICP-MS/MS in environmental samples^{37,43,44}. It is therefore necessary to confirm this mathematical consideration and to investigate the real limit of the developed method by measuring samples with certified $^{236}\text{U}/^{238}\text{U}$ isotopic ratios.

UO⁺ SENSITIVITY USING O₂ VERSUS N₂O. The uranium sensitivity in UO⁺ form was studied using O₂ and N₂O as the reaction gas. According to thermodynamic data, the oxygen affinity in the N₂O molecule is significantly lower compared to other reaction gas (CO, NO, CO₂, O₂ and NO₂).⁵⁹ In particular, affinity values for the N₂O and O₂ are 1.8 eV and 5.2 eV respectively^{50,60}, which means that N₂O readily reacts and donates an oxygen atom to react with uranium ions. From these values of bond dissociation energies, the reaction enthalpy for the formation of UO⁺ ions could be deduced and shows a higher reactivity using N₂O ($\Delta_r H = -6.72$ eV) than O₂ ($\Delta_r H = -3.28$ eV).⁶¹⁻⁶³ Therefore, a higher signal intensity of the UO⁺ is expected using N₂O compared to O₂. Findings of a previous study⁵⁰ seem to support the benefit of using N₂O; during radium analysis a sensitivity improvement was observed using N₂O instead of O₂.

However, our results have not shown a sensitivity increase using the N₂O as the reaction gas. Both N₂O and O₂ have led to the same sensitivity that was found to be $\sim 5 \times 10^5$ cps of $^{238}\text{U}^{16}\text{O}^+$ per ppb of U in MS/MS mode (see also Table 1). This can be explained by the fact that part of U⁺ ions can also react with N⁺ ions to form UN⁺ ions. Indeed, in presence of N₂O gas, the reaction enthalpy for the formation of UN⁺ ($\Delta_r H = -6.64$ eV) is similar to that of UO⁺ ($\Delta_r H = -6.72$ eV)^{60,61} creating thus a competition between the formation of the UO⁺ and UN⁺ species. During our measurements using N₂O in the CRC, the UN⁺ and UO⁺ formation was quantified to be about 28% (UN⁺/U⁺_{no gas}) and 47% (UO⁺/U⁺_{no gas}, that compares with 51% using O₂) respectively, which is in fair agreement with thermodynamic data.^{60,61} It should be noted that the fact that no signal increase was observed using N₂O gas points out that the main process leading to the hydride rate decrease is competitive protonation reactions between UO⁺ and N_x⁺.

One major concern is the uranium concentration needed to measure ^{236}U in such low ratios. Based on the sensitivity reached in this work and considering a $^{236}\text{U}/^{238}\text{U}$ isotope ratio as low as 10^{-10} , a minimum concentration of $20 \mu\text{g}\cdot\text{g}^{-1}$ is needed in order to obtain at least 1 cps in $^{236}\text{U}^+$. Considering a minimum volume of the analysed solutions of about 2 mL, $\sim 40 \mu\text{g}$ of U are needed for a complete analysis of the $^{236}\text{U}/^{238}\text{U}$ ratio (including $^{236}\text{U}/^{234}\text{U}$ and $^{234}\text{U}/^{235}\text{U}$ determination). This value is to be compared with the needs of the AMS technique which is capable of detecting lower $^{236}\text{U}/^{238}\text{U}$ ratios with $\sim 1 \mu\text{g}$ of U.²⁹ However, the ICP-MS/MS is a low cost widespread technique compared to the AMS and for samples with low uranium concentrations, acid leaching (HCl, HNO₃) of high sample volumes and preconcentration procedures can be used to achieve the appropriate uranium concentration.

VALIDATION OF THE METHOD WITH CERTIFIED REFERENCE MATERIALS. The new method was validated

using certified standard materials from the Joint Research Center (Figure 2 a-c). Three certified solutions (IRMM184, IRMM-075/5 and IRMM-075/6) were analysed, with $^{236}\text{U}/^{238}\text{U}$ isotope ratios ranging from 1.2×10^{-7} to 1.1×10^{-9} . As can be seen in figure 2, the measured $^{236}\text{U}/^{238}\text{U}$ isotope ratios are in good agreement with the certified values reaching a trueness better than 2%. Isotope ratio uncertainties and repeatabilities (relative standard deviation of n measurements expressed for a coverage factor k = 2) were found to be lower than 5% and 10%, respectively. Measurements of these certified reference solutions validated the analytical method for isotope ratios down to 10^{-9} . It should be noted that this is the first time that $^{236}\text{U}/^{238}\text{U}$ isotope determination by ICP-MS/MS down to 10^{-9} was validated with the use of isotopically certified materials. For lower ratios, as no isotopically certified material is available, environmental samples previously characterised by AMS were used.

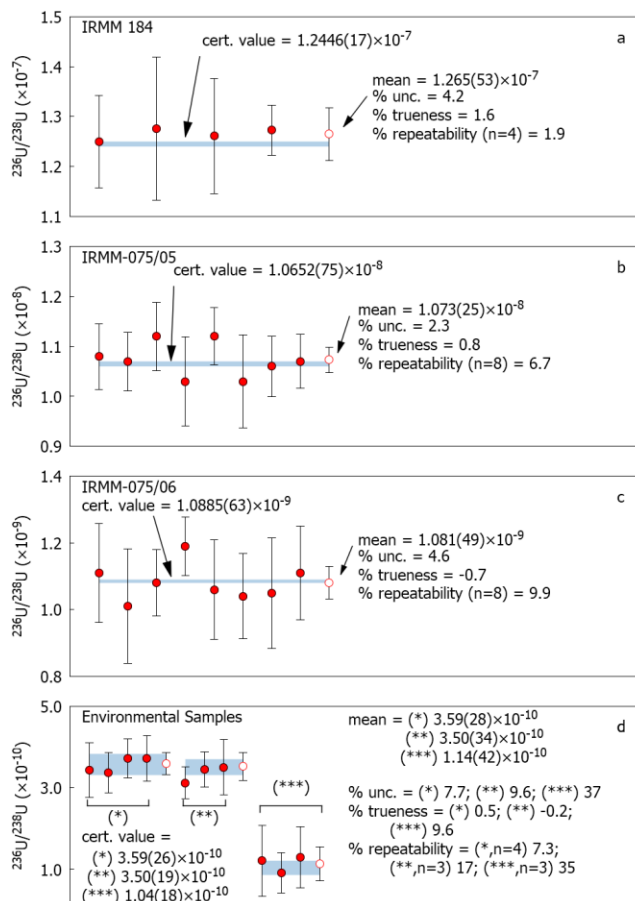


Figure 2: Measurements of certified reference solutions: (a) IRMM 184; (b) IRMM-075/5; (c) IRMM-075/6 and environmental samples previously measured by AMS (d): (*) C2-5, (**) C2-30 and (***) MBN. Open dots correspond to the means of the measurements. Blue shaded rectangles highlight certified values uncertainty. Isotope ratio uncertainties of this work were calculated by taking into account uncertainties of the mass fractionation factor and of the measured isotope ratios used for the calculation of the $^{236}\text{U}/^{238}\text{U}$ ($^{236}\text{U}/^{234}\text{U}$ and $^{234}\text{U}/^{235}\text{U}$). Trueness is expressed as the difference between the certified and measured isotope ratios. Repeatability was calculated as the standard deviation of n repeated measurements. Uncertainties and repeatabilities are extended using a coverage factor of 2.

VALIDATION WITH ENVIRONMENTAL SAMPLES. Three samples (C2-5, C2-30 and MBN) were characterised by AMS. Samples C2-5 and C2-30 have similar $^{236}\text{U}/^{238}\text{U}$ isotope ratios close to 3×10^{-10} and the MBN presents a lower ratio of 1×10^{-10} . As can be seen in figure 2 d, the results obtained with the new ICP-MS/MS method are in good agreement with those obtained with AMS (trueness close to 10 %). The uncertainties are below 10 % for the C2-5 and C2-30, while for the MBN the achieved uncertainty is about 37 %. Even if this uncertainty is still high, it allows the discrimination between the different U sources due to their important $^{236}\text{U}/^{238}\text{U}$ isotope ratio variation (higher to the analytical uncertainty). Therefore, these results validate the proposed analytical method for the determination of low $^{236}\text{U}/^{238}\text{U}$ isotope ratios with ICP-MS/MS, down to 1×10^{-10} .

The proposed method was also tested using the in-house standard Vienna-KkU, whose the $^{236}\text{U}/^{238}\text{U}$ isotope ratio was determined by AMS at $(6.98 \pm 0.32) \times 10^{-11}$.³ Our results showed a systematic overestimation of this ratio that clearly points out the presence of an additional interference at m/z 252. The generation of $^{238}\text{U}^{14}\text{N}^+$ ions in the CRC has been suspected as the most probable interference. Although sequential transmission of U isotopes into the CRC prevents spectral overlaps at $m/z = 252$ due to the presence of different oxygen isotopes ($^{234}\text{U}^{18}\text{O}^+$, $^{235}\text{U}^{17}\text{O}^+$), accurate $^{236}\text{U}/^{238}\text{U}$ isotope ratio measurement can be hampered by the contribution of $^{238}\text{U}^+$ peak tailing on $^{236}\text{U}^+$ (at $m-2$). During $^{236}\text{U}^+$ measurement, $^{238}\text{U}^+$ tail is simultaneously transmitted with $^{236}\text{U}^+$ ions through Q1 mass filter to the CRC. As previously shown, in presence of N_2O in the CRC, UN^+ formation is favorable at $\sim 28\%$ (according to the experimental settings of this work) and thus part of the $^{238}\text{U}^+$ ions in the CRC from $^{238}\text{U}^{14}\text{N}^+$. Therefore, these species interfere with $^{236}\text{UO}^+$ leading to an overestimation of the $^{236}\text{U}/^{238}\text{U}$ isotope ratio. A simplified schematic of the interference formation mechanism at $m/z = 252$ is presented in figure 3. Finally, $\sim 1 \times 10^{-10}$ is the lower achievable limit with the proposed configuration.

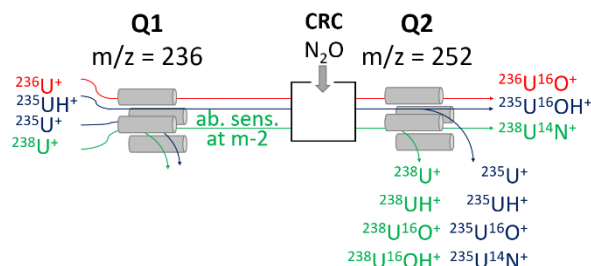


Figure 3: Illustration of the UH^+ and UN^+ interference mechanisms at $m/z = 252$.

CONCLUSION

A new analytical method for the determination of ultra-low $^{236}\text{U}/^{238}\text{U}$ isotope ratios by ICP-MS/MS was developed. The major novelty is the use of N_2O as the reaction gas in the CRC. Hydride rate formation (measured as $^{238}\text{U}^{16}\text{O}^{1}\text{H}^+$ / $^{238}\text{U}^{16}\text{O}^+$) was decreased to 6×10^{-9} , which is an improvement of 2 orders of magnitude, compared to the “standard” configuration, in which O_2 is used. By reducing this

main interference, $^{236}\text{U}/^{238}\text{U}$ isotope ratios down to 1×10^{-10} from certified reference materials and environmental samples previously measured by AMS were successfully characterised. Below this boundary and with the proposed configuration, it seems that our method limits are reached, as interferences become more and more significant to perform an accurate determination of the $^{236}\text{U}/^{238}\text{U}$ isotope ratio. At this level, AMS is still the most reliable measurement technique, with lower uncertainties (31 % of difference between the two techniques for MBN sample) and lower detection limits.²⁸

To decrease even further the limits of the ICP-MS/MS, it is important to focus on the reduction of interferences. Improving the performances of Q1 mass filter in terms of abundance sensitivity could open the way for the investigation of $^{236}\text{U}/^{238}\text{U}$ isotope ratios lower than 10^{-10} . Another possible way that remains to investigate is the use of the Agilent’s second generation of ICP-MS/MS (Agilent 8900). This instrument is equipped with enhanced mass filters that offers an extended mass range and enable the detection of uranium dioxide (UO_2^+).⁶⁴ According to the manufacturer data, in UO_2^+ form hydride formation rate is reduced to 5.7×10^{-8} with the use of O_2 as reaction gas. With this instrument, an effective desolvating system and N_2O as reaction gas, hydride formation rate could be decreased below 10^{-10} allowing thus and accurate detection of $^{236}\text{U}/^{238}\text{U}$ isotope ratios down to 10^{-11} .

ASSOCIATED CONTENT

Supporting Information

Demonstration of Eq. 1 and Eq. 2. and a figure on the influence of the $^{235}\text{UH}^+$ interference on the measurement of $^{236}\text{U}/^{238}\text{U}$ isotope ratio for a given hydride formation rate.

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Author Contributions

HJ, AG, OD and CC performed the ICP-MS/MS investigations, while PS and RG did the AMS measurements. All authors have given approval to the final version of the manuscript.

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