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# Determination of $^{234}\text{U}/^{238}\text{U}$ isotope ratios in environmental waters by quadrupole ICP-MS after U stripping from alpha-spectrometry counting sources

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**Abstract** The  $^{234}\text{U}/^{238}\text{U}$  isotope ratio has been widely used as a tracer for geochemical processes in underground aquifers. Quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS) equipped with a high-efficiency nebulizer and a membrane desolvator was employed for the determination of  $^{234}\text{U}/^{238}\text{U}$  isotope ratios in natural water samples. The instrumental limit of detection for  $^{234}\text{U}$  was at the low  $\text{pg L}^{-1}$  level with very low sample consumption. Measurement precision ( $^{234}\text{U}/^{238}\text{U}$ ) was 3–5% for bottled mineral water with elevated uranium concentration ( $>1 \mu\text{g L}^{-1}$ ). For the analysis of groundwater samples from the Almonte-Marisma underground aquifer (Huelva, Spain), uranium was stripped from stainless steel planchets that had previously been used as radiometric counting sources for alpha-particle spectrometry. Potential spectral interferences from other metals introduced during the dissolution were investigated. Matrix-matched blank solutions were needed to subtract the background on  $^{234}\text{U}$  due to the formation of platinum argides, and to allow for mass bias correction and background correction. The Pt appears to be an impurity present in the stainless steel, either as a minor component

by itself or after extraction from the anode and a subsequent uranium electrodeposition. The  $^{234}\text{U}/^{238}\text{U}$  isotope ratio data were in very good agreement with those of alpha spectrometry, while precision was improved by a factor of up to 10 and counting time was reduced down to ~20 min (10 replicate measurements).

**Keywords** Mass spectrometry/ICP-MS · Water · Radiochemical methods · Isotope ratio

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## Introduction

There are natural systems where secular equilibrium between  $^{234}\text{U}$  and  $^{238}\text{U}$  ( $t_{1/2, \text{U-}^{234}}=244.5$  kyears;  $t_{1/2, \text{U-}^{238}}=4,468$  Myears) can be broken. Among these systems, underground aquifers are especially representative. Uranium atoms in the rock substrate are leached into water. The alpha emission from  $^{238}\text{U}$  provokes a recoil of the daughter product ( $^{234}\text{Th}$ , which decays to  $^{234}\text{U}$  following beta decay through  $^{234}\text{Pa}$ ). This is the process for preferential leaching of  $^{234}\text{U}$  over  $^{238}\text{U}$ , affecting the isotope ratio in the groundwater; the isotope ratio deviates from that corresponding to the secular equilibrium condition [1]. The magnitude of these deviations can be slight or very large, depending on factors such as uranium content in the rock substrate and environmental conditions [2, 3].

This fact has been successfully applied in the environmental sciences for geological tracing, geochemical processes characterisation, etc [4, 5]. In the same way, the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio (natural value  $7.25 \times 10^{-3}$ , [6]) has been used for the identification of anthropogenic pollution scenarios [7].  $^{235}\text{U}$  is a key isotope in nuclear fuel manufacture and reprocessing, and any deviation from the expected isotope ratio in environmental samples is an indication of contamination from nuclear activity. In the same way, large increases in the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio represent a clear indicator of the presence of irradiated uranium [8].

Compared with alpha-particle spectrometry, mass spectrometric determination of these isotope ratios offers

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several advantages, including that of requiring short counting times, despite the very large differences in their respective isotope abundances.

Thermal ionisation mass spectrometry (TIMS) has traditionally been used for the analysis of uranium isotope ratios. New advances in this technique have allowed the determination of both  $^{234}\text{U}/^{238}\text{U}$  and  $^{235}\text{U}/^{238}\text{U}$  isotope ratios with uncertainty in the range of 0.1–0.2% [9]. However, this technique is now in competition with inductively coupled plasma mass spectrometry (ICP-MS).

Quadrupole ICP-MS (ICP-QMS) instruments became an alternative analytical tool for isotope ratio determination from the very beginning, when the first commercial instruments were available, despite the difficulties created by the extremely different isotope relative abundances. This translates to a very large difference in their absolute concentrations. Early works reported uncertainties as low as 0.5% for  $^{235}\text{U}/^{238}\text{U}$  isotope ratio and within the range 4–12% for  $^{234}\text{U}/^{238}\text{U}$  for solutions containing uranium concentrations in the range of 0.5–4.6  $\mu\text{g mL}^{-1}$  [10]. These performances can be improved using instruments operating collision cells [11]. However, the analytical limitations of quadrupole-based ICP-QMS for isotope ratio determinations prompted the use of sector-field ICP-MS systems, coupled with both single- and multiple-ion collectors [12–14], which can provide relative uncertainties similar to those of TIMS.

During the last two decades, many improvements have been developed in isotope-ratio determination using ICP-QMS, including a full characterisation of background sources, analytical signal fluctuations and sources affecting counting precision and mass bias [15]. Analytical preconcentration methods including both on-line [16] and off-line [17] setups were established for isotope ratio determinations in environmental samples. A recent characterisation of the analytical quality of results as a function of the nebulizer system has been described in the literature [18]. A high-efficiency sample introduction system can improve signal stability by minimising signal fluctuations while enhancing sensitivity.

In this work, we show the results for  $^{234}\text{U}/^{238}\text{U}$  isotope ratios in underground and drinking-water samples. Underground water samples coming from an aquifer located in southwestern Spain were selected to test the performances of the instrumental setup. To do that, a conventional ICP-QMS system coupled to a new high efficiency nebulizer was used. The samples had previously been analysed using alpha-particle spectrometry; following that, uranium atoms were stripped from the radiometric counting sources in order to get solutions compatible with the sample introduction system. The application of this methodology was a consequence of the lack of statistical significance of results previously achieved by alpha-particle spectrometry. Due to the low uranium concentrations obtained, poor alpha counting (and thus, poor counting statistics) resulted in large analytical uncertainties. Those uncertainties were in turn translated into a lack of statistical significance of the geochemical interpretation of results. Thus, this methodology could offer the possibility of testing and evaluating a

second time, if required, the very large inventory of U sources prepared for alpha-particle spectrometry at many radiochemical laboratories. Analytical performances of the instrumental setup are shown. The role of possible interferences is experimentally determined, both in terms of the effect on limits of detection and accurateness of isotope ratios.

## Experimental

### Instrumentation

Quadrupole-based ICP-MS was an Agilent 4500 c. Instrumental conditions are provided in Table 1. They were selected after successive approximations: (1) a conventional instrumental tuning was performed in order to maximise the signal-to-background ratio using a solution containing 10  $\text{ng mL}^{-1}$  of  $^{209}\text{Bi}$ , (2) for uranium isotope ratio measurements, counting times for each mass were determined according to the experiment described below. An automatic mass bias-correction routine was performed via the instrument software. First, a standard solution containing a known/certified isotope ratio was analysed. The calculated isotope ratio was normalised by the true isotope ratio (i.e., a linear correction factor was determined). This correction factor was subsequently applied to any isotope ratio calculated from that moment. Background subtraction was also possible.

A conventional Babington nebulizer with a double-pass spray chamber was used for total uranium concentration measurements. Uranium isotope ratios were determined using the high efficiency nebulizer ESI Apex-Q (ESI, Omaha, NE, USA), which provides both a chilling and a heating stage. The introduced sample was carried to a cyclonic spray chamber heated to 100 °C (heating temperature could also have been established at 140 °C for high sample intake rates). The vaporised stream traveled thereafter to a condenser loop, then to a Peltier-cooled

**Table 1** Operating conditions of Agilent 4500 and ESI Apex-Q

Part/area considered	Value/condition
RF power (W)	1,369
Depth (mm)	6.9
Sampler and skimmer cones	Ni
Carrier gas ( $\text{L min}^{-1}$ )	1.05
Nebulizer	Microconcentric, PFA
Sample uptake ( $\mu\text{L min}^{-1}$ )	50
Heating stage (°C)	100
Chilling stage (°C)	2
Ce <sup>+</sup> /Ce <sup>+</sup> (%)	<0.06
Ba <sup>++</sup> /Ba <sup>+</sup> (%)	<0.2
PtAr <sup>+</sup> /Pt <sup>+</sup> (%)	$\sim 10^{-3}$
N <sub>2</sub> supply pressure (kPa)	300
Counting mode	Isotope ratio (peak hopping)
No. of points per peak	3
$^{238}\text{U}$ counting time (s)	1.5

multipass condenser, where temperature could be selected as  $-5$  or  $2$  °C, depending on the organic or inorganic nature of the solution. An additional  $N_2$  stream was added within the last loop of the condenser in order to improve the signal stability and reduce oxide formation.

Different concentric PFA nebulizers could be coupled to the Apex system. In this work, we used a factory-made PFA microconcentric nebulizer, with a flow intake of about  $50$   $\mu\text{l}/\text{min}$  working under free aspiration.

Model Q of the Apex nebulizer also provided an additional membrane desolvation system, the so-called ACM (actively coupled membrane) module. The sample passed inside Peltier-cooled nafion membrane wall, which can be crossed by the solvent water molecules, but not by the analyte droplets. Thereafter, solvent molecules were removed by a sweep gas stream. Previous works developed by the manufacturer have shown the independence of analyte signals on the sweep gas flow [19].

Radiometric analyses were performed using an eight-detector ensemble Ortec SOLOIST (Ortec, Oak Ridge, TN, USA). Each detector works as an ion-implanted barrier silicon spectrometer, with eight independent vacuum systems. The spectrometric efficiency and accurateness of extracted results were tested in different intercomparison experiments [20].

#### Standards, reagents and samples

Underground water samples were collected in the year 2000 from different points along the underground aquifer of Almonte-Marisma (Huelva, SW Spain; Fig. 1), which consists of a confined aquifer with a sandy substrate and with a free zone, which is exposed to weathering.

The experimental setup (i.e., HP 4500 c coupled with the Apex nebulizer) had previously been tested using six brands of commercially available drinking-water samples. These samples were acidified with high-purity (Aristar)

nitric acid and diluted 1:10 v/v without further uranium preconcentration.

A uranium standard solution (Sigma Aldrich ALPHA) with a nominal concentration of  $960 \pm 50$   $\mu\text{g mL}^{-1}$  was successively diluted to the required concentrations. Isotope ratios were determined by measuring five aliquots of this solution at different concentration levels over an order of magnitude using alpha-particle spectrometry following a chemical scheme based on electrodeposition of uranium isotopes onto stainless steel disks [21]. Determined isotope ratios were  $(5.325 \pm 0.029) \times 10^{-5}$  ( $^{234}\text{U}/^{238}\text{U}$ ) and  $(5.882 \pm 0.069) \times 10^{-3}$  ( $^{235}\text{U}/^{238}\text{U}$ ), showing a certain deviation from the natural IUPAC isotope ratios [6].  $^{236}\text{U}$  relative isotope abundance was not determined due to spectral overlap by several of the  $^{235}\text{U}$  alpha emissions. With a long counting time ( $\sim 1$  month) and high activities, the uncertainties associated with individual aliquots due to counting statistics can be drastically reduced to less than 0.5% for  $^{238}\text{U}$  and  $^{234}\text{U}$  ( $\sim 2\%$  for  $^{235}\text{U}$ ).

#### Methods

The isolation of U isotopes before alpha-particle spectrometry was carried out according to a chemical extraction method developed by Holm and Fukai [21], conveniently adapted to our operational requirements (Fig. 2). A full characterisation of this method has been previously developed, hence only a basic description will be given here. First, water samples (0.5–2 L each) were evaporated to almost dryness following filtration through a Whatman A glass fibre filter, and about 40 mBq of  $^{232}\text{U}$  ( $\sim 48$  fg) was spiked to the sample for chemical yield calculation. The residue was dissolved in HCl, and then U isotopes were extracted by liquid-liquid extraction using trybutyl phosphate (TBP). Po isotopes remained concentrated in the aqueous phase for subsequent chemical isolation. Two back-extraction steps were applied, using first xylene in order to remove the Th isotopes and then deionised water, where uranium isotopes remained concentrated. This solution was adjusted to a basic  $\text{NH}_4\text{OH}$  matrix, which was finally submitted to electrodeposition of U isotopes onto a stainless steel disk using a Pt wire as the anode. The disks were then analysed by alpha-particle spectrometry. Chemical yields are usually in the range of 50–70% for uranium isotopes. The analysis of blank samples allowed the determination of the contribution of  $^{232}\text{U}$  impurities to  $^{234}\text{U}$  and  $^{238}\text{U}$  background levels. The different tests carried out showed a negligible contribution to these levels.

As previously explained, these disks have been used as a convenient tool for storing and transporting the samples, as the major goal of this work is the determination of uranium isotope ratios using ICP-QMS instead of the determination of uranium concentrations themselves. A new determination of uranium concentrations would require the use of a new chemical yield tracer for the calculation of the chemical yields associated with the stripping step, increasing the uncertainties of the whole process.

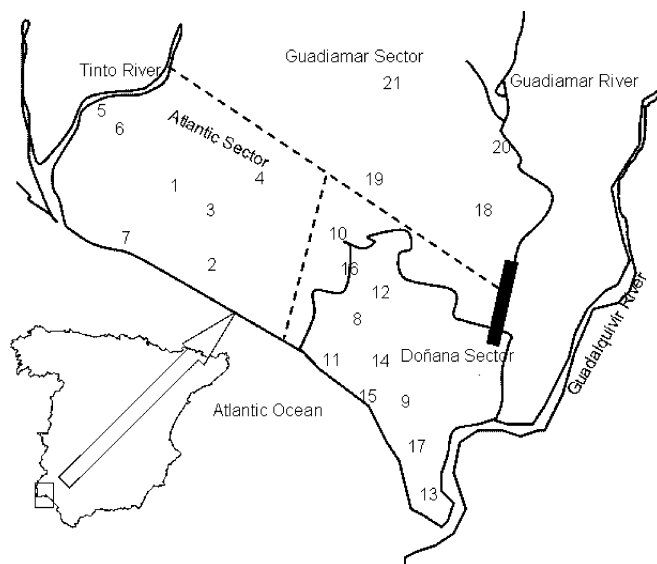
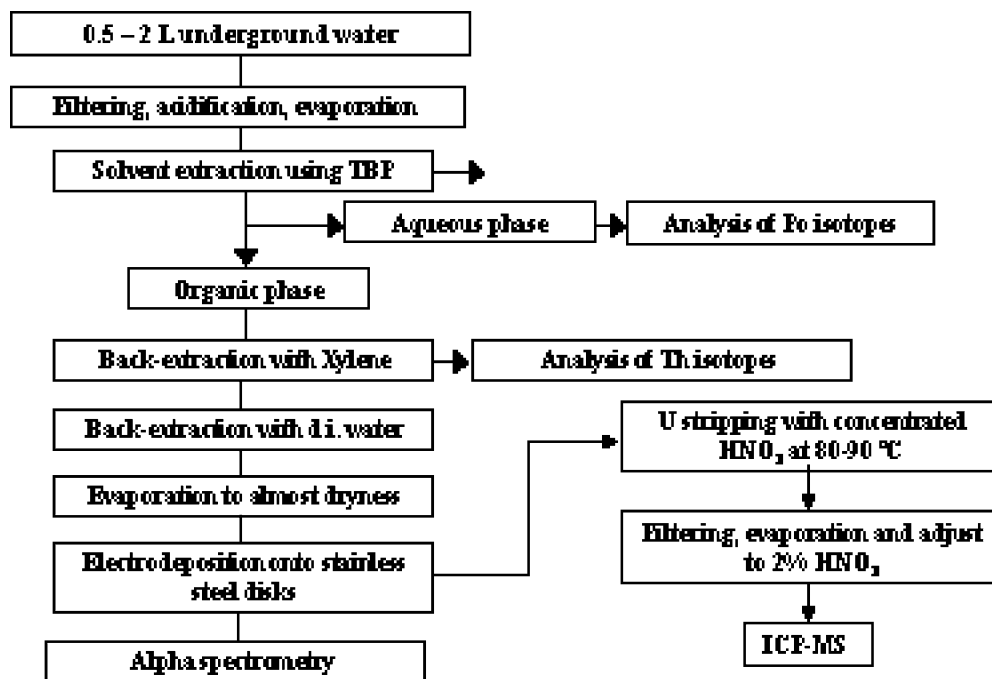


Fig. 1 Location of the sampling points in southwestern Spain

Fig. 2 Summary of the radiochemical method used in this work



Hence, the disks were submitted to a stripping process in order to extract the uranium atoms. To do that, the disks were leached in 20 mL of concentrated nitric acid within a Teflon beaker for 90 min at 80–90 °C. After cooling to room temperature, the solutions were filtered and evaporated to almost dryness at 140 °C on a hot plate. Finally, uranium atoms were recovered in 10 mL of 2% HNO<sub>3</sub>.

The efficiency of this stripping method was checked by submitting stainless steel disks containing known amounts of electrodeposited U isotopes to stripping, and comparing the corresponding activities before and after the stripping. More than 85–90% of previously electrodeposited uranium was removed from each disk. Thus, this method would produce enough uranium as to measure the isotope ratios, especially bearing in mind that this chemical scheme would introduce no isotope fractionation. Unfortunately, this stripping method would be not specific to uranium, hence different interferences could appear in the mass spectra. An example can be found in Fig. 3, where the total mass amount of several elements extracted from one of these disks (in this case, a true sample) is shown.

The major interferences in the masses under study are Sn dimers, Th hydrides, Pt/Hg argides and Au/Hg chlorides. Gold, mercury and thorium could eventually be rejected as sources of important interferences as their corresponding count rates in true samples were no different from background count rates in the analysed solutions. In contrast, the concentrations of Pt and Sn were relatively high. The effect caused by these interfering elements will be detailed below.

Drinking-water samples contained variable amounts of dissolved solids, as much as nearly 1,000 µg mL<sup>-1</sup>. In order to keep the same treatment for all of them, the most conservative option was chosen. Hence, all the samples were directly analysed after a 1:9 v/v dilution in 2% HNO<sub>3</sub>.

Blanks and determination of isotope ratios

Instrumental conditions can affect both accuracy and reproducibility of results, so several experiments were carried out in order to optimise the procedure. They are detailed in the following section. Furthermore, ICP-MS determination of isotope ratios requires the introduction of mass bias correction. However, as we will show below, our measurements for stripped samples will be affected in a very important way by the presence of Pt argides within the plasma.

This fact is clearly reflected in Fig. 4, where the spectrum corresponding to a standard solution containing 1 µg mL<sup>-1</sup> of both Pt and Sn was analysed. It is easy to see large peaks two orders of magnitude above the background level for masses 234, 235 and 236. These peaks do not

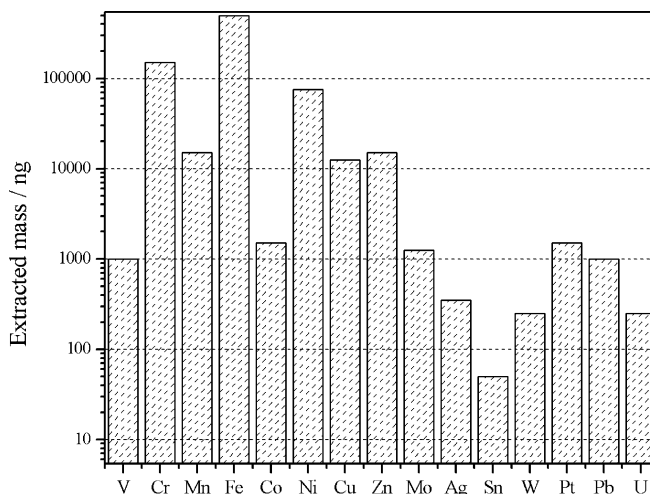


Fig. 3 Extracted elements from a test stainless steel disk

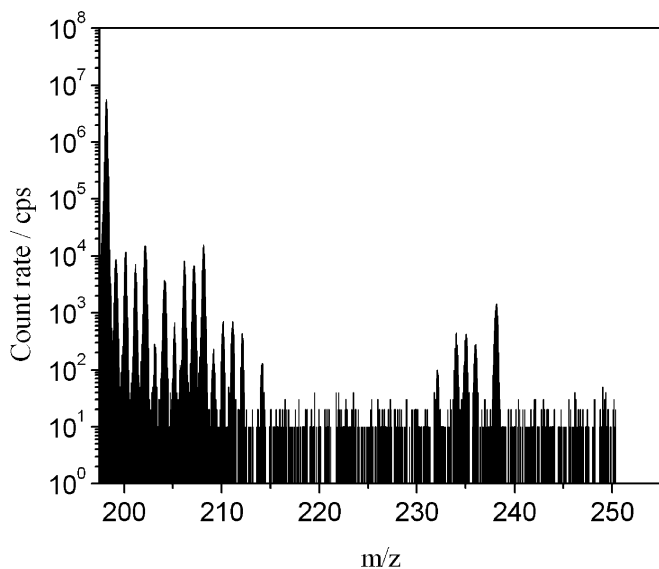


Fig. 4 Spectrum of a standard solution containing  $1 \mu\text{g mL}^{-1}$  of Pt and Sn

correspond to relative abundances of U, and they are only one order of magnitude less than that of  $^{238}\text{U}$ . This demonstrates the increase in count rates due to the presence of overlapping interfering ions.

Pt argides (bearing in mind only the major Ar isotope) could be produced at  $m/z$  values 230, 232, 234, 235, 236 and 238. Regarding Sn dimers, different combinations can appear. The relative appearance rate is dependent on the relative isotope abundances. Let us focus on  $m/z$  ratios 233 and 234. For  $m/z=233$ , the possible combinations are  $^{119}\text{Sn}-^{114}\text{Sn}$  (8.6%, 0.7%),  $^{118}\text{Sn}-^{115}\text{Sn}$  (24.2%, 0.3%) and  $^{117}\text{Sn}-^{116}\text{Sn}$  (7.8%, 14.5%). The superposition of these possible sources produces a relative probability of 0.012. That probability, after multiplying by the dimer formation rate, should produce the relative magnitude of tin dimers at  $m/z=233$ . Applying the same reasoning for  $m/z=234$ , the possible combinations are  $^{112}\text{Sn}-^{122}\text{Sn}$  (0.97%, 4.63%),  $^{114}\text{Sn}-^{120}\text{Sn}$  (0.65%, 32.6%),  $^{115}\text{Sn}-^{119}\text{Sn}$  (0.34%, 8.59%) and  $^{116}\text{Sn}-^{118}\text{Sn}$  (14.5%, 24.2%). That produces a relative probability of 0.038, i.e., the coupled probability of tin dimers at  $m/z$  ratio 234 is only three times higher than the corresponding probability for  $m/z$  ratio 233. However, during the Pt/Sn standard analysis (at  $1 \text{ mg L}^{-1}$  level), the gross count rate increase over background for  $m/z$  234 was a factor of almost 500, while the increase in gross count rate for  $m/z$  233 was within the counting uncertainty. This lack of correspondence between response increase and relative probability of dimer formation showed that the contribution of tin dimers to interference counting is negligible when compared to that of the Pt argides, which constitute the source of count rate increases at  $m/z$  234 in the absence of U isotopes.

Theoretically, this issue could be solved by introducing an interference correction equation for gross count rate at  $m/z=234$ . To do that, an estimation of the PtAr contribution at  $m/z$  234 must be evaluated. Among the different possibilities to be considered for the count rate correction,

the count rates measured at  $m/z$  ratios 230 and 232 were associated with low abundance Pt isotopes combined with Ar, but they were overlapped by natural Th isotopes. 234 was the target  $m/z$  ratio;  $m/z$  235 and 238 were overlapped by natural  $^{235}\text{U}$  and  $^{238}\text{U}$  isotopes (in more detail, within the concentration ranges used in this work, the count rates associated with U isotopes at  $m/z$  ratios 235 and 238 were at least two orders of magnitude higher than the count rates arising from Pt argides). Hence, it seems that  $m/z=236$  is a good choice for controlling the Pt argide instrumental response, especially bearing in mind that the relative isotope abundances of the argide generators  $^{196}\text{Pt}$  and  $^{194}\text{Pt}$  are quite similar to each other (32.3 and 25.9% respectively).

However,  $^{235}\text{U}$  also generates hydrides at  $m/z$  236. This additional contribution to the gross count rate at  $m/z$  236 should be accounted for in the previously mentioned interference correction equation. The U hydride generation rate could be estimated by control of the instrumental response at  $m/z=239$ , which corresponds to  $^{238}\text{U}^1\text{H}$ . Therefore, the interference correction equation should be given by:

$$N_{U-234} = N_{234} - \frac{I_{Pt-194}}{I_{Pt-194}} \left( N_{236} - \frac{I_{U-235}}{I_{U-238}} N_{239} \right)$$

where  $N_{234}$ ,  $N_{236}$  and  $N_{239}$  are the gross count rates at  $m/z=234$ , 236 and 239 respectively,  $N_{U-234}$  is the net count rate at  $m/z=234$  that is due to  $^{234}\text{U}$ , and  $I_k$  is the natural relative isotope abundance of isotope  $k$  ( $k=^{194}\text{Pt}$ ,  $^{196}\text{Pt}$ ,  $^{235}\text{U}$  or  $^{238}\text{U}$ ).

Once the uncertainties are propagated, it is possible to see that the absolute uncertainties associated with the first, second and third terms are similar to each other. That means that the net count rate is reduced from the gross count rate, while the resulting uncertainty is about three to six times higher than the gross uncertainty. Under these conditions, we've found that the relative uncertainties obtained in such a way are higher than when the method detailed in this work is applied.

It is not easy to locate accurately the origin of these interferences. The scarce Pt arising from the environmental waters should be not concentrated during the preparation of the radiometric counting source. Thus, it could arise either from the Pt wire used during the electroplating or as an impurity in the stainless steel disks. The effect of these interferences was translated into the following analytical consequences: first, the true instrumental limit of detection should be affected, i.e., it should increase. Second, that would produce an increase in gross count rate at  $m/z$  234. The mass bias correction should be applied to net count rates; therefore if this correction is not taken into account, a systematic deviation of the calculated isotope ratio from the true isotope ratio could occur (see below for details).

In order to fix this problem, an immediate solution should consist of data correction by a background, Pt-spiked blank sample. However, due to the characteristics of this software-driven data correction, that background subtraction would also affect the U standard count rate. U standard does not contain any Pt; hence the application

of such a correction would result in the subtraction of a certain count rate proportion which, in fact, would correspond to actual uranium atoms. That would produce a systematic deviation of the calculated isotope ratio from the true isotope ratio.

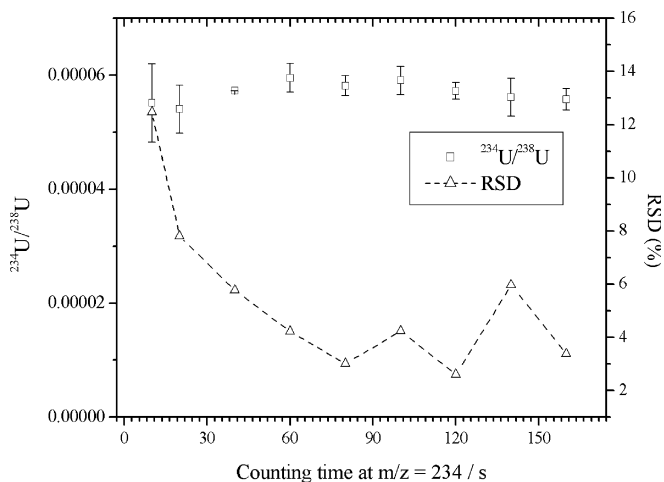
An alternative solution would consist of spiking both a blank sample and a certified standard with known Pt concentrations. In this way, the final calculated result would consider only the net count rates for each mass because the same correction should be established for all the solutions involved in the determination: blanks, standards and unknown samples. Although this methodological approach of double spiking introduces higher uncertainties and more sources of instrumental instability than the usual method (i.e., chemical off-line separation), it could be a reasonable method for performing calculations while avoiding the use of further radiochemical methods for a greater purification of uranium in the solutions. Hence, every analysis of an unknown sample set requires the analysis of a sequence consisting of (1) a fortified blank solution containing an adequate concentration of Pt, (2) a uranium standard solution containing a similar concentration of Pt, which is used to calculate the mass bias correction factor, and (3) the unknown sample.

## Results

### Counting conditions and concentration lower limit

Several parameters are crucial for achieving sufficient measurement precision, including counting times, particularly for low-abundance isotopes and concentration levels.

Different counting times were tested for mass 234 once a counting time of 1.5 s was fixed for mass 238 (and 9 s for mass 235). Both reproducibility and relative deviation were evaluated as a function of mass 234 counting time. Results are shown in Fig. 5, with reference to a uranium standard solution of 1.0 ng mL<sup>-1</sup>. The mass bias-corrected isotope ratios were the same within the uncertainty intervals.



**Fig. 5** Dependence of  $^{238}\text{U}/^{234}\text{U}$  isotope ratio precision and accurateness on  $^{234}\text{U}$  counting time

Furthermore, the relative uncertainties drastically decreased when increasing the counting time for mass 234, as expected. Thus, 120-s counting time was selected for  $^{234}\text{U}$ .

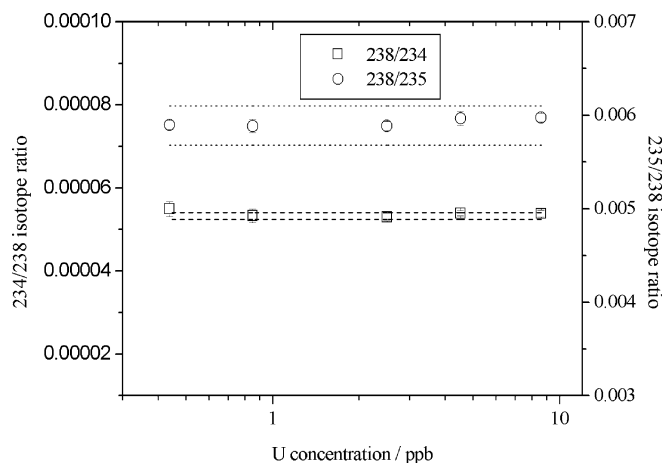
It is interesting to test the dependence of results on the overall uranium concentrations within the expected range of concentration. In this way, we could determine the range of uranium concentrations that could be analysed.

Several solutions of different uranium concentrations, at the same isotope ratio level, were analysed using the previously established counting times. Results are depicted in Fig. 6. Dashed lines show the 99.5% uncertainty interval for the standard. Regarding the lower concentration range, a larger deviation occurred because of the proximity to the limit of detection for mass 234 (approx. 2 pg L<sup>-1</sup>). Hence, analysis of solutions containing less than 0.5–0.6 ppb U was avoided. Regarding the  $^{238}\text{U}/^{235}\text{U}$  isotope ratio measurements, our results show that they are not affected by the U-concentration level within this range. In our previous works using a different high-efficiency nebulizer and the same quadrupole ICP-MS instrument, a lower cut-off level was established for uranium concentrations near 10 pg mL<sup>-1</sup> for analysing  $^{235}\text{U}/^{238}\text{U}$  ratio, which is usually about two orders of magnitude higher than the  $^{234}\text{U}/^{238}\text{U}$  isotope ratio.

It is interesting to note that during the experiments described here, the relative uncertainties of  $^{234}\text{U}/^{238}\text{U}$  and  $^{235}\text{U}/^{238}\text{U}$  isotope ratios were quite similar to each other. This fact is probably due to the lack of an ad hoc optimisation of the counting conditions for the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio, as this was not the major goal of this work.

### Effect of Pt concentration on the limit of detection and the $^{234}\text{U}/^{238}\text{U}$ isotope ratio

Different Pt concentrations in a blank solution were analysed for m/z ratio 234. The expected increase in the counting rates for 234 should be reflected in an increase in the calculated limit of detection, which is calculated as the



**Fig. 6** Dependence of calculated  $^{238}\text{U}/^{234}\text{U}$  and  $^{238}\text{U}/^{235}\text{U}$  isotope ratios on the overall U concentration. *Dashed lines* indicate the 99.5% confidence interval for the used standard. Please note the *double scale*

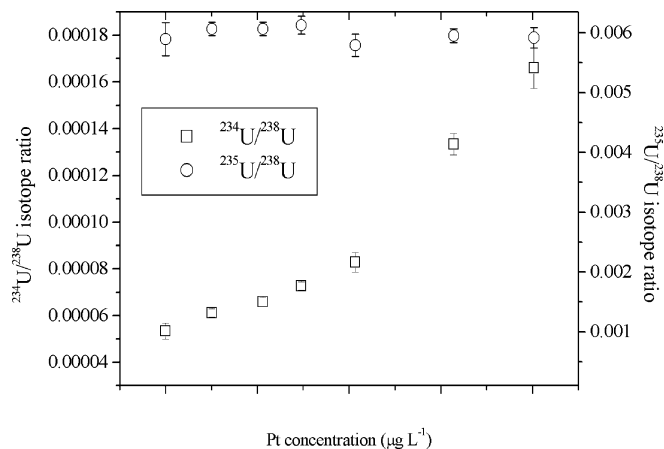
concentration corresponding to three times the standard deviation of these “spiked blank” solutions. Results for limit of detection are shown in Table 2, while the deviation of the calculated isotope ratio from the true isotope ratio is shown in Fig. 7. When Pt concentration is zero, the IUPAC expression for the limit of detection is obtained. A severe increase in the limit of detection for  $^{234}\text{U}$  was reflected once the Pt concentration became larger than  $20\text{ ng mL}^{-1}$ . This fact establishes a very important restriction compared to the performances achieved using “ideal” standard solutions.

Furthermore, the effect of the Pt concentration on the calculated uranium isotope ratio can be seen in Fig. 7. Different aliquots of a certified standard solution containing  $1\text{ }\mu\text{g L}^{-1}$  of uranium were spiked with increasing masses of Pt until the Pt concentrations were within the range  $0\text{--}50\text{ }\mu\text{g L}^{-1}$ . This is the corresponding expected range of concentrations of platinum, according to the previous tests. Pt concentration 0 corresponds to a  $1\text{ }\mu\text{g L}^{-1}$  standard solution of uranium, with no Pt, which is used for calculating the mass bias factor. The true uranium isotope ratio was hence always the same throughout the experiment. In the absence of interferences, the application of the mass bias correction should produce the same calculated isotope ratio. However, the figure shows that, as previously explained, the calculated isotope ratio drastically deviates from the true value as the Pt concentration increases.

The applied mass bias factor ( $k$ ) under these conditions was always the same (approximately 1.13).  $k$  must be applied to net count rates. However, due to the effect of interferences, additional corrections should be established, as previously explained in order to avoid this deviation from the true isotope ratio.

A radiochemical separation method could be applied [17] in order to remove the Pt present in the solutions; however, we preferred to use the double-spiking method as a contingency, even establishing further limitations on instrumental performances. It is interesting, anyway, to see that once again, no important effect was detected when attempting to calculate the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio with Pt present in the solution. This fact is in agreement with the greater isotope abundance of  $^{235}\text{U}$  (compared with that of  $^{234}\text{U}$ ), hence a certain insensitivity of the method to the presence of Pt atoms in the solution has been demonstrated (at least within this range of Pt concentrations).

Thus, mass bias factors have been independently determined for isotope ratios  $^{235}\text{U}/^{238}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$ .



**Fig. 7** Dependence of the calculated  $^{238}\text{U}/^{234}\text{U}$  isotope ratio on the Pt concentration in a  $1\text{ ng mL}^{-1}$  U standard solution

For the first one, only a traditional correction was applied. No further correction has been introduced in the presence of Pt, as the effect of this element on the corresponding mass bias ratio has been shown to be negligible. On the contrary, when Pt is present, both a blank solution and a uranium reference standard were spiked with an adequate mass of Pt, and mass bias correction and background subtraction algorithms were applied as detailed above.

#### Application: isotope ratios in drinking water and underground water samples

Results for drinking-water samples are shown in Table 3. Due to the tested absence of remarkable Pt contents, only typical mass bias factors were calculated. Total uranium concentrations lie within a range of  $0.3\text{--}7.6\text{ ng mL}^{-1}$ , which is quite typical for natural waters. Buxton and Rapido waters are from regions known to be geologically rich in uranium. Several of the water samples were not analysed for uranium isotope ratios due to the low U content. It is interesting to note that all the measured  $^{234}\text{U}/^{238}\text{U}$  isotope ratios were well below that of the secular equilibrium condition. In addition, all of them were very different from the seawater average value ( $\sim 6.25 \times 10^{-5}$ ). For both  $^{235}\text{U}/^{238}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  ratio measurements, precision was better than 5%.

Results for underground water samples using both ICP-QMS and alpha-particle spectrometry are shown in Table 4.

**Table 2** Background enhancement factor and  $^{234}\text{U}$  instrumental limits of detection depending on the Pt concentration in the analysed sample

Pt ( $\text{ng mL}^{-1}$ )	Enhancement factor at m/z 234	Enhancement factor at m/z 235	Enhancement factor at m/z 238	$^{234}\text{U}$ LOD ( $\text{pg L}^{-1}$ )
0	1.0	1.0	1.0	1.5
5	1.9	1.1	0.8	2.7
10	3.5	1.2	1.1	2.6
15	4.1	0.9	1.3	2.8
20	6.3	1.2	1.2	3.4
31	7.6	1.1	1.0	5.8
39	8.8	1.3	1.2	13.0

**Table 3** Uranium concentrations and uranium isotope ratios determined in drinking-water samples

Sample	[U](ng mL <sup>-1</sup> )	RSD (%)	<sup>235</sup> U/ <sup>238</sup> U (×10 <sup>-3</sup> )	RSD (%)	<sup>234</sup> U/ <sup>238</sup> U (×10 <sup>-5</sup> )	RSD (%)
Volcano	0.29	2.2	7.179	2.0	NM	–
Vittel	0.47	1.0	7.457	1.7	NM	–
Badout	0.58	0.2	7.283	2.8	NM	–
Evian	1.86	1.9	7.215	3.8	6.543	3.3
Buxton	3.23	0.4	7.294	3.5	9.533	3.0
Rapido	7.58	1.2	7.042	4.1	7.559	4.6

All the results show a good agreement with the results collected using radiometric methods within the uncertainty intervals corresponding to ICP-QMS measurements, despite the higher uncertainties introduced with the correction algorithm. Of course, the same could be said when considering the uncertainty intervals related to alpha-particle spectrometry, as the corresponding uncertainties are quite higher than those collected using our experimental setup. Indeed, the average uncertainty has decreased drastically by a factor of four, from 17% (alpha-particle spectrometry) to about 4% (ICP-QMS + Apex Q nebulizer), showing the advantages of this approach. Reducing uncertainties would require an initial radiochemical separation of uranium from Pt isotopes.

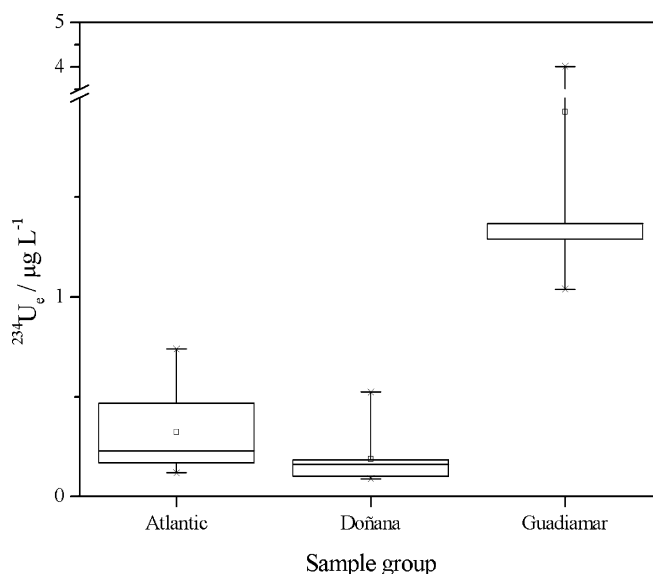
It can be seen that the range of variation in the isotope ratios is quite narrow (5.24–8.93)×10<sup>-5</sup>. Much higher values have been described in the literature [1, 12, 16], although it is well established that the degree of the variation range is dependent on the nature of the aquifer substrate and the water

charge rate. In the shallow oxidised zone (in this case, the recharge area), the uranium concentration increased along the flow line, and so, <sup>234</sup>U/<sup>238</sup>U activity ratio will be depleted as a consequence of the preferential leaching effects. In case there is a redox front, a high fraction of U precipitates, a fact that is reflected in a great decrease in U concentration in dissolution. However, under near chemical equilibrium conditions at the redox front, preferential leaching of <sup>234</sup>U from previously precipitated material could occur. In this way, the <sup>234</sup>U/<sup>238</sup>U isotope ratio could quickly decrease [12].

Rainwater is the main water source for the aquifer [22]. The aquifer's substrate is sandy and homogeneous, so that the properties of the substrate should not be the origin of the variations. The recharge area of the aquifer is located at its northern sector (samples 17–20). Therefore, that sector should be associated with environmental oxic conditions where uranium remains dissolved as the quite stable UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> or UO<sub>2</sub><sup>2+</sup> ions. As preferential leaching occurs for <sup>234</sup>U, the <sup>234</sup>U/<sup>238</sup>U isotope ratio should increase from the secular equilibrium value. In contrast, if the water leaching efficiency throughout the sandy top layer of the aquifer were not important, the contribution of rain water could drastically affect the isotope ratio. According to Martínez-Aguirre et al. [23], uranium isotope ratios in rainwater samples collected close to this area during the second half of the 1980s were in the range of

**Table 4** Uranium isotope ratios as determined using ICP-QMS and alpha-particle spectrometry in underground water samples

Sample	T (°C)	pH	Conductivity (mSm/cm)	<sup>234</sup> U/ <sup>238</sup> U (×10 <sup>-5</sup> , ICP-QMS)	<sup>234</sup> U/ <sup>238</sup> U (×10 <sup>-5</sup> , α-spectrometry)
1	19.8	9.2	0.7	6.13±0.23	5.71±0.95
2	19.3	7.5	0.4	6.25±0.16	5.49±1.33
3	19.9	9.1	0.4	6.80±0.14	7.30±2.29
4	18.6	7.4	0.5	6.21±0.23	6.21±1.27
5	18.2	6.8	0.7	6.76±0.18	6.58±0.82
6	21.9	8.7	0.8	5.85±0.34	5.71±1.21
7	20.8	8.9	0.8	5.95±0.18	5.81±1.05
8	16.1	6.3	0.1	5.59±0.25	5.49±0.72
9	16.8	7.2	3.6	7.09±0.20	7.46±1.11
10	18.8	7.6	0.3	5.24±0.19	5.49±1.00
11	17.3	4.7	0.6	5.75±0.40	5.85±0.55
12	16.5	5.4	0.7	NM	5.49±0.78
13	18.3	7.7	5.4	6.17±0.27	6.29±0.83
14	15.8	6.1	0.2	6.25±0.23	5.99±0.72
15	16.8	7.4	0.5	5.56±0.19	5.49±1.21
16	17.6	8.0	0.2	8.93±0.48	7.75±1.26
17	17.3	8.5	1.2	7.69±0.36	7.46±1.62
18	22.3	7.9	0.6	5.68±0.39	5.81±0.78
19	20.3	6.3	0.2	5.68±0.39	5.85±0.55
20	19.6	7.5	0.5	6.25±0.23	6.37±0.97
21	15.8	7.9	1.2	7.19±0.36	6.94±1.01

**Fig. 8** Box and whisker plot of <sup>234</sup>U<sub>e</sub> values for the dissolved fraction of underground water samples described in the text



$5.92 \times 10^{-5}$ . Interestingly, the isotope ratios measured at the recharge zone (samples 17 and 18) showed either similar or slightly lower isotope ratios than those of rainwater. Therefore, the actual isotope ratio seems to be the result of the competition between both trends: values only slightly higher than secular equilibrium condition describe the sectors where rain water is recharging the underground aquifer.

The southern sector of the aquifer is not a recharge area; hence, no additional supply of  $^{234}\text{U}$ -enriched water occurs. For the samples taken in this sector, the isotope ratio decreased to values close to the secular equilibrium condition. It has been established that a drastic decrease in the isotope ratio (coupled to a decrease in the uranium concentration) should demonstrate the existence of a reducing (i.e., anoxic) environment. The uranium concentration decreased due to precipitation processes, which does not affect the isotope composition, but if leached  $^{234}\text{U}$  atoms rapidly precipitate, no  $^{234}\text{U}$  excess occurs, affecting the overall isotope ratio due to a lack of "excess" supply. As an additional tool,  $^{234}\text{U}$  in excess ( $^{234}\text{U}_e$ ) has been calculated for the collected samples.  $^{234}\text{U}$  in excess is defined as:

$$U_e = [U] \left( \frac{a_{234}}{a_{238}} - 1 \right)$$

where  $a_i$  is the concentration activity of radionuclide  $i$  and  $[U]$  is the uranium concentration ( $\mu\text{g L}^{-1}$ ). This magnitude was introduced as a useful marker of water masses having similar geochemical properties [1]. The term in brackets indicates the relative magnitude of deviation of uranium in the sample from radioactive equilibrium. The summary of the calculated  $^{234}\text{U}$  in excess can be seen in Fig. 8, and at least two value groups can easily be distinguished. The Guadamar group samples come from the recharge sector, producing clearly large  $^{234}\text{U}_e$  values. It can be deduced that this fact is more related to relatively large uranium concentrations than to large isotope ratios. In contrast, both the Atlantic and Doñana sectors are characterised by relatively homogeneous  $^{234}\text{U}_e$  distributions, which could be associated with a certain loss of the uranium conservative behaviour. This fact could demonstrate the presence of a reducing environment, hence the transition zone from high  $^{234}\text{U}_e$  values (oxic environment) to low  $^{234}\text{U}_e$  values (reducing environment) could be defined as a redox front. This preliminary hypothesis should be tested after additional sampling campaigns by the analysis of both dissolved and suspended matter, which could be used as a useful marker of uranium capacity for adsorption onto scavenging particles.

## Conclusions

These results show that stripping the uranium from radiometric counting sources prior to analysis by ICP-QMS allowed the researchers to compare measurements

and test the reproducibility of results, improving the precision of the analysis. This procedure provides several advantages involving ease of storage and transportation of the samples. However, special attention must be paid to the presence of interferences, which are related to formation of Pt argides in the plasma. However, it would be quite strange to find this kind of interference in natural samples directly analysed by ICP-MS.

The effect of these argides on calculated uranium isotope ratios has been shown, and the limitations that they pose on limits of detection, precision and accuracy of results. This effect was negligible when attempting the calculation of  $^{235}\text{U}/^{238}\text{U}$  isotope ratios due to the higher isotope abundances of  $^{235}\text{U}$ . Results obtained using the developed instrumental setup have been in good agreement with those obtained using radiometric counting, improving the precision of results. These results seem to confirm the existence of a change in redox conditions within the underground aquifer.

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