Further investigations on optimized tail correction and high-precision measurement of uranium isotopic ratios using multi-collector ICP-MS

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Abstract

In the present paper, we further examine the optimum conditions for rapid, precise and accurate determination of $^{234}U/^{238}U$ ratios in geological materials by multiple collector (magnetic-sector) inductively coupled plasma mass spectrometry (MC-ICP-MS). In our experiments, isotopic measurements were performed on a Micromass IsoProbe™ instrument, using Faraday collectors in static mode only. Unlike the ion counting system coupled with an energy filter, this technique eliminates the difficulty of proper calibration of the Daly/Faraday gain ratio. On the other hand, since our Micromass instrument has a poor abundance sensitivity (the proportion of the ^{238}U ion beam measured at mass 237 is ∼ 25 ppm), the major issue to be addressed is the tail correction. For this purpose, we have developed a tail correction method slightly modified from Thirlwall [J. Anal. At. Spectrom. 16 (2001) 1121]. This method is based on correction of the actual tail contribution under each peak, as assessed by the tail shape measurements on mono-isotopic ion beams, instead of the usual half-mass zeroes baseline estimation. Our approach enabled us to correct for the large offset that can be observed on isotopic data when tail correction is done by means of linear interpolation between half-mass zeroes, and showed that this latter tail correction method results in nearly 3% underestimation of $^{234}U/^{238}U$ ratios on the GEOTOP IsoProbe™ for material at secular equilibrium.

A $^{236}U-^{233}U$ double spike was employed to correct for mass discrimination bias. Using an Aridus™ micro-concentric, desolvating nebulizer sample introducing system, a minimum of 200 ng of sample-U was consumed to carry out a precise $^{234}U/^{238}U$ analysis, thereby allowing a ^{234}U signal of ∼ 4–5 mV to be monitored for 50 measurement cycles of 5 s each. This time-consuming, 10-min procedure allowed us to obtain an external reproducibility of 0.8‰ (2σ) for isotopic measurements of the NBL-112a standard solution. Replicate measurements of this reference material yielded a mean $\delta^{234}U$ value of − 36.42 ± 0.80‰ (2σ, n = 19), which is highly consistent with values reported by other laboratories. The total

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reproducibility, including both chemical separation and spectrometric measurement, was assessed using geological samples (a coral and a carbonate rock); the long-term reproducibility obtained was about 1.3‰ (2σ).

Keywords: Uranium isotopes; Multiple collector ICP-MS; Tail correction; Standard; Accuracy; Precision

1. Introduction

Multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has proved to be a powerful tool for high-precision measurement of isotopic compositions, leading to a wide array of new applications in Earth and planetary sciences and cosmochemistry (Halliday et al., 1998).

This technique has been successfully used for precise measurements of U and Th isotopic compositions (Luo et al., 1997; Stirling et al., 2000, 2001; Henderson, 2002; Robinson et al., 2002; Shen et al., 2002). MC-ICP-MS, and more generally, ICP sources, have several advantages over conventional thermal ionization mass spectrometry (TIMS), which many other studies have already reported (e.g. Halliday et al., 1998; Stirling et al., 2000):

(a) The plasma source yields a very high ionization efficiency (>90%) of nearly all elements having a low first ionization potential (Jarvis et al., 1992; Taylor, 2001);
(b) Ionization efficiency is not a function of load size;
(c) To a first approximation, the mass discrimination is time-independent during data acquisition, since fresh aerosol sample is continuously introduced into the ICP;
(d) Fewer chemical steps are needed during sample preparation.

Nevertheless, MC-ICP-MS has two major drawbacks not encountered in TIMS with respect to U($-$Th) isotopic analysis: (i) high plasma-generated ion source instability (Shen et al., 2002); and (ii) poor abundance sensitivity of some instruments (Thirlwall, 2001). The abundance sensitivity is a parameter that allows the estimation of the magnitude of the tail contribution, and is usually defined as the proportion of ^{238}U ion beam measured at mass 237 (Chen et al., 1992; Thirlwall, 2001). Because of the large atom ratios encoun-

tered in the U($-$Th) systematics (for example, the ^{238}U/^{234}U atom ratio is close to 18,200 for a sample in secular equilibrium), the tail effect may limit the analytical accuracy (see discussion in Chen et al., 1992). With TIMS analyses, this problem is generally circumvented by using a Daly detector coupled with an energy filter: electrostatic (ESA), Retarding Potential Quadripole (RPQ) or Wide Aperture Retarding Potential (WARP) filter (Edwards, 1988; Chen et al., 1992; Cheng et al., 2000; Rubin, 2001). With such a system, abundance sensitivity is greatly improved to ≪1 ppm, and the remaining tail contribution is corrected by using a linear interpolation between half-mass zeroes. The stable thermal-generated ion source allows an analysis in magnet-controlled peak jumping mode on a single detector placed behind the energy filter.

In MC-ICP-MS, the high instability of the ion beam produced by the plasma source makes this approach impractical. Depending on the instrument, different protocols were adopted to overcome this problem.

In this paper, we outline and discuss the advantages and limitations of the technique we developed for precise measurement of uranium concentration and isotopic composition using a Micromass IsoProbe™ MC-ICP-MS instrument. In contrast to what other MC-ICP-MS users have done (Luo et al., 1997; Robinson et al., 2002; Shen et al., 2002), we used Faraday detectors in static mode only. This strategy obviates many of the problems related to gain calibration of the Daly/Faraday detectors. However, since we did not use a Daly detector and the energy filter normally coupled with it, the tail contribution induced by the high abundance sensitivity of the instrument (∼ 25 ppm) proved to be a critical bias. We addressed this issue following an approach slightly modified from Thirlwall (2001).

In the forthcoming sections, we outline the general protocol used to optimize correction for significant tailing effects. We also describe the entire mass

spectrometric procedure that can be used with an IsoProbe™ MC-ICP-MS instrument for precise measurement of $^{234}U/^{238}U$ ratios. Finally, based on measurements of standard reference materials and geological samples (corals and limestones), we address the issue of the overall analytical precision and accuracy that can be achieved using this technique.

2. Overview of current procedures for U isotopic analysis by ICP-MS

Using a VG Elemental Plasma 54™ MC-ICP-MS instrument, Luo et al. (1997) proposed to perform U(−Th) analyses by combining Faraday cups and a Daly detector coupled with an energy filter, either in static or in multi-static mode. Since Faraday and Daly detectors are used simultaneously, their relative gain must be carefully determined in order to achieve maximum precision and accuracy. Two data acquisition protocols were developed. They differ in the way variations in the relative Faraday/Daly gain are monitored. With the static procedure, it is determined externally by a standard bracketing method. With the multi-static procedure, the relative Faraday/Daly gain is monitored and calibrated during the sample analysis by comparing the results of two sequential $^{235}U/^{238}U$ measurements with two different collector configurations (Daly/Faraday and Faraday/Faraday). Luo et al. (1997) and Stirling et al. (2000) argued that the latter approach is superior even though it requires slightly larger sample sizes and is more time-consuming. Because a Daly detector coupled with an energy filter is used to measure the minor mass (^{234}U), the contribution of the tail effect underneath this peak may be considered negligible or, at least, well corrected for by the linear interpolation between half-mass zeroes.

Using a Nu™ MC-ICP-MS, Robinson et al. (2002) proposed to perform measurements in static mode on Faraday collectors for major peaks and on an ion counting channel for the minor peak (^{234}U). In contrast to observations made on the Daly detector of the Plasma 54™ instrument (Luo et al., 1997) and our IsoProbe™ instrument, the relative gain between the ion counting channel and the Faraday cups remains constant throughout an analysis with the Nu™ collector system, so that no internal drift correction is required. However, because the ion counting channel

is not coupled with an energy filter, abundance sensitivity is in the order of 5 ppm at 1 amu. With this instrument, this causes an offset of < 0.5‰ to the measured $^{235}U/^{234}U$ ratio (Robinson et al., 2002). Robinson et al. (2002) argued that the standard bracketing measurement procedure they followed corrects not only for the relative gain between Faraday cups and the ion counting channel, but for this tail offset as well. This means that all sample measurements are taken with reference to a given standard, in this case, CRM-145, and that one makes the assumption that the system behaves linearly. They assessed the validity of their approach by comparing analyses of the CRM-145 standard (also called NBL-112a, NIST-4321, and formerly U-960 or NBS SRM-960) with analyses of the Harwell uraninite (HU-1), which Cheng et al. (2000) have shown to be in secular equilibrium for the $^{238}U-^{234}U$ sequence.

Using a sector-field ICP-MS equipped with a single electron multiplier, Shen et al. (2002) also performed a precise, accurate U−Th isotopic analysis. Their approach obviates many of the problems associated with the intercalibration of ion-counting and Faraday detectors, but requires (i) that the error introduced by source instabilities be minimized; and (ii) more particularly, that the tail correction problem be addressed. The first problem is overcome by installing a guard electrode (GE) sheath around the torch and by employing a rapid peak switching method. The second problem requires precise determination of the tail shape between each mass. Furthermore, the intensity bias inherent in the electron multiplier (see also Cheng et al., 2000) must be corrected for. The correction value is determined once a day by comparing the CRM-145 measured $\delta^{234}U$ with its accepted value. In much the same way as the experiments conducted by Robinson et al. (2002), this protocol requires that all sample analyses be done with reference to a standard sample.

3. Experimental procedure used for U-isotope measurements

3.1. Instrumentation and data acquisition

All the results presented here were obtained using a Micromass IsoProbe™ MC-ICP-MS at the GEOTOP-

UQAM-McGILL Research Center from July 2001 to May 2002. The instrument is similar to that used by Thirlwall (2001, 2002). It is equipped with an array of nine Faraday cups with 10^{11} Ω positive feedback resistors, two ion counting detectors (Channeltron) and a Daly ion counting system inserted immediately behind a retarding filter (WARP).

The U isotopic data are acquired in static multi-collection mode by means of Faraday collectors with cup efficiencies set at unity. The Faraday amplifier gain is calibrated daily before the analytical session. Ignition of the plasma and application of the accelerating high voltage is followed by a warm-up period of about 90 min. Collectors are aligned H1: mass 233 to H6: mass 238, using the configuration shown in Table 1. For uranium isotopic determinations, since the ^{234}U ion beam has to be measured on a Faraday cup with a minimum intensity of $\sim 4-5$ mV, the ^{238}U beam would exceed 80 V for a sample assumed to be in secular equilibrium for the ^{238}U$-^{234}$U sequence. This greatly exceeds the capacity of Faraday cups equipped with a 10^{11} Ω resistor. In such cases, the H6 detector is moved away from the ^{238}U beam in order to avoid any beam collection. However, this collector is occasionally used to determine U concentration in low U-content samples as well as to conduct specific tests (for instance, spike calibration). Abundance sensitivity, usually defined as the proportion of the ^{238}U ion beam tail measured at mass 237, is monitored online during each analysis from H5 output, with H5 set for mass 237. The ^{238}U intensity is calculated from the ^{235}U ion beam (H3) using the natural ^{238}U/^{235}U ratio of 137.88 (see Section 4.2). A double spike (^{236}U$-^{233}$U) with a ratio of ≈ 0.7 is used to correct for mass discrimination. The measured isotope ratios are then normalized using a linear law (see Section 5.2). In general, samples are spiked so that the resulting ^{235}U/^{233}U and ^{233}U/^{234}U ratios are close to 11, thereby optimizing dynamic range and precision.

All measurements are performed using a high-efficiency desolvating microconcentric nebulizer system, the ARIDUS MCN 6000™. The sweep gas (Ar and N_2) settings are optimized to maximize the sensitivity and minimize oxide levels. The uptake rate of the nebulizer is kept constant at ~ 50 µl/min. Under such conditions, a $6-7$ ppb ^{238}U solution generates a signal over 1 V. The total sensitivity, combining ionization with MS transmission efficiencies, is about 5‰. Argon flows are set at ~ 15.0 l/min for the cool gas, at ~ 1.03 l/min for the intermediate gas and at $\sim 0.90-0.99$ l/min for the nebulizer gas.

The sample is introduced into the mass spectrometer in a 2% HNO_3 solution. The inlet system is cleaned with 4% HNO_3 followed by 2% HNO_3 between sample runs until a negligible U background is achieved (see Section 3.2). Depending on the cleanliness of the nebulizer, the washout procedure requires from 10 to 20 min. The first step of the data acquisition procedure consists of a 1-min measurement of the electronic backgrounds of each Faraday cup, subsequently defined as the Mass Spectrometer Background (MSB), with no ion beam (valve off) in the analyzer, in order to determine the amplifier drifts. After the valve (LOS) is opened, the "on-peak zero" baseline (OPZ) is measured for 1 min with the same 2% HNO_3 batch solution that was used to dilute samples. Finally, samples are analyzed for one block of 50 scan cycles with a 5 s integration time per cycle. A routine analytical procedure time is around 10 min. With this protocol, the amount of U consumed per analysis is at least 200 ng. This produces a signal of ~ 1 V for ^{235}U and >0.005 V for ^{234}U (for samples close to ^{238}U$-^{234}$U secular equilibrium).

Raw signal intensities are corrected for resistor gains only. They are then transferred to an Excel spreadsheet for further offline cycle-by-cycle manipulations (correction for OPZs, tailing and mass discrimination).

3.2. Accuracy and background

In the Excel spreadsheet, the on-peak zeroes (OPZs), determined before sample acquisition, are subtracted from sample peak intensities to correct for: (i) amplifier drifts; (ii) U in the blank solution; (iii) U memory effect in the inlet system; and (iv) potential isobaric interferences that may be associated with the 2% HNO_3 solution. The OPZ correction significantly controls the precise determination of

Table 1
Collector configuration for U isotopic analysis on the GEOTOP IsoProbe™ MC-ICP-MS

Collector	Axial	High 1	High 2	High 3	High 4	High 5	High 6
Uranium	–	^{233}U	^{234}U	^{235}U	^{236}U	(237)	^{238}U

the small ^{234}U signal and thus the accuracy of U isotopic measurements. The effect of MS backgrounds and absolute on-peak zero (OPZ$_{abs}$) intensities (estimated by subtracting the MSB from OPZ) on accuracy and precision are discussed separately in the next sections.

3.2.1. MS background

Daily variations in the electronic background (MSB) were monitored during 64 s on each Faraday cup throughout the first step of the sample analytical procedure. These were around 20–30 μV (2σ; $n ≈ 20$ analysis per day) depending on the day of analysis. However, a general drift was observed on all the Faraday cup baselines in the course of a day, demonstrating that, to a first approximation, the electronic backgrounds monitored on each cup co-varied with time. This phenomenon might be associated with temperature fluctuations of the system (MC-ICP-MS, room temperature).

We define dark noise here as the fluctuation around this first-order drift. This noise is below 10 μV (2σ) for the MSB measurements of each Faraday cup, based on a 64-s integration time. Included in this value is the intrinsic error associated with the amplifier noise (see discussion in Ludwig, 1997), and also the error related to the drift in the amplifier background, during the integration. This value represents the actual irreproducibility associated with the background correction. It also provides an estimate of the limits, in terms of precision and accuracy, which can be achieved on the GEOTOP IsoProbe™. Thus, in order to obtain an external reproducibility and an internal precision of 1‰ to 2‰ on each measured ratio, the signal/dark noise ratio must be equal to or greater than 500 for each ion beam. For the minor isotope (^{234}U), this requires monitoring a signal intensity of at least 5 mV. Under such conditions, baseline variations occurring during data collection will not affect signals measured within the desired level of precision. However, large fluctuations we observed within a day made it necessary to monitor the MS background during each analysis.

3.2.2. Absolute OPZ values

The OPZ$_{abs}$ values give direct indications about the U content in the blank solution, U-memory effects in the inlet system and potential isobaric contributions. The 2% HNO$_3$ blank solution is prepared with ultra-pure reagents and is identical to the blank solution used to dilute samples and standards. Theoretically, this should make it possible to thoroughly correct for any U contamination present and to avoid any change in the acid molarity that could remove additional U from the inlet system (Thirlwall, 2002). During our U isotopic measurements, constant contamination associated with the 2% HNO$_3$ remained undetectable on ^{235}U and thus, a fortiori, on ^{234}U.

Concerning sample cross-contamination, a longer washout time (up to 20 min) is sometimes required between two successive analyses in order to make OPZ$_{abs}$ values negligible in comparison with signal intensities (i.e. signal/OPZ$_{abs}$ ≫ 500). Memory effects do not appear to be directly related to the most recent sample intensity. In practice, for uranium isotopic determinations, data acquisition is initiated when measured OPZs do not differ from MS background values for masses 233, 234 and 236 within the range of dark noise irreproducibility (i.e. -20 μV < OPZ$_{abs}$ < 20 μV, where OPZ$_{abs}$ = OPZ $-$ MSB). With respect to ^{235}U measurement, the analysis criterion is that the OPZ$_{abs}$ value on H3 remains < 50 μV. However, while memory effects are well constrained using the suggested cleaning procedure for routine ^{234}U/^{238}U isotopic measurements, they remain a serious problem for standards such as U-500 or NBL-117, as well as for tests and spike analyses that require monitoring ^{238}U ion beams. In fact, such standard or spike solutions have ^{238}U/^{235}U ratios (e.g. ^{238}U/^{235}U ≈ 1, for NBL-117 and U-500) that are very different from natural uranium (^{238}U/^{235}U = 137.88). During such analyses, any variations in the uranium baseline from the OPZ measurement will cause significant inaccuracies in the final results.

No isobaric interferences were observed on the monitored masses of uranium. If there were any, they remained within the dark noise range. However, we identified a substantial constant interference on mass 237, with an OPZ$_{abs}$ significantly higher than the MS background (OPZ$_{abs}$(mass 237) ≈ 60 to 100 μV). This suggests a mono-isobaric interference, which might be associated with the presence of Au (gold coating of the hexapole ion guide, cf. Rehkämper and Mezger, 2000) and Ar in the inlet system.

4. The tailing contribution

4.1. The half-mass zero estimation of the baseline

Correction for tail from adjacent peaks onto a given mass is commonly done by subtracting values interpolated from signals measured at half-mass positions (± 0.5 amu) from the peak to be corrected (Chen et al., 1986; Edwards et al., 1987). This approach has the advantage of an online correction of the tailing contribution, but also has two major drawbacks. First, each peak is corrected for its own tailing. Second, because the tail profile has a negative curvature, linear interpolation between half-mass backgrounds overestimates the actual tail contribution under the peak. This problem was first reported by Chen et al. (1986) and Bard et al. (1990) for U–Th analyses. Bard et al. (1990) have shown that the linear tailing correction is no longer appropriate for U–Th TIMS analyses when abundance sensitivity increases due to vacuum deterioration. They proposed a parabolic interpolation to correct for the total tail contribution under the ^{234}U and ^{235}U peaks. Nevertheless, they acknowledged that this parabolic fit was not able to correct properly for tailing

biases under the ^{236}U peak. Shen et al. (2002) also used the log-mean of the signals measured at half-masses to subtract tail contribution from ^{233}U, ^{234}U and ^{235}U intensity beams. However, they showed that this calculation was no longer appropriate for mass 236 because of the significant contribution of the ^{235}U peak, superimposed on the major ^{238}U tailing, over the mass interval 235.5–236.5. They therefore established an empirical formula, which was a function of the signal measured at mass 236.5, to estimate the total tail contribution at mass 236.

When applied to our IsoProbe™ MC-ICP-MS data, the linear and exponential interpolation result in a systematic offset, which is illustrated by δ^{234}U values of $-26‰$ and $-15‰$, respectively, for the Harwell uraninite standard (see Fig. 1 and Section 6.1 for more details) instead of the expected value for secular equilibrium, δ^{234}U $= 0‰$ (Ludwig et al., 1992; Cheng et al., 2000). This large offset is due to the poor abundance sensitivity (~ 25 ppm) of the GEOTOP IsoProbe MC-ICP-MS. Below, we will show that with this instrument, even exponential corrections (i.e. the log-mean of the signals measured at half-mass positions) overestimate the real tail contribution.
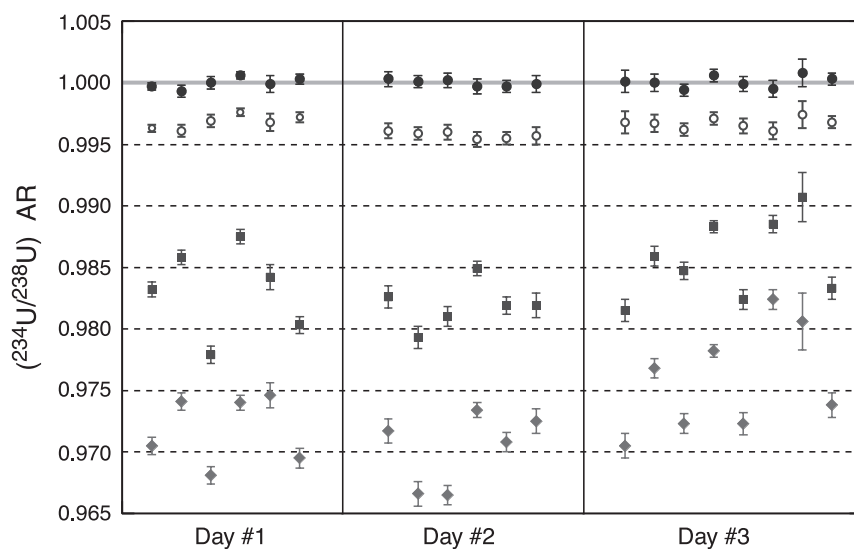

Fig. 1. Repeated analyses of the (^{234}U/^{238}U) activity ratio of the HU-1 uraninite conducted on the Micromass IsoProbe™ MC-ICP-MS instrument over a 3-day analytical run. Results obtained using a tail correction based either on linear (filled diamonds) or exponential (filled squares) interpolation of half-mass zeroes are compared with results obtained using the tail correction method we developed (circles). The latter approach is based on the actual, precise quantification of tail contributions underneath each peak due to adjacent ion beams, as assessed by tail shape measurements on mono-isotopic ion beams. Blank circles refer to the correction which is done when the measured tail shape only is used; filled circles refer to results obtained by this same model using the tail shape corrected according to the θ coefficient (see full explications in the text).

4.2. The tail correction method

The method that we finally retained for tail correction is based on the actual, precise quantification of tail contributions underneath each peak due to adjacent ion beams. Thirlwall (2001, 2002) used the same method for optimizing tail corrections on MC-ICP-MS instruments with poor abundance sensitivity, such as the IsoProbe™. He showed, for example, that for high-precision Pb isotope measurements, his method corrects for discrepancies of up to ~ 700 ppm relative to the standard half-mass zero correction for the $^{208}Pb/^{206}Pb$ ratio on the NIST SRM-982 reference standard (Thirlwall, 2001).

Our approach requires precise determination of the tail profile on both sides of a mono-isotopic peak in an array of several atomic mass units (amu). This is accomplished by measuring mono-isotopic solutions within the mass range of the element of interest (see Section 4.3). The total tail under a given peak then becomes the sum of contributions from all adjacent peaks. This can be mathematically formalized by:

$$I^m_{\text{Tailcor}} = I^m_{\text{Measured}} - \sum_{\substack{i=-5 \\ i \neq 0}}^{+3} Z_i \times I^{m-i}_{\text{Tailcor}} \qquad \text{(S)}$$

where I^m_{Tailcor} is the tail-corrected beam intensity on mass m, I^m_{Measured} is the measured beam intensity, and Z_i is the proportional tail, expressed in ppm, at i amu away from a mono-isotopic peak. This expression is similar to that proposed by Thirlwall (2001), but it dispels one ambiguity. From a theoretical point of view, one must consider the tail-corrected beam intensity in the right part of the expression (S). In the equation proposed by Thirlwall (2001), it is unclear whether the tail-corrected intensities or the measured ones are considered. However, for uranium analysis, the artefact induced by using the measured intensities is small: 0.2‰ for the $^{234}U/^{238}U$ ratio and 0.5‰ for the concentration.

Since we do not monitor the ^{238}U ion beam, its intensity is calculated using ^{235}U intensity, corrected for mass discrimination according to:

$$I^{238}_{\text{Estimate}} = 137.88 \times I^{235}_{\text{Tailcor}}(1 + \Delta_m \varepsilon)^{-1}.$$

where ε is the linear discrimination bias (see Section 5) calculated by using the $^{236}U/^{233}U$ double-spike ratio and Δ_m is the mass difference between ^{238}U and ^{235}U.

Thus, for the determination of the $^{234}U/^{238}U$ ratios, this approach leads to a linear system of four equations for four unknowns (I^{233}_{Tailcor}, I^{234}_{Tailcor}, I^{235}_{Tailcor}, I^{236}_{Tailcor}), which is solved offline by inverting the associated matrix in the Excel spreadsheet. This calculation is done cycle by cycle.

4.3. Determination of the tail profile

The tail profile was determined using separate isotope solutions. ^{233}U solutions were used for the range from -5 to -1 amu. Both ^{238}U and ^{232}Th solutions were analyzed for the range from $+1$ to $+3$ amu. Before dilution and analysis, the parent solutions of ^{233}U and ^{232}Th were purified by means of anion exchange resin to avoid any presence of uranium in ^{232}Th solutions and of thorium in ^{233}U solutions.

We took great care in precise quantification of the tail profile over the range from -5 to -1 amu because this is the tail contribution of the major ^{238}U ion beam that mainly controls the accuracy of uranium isotopic analysis. Four ^{233}U mono-isotopic solutions were prepared in order to yield ^{233}U ion beam intensity over the range from 25 to 140 V. That way, the experiments were carried out in the same intensity conditions as for uranium analyses. The alignment of the Faraday cups, optimized for uranium isotope analysis (H1: mass 233 to H5: mass 237; see Table 1), was conserved. The ion beams monitored at masses 228 (H1) to 232 (H5) were measured with an intensity of at least 0.05 mV. Since the ^{233}U intensity beam was not monitored for these solutions, the "abundance sensitivity", defined here as Z_{-1}, could not be determined online. However, we were able to determine the (Z_{-i}/Z_{-1}) ratios precisely.

Two dilute solutions of a shelf of thorium and two HU-1 uraninite solutions were prepared to yield ion beam intensities on the main peak (^{238}U or ^{232}Th) over the 4–8.5 V range. The major isotope was monitored on the H2 Faraday cup. This permitted online calculation of abundance sensitivity Z_{-1}, using the H1/H2 ratio, as well as the other $Z_{\geq +1}$ parameters.

Tests were performed on 2 days in July and November 2001. In July, three ^{233}U solutions yielding a ^{233}U beam intensity over the 25–100 V range and the two ^{232}Th solutions were analyzed. In November, we performed three analyses of a ^{233}U solution with a 140 V signal intensity together with the two ^{238}U solutions. Each analysis consisted of three blocks of

12-scan cycles with a 5-s integration time per cycle. Prior to each block, half-mass zeroes ($+0.5$ and -0.5 amu) were measured for 1 min. Using this protocol, we determined the tail contribution at half-masses (that is to say the $Z_{\pm i.5}$ values) with the same precision as at unit masses.

The results are presented in Tables 2a and 2b and illustrated in Fig. 2. For the ^{233}U tests, we determined all the results ($Z_{-5.5}$ to $Z_{-0.5}$), fixing the abundance sensitivity (Z_{-1}) arbitrarily at 27 ppm. That way, the GEOTOP tail profile could be directly compared with the one determined by Thirlwall in 2001, who measured a mean abundance sensitivity of 27 ppm on the Royal Holloway IsoProbe™ (Thirlwall, 2001). Since then, following repairs to two major leaks in the analyzer, the abundance sensitivity of the Royal Holloway Isoprobe™ has been improved to 8 ppm (Thirlwall, 2002).

For the ^{238}U and ^{232}Th tests, the data were also normalized to the reference value of 27 ppm. In correcting for tail effect on standard and sample data, we used the average results obtained in July and November, except for Z_{+2} and Z_{+3}, for which the half-mass log-mean estimation appears to be better. In fact, for these two parameters, we observed interferences and/or contamination during measurements at unit mass. For the ^{232}Th tests, this can be easily attributed to the presence of ^{235}U traces on H5. For the ^{238}U tests, however, interferences observed on masses 240 and 241 are not explained.

In Tables 2a and 2b, we calculate (1) the theoretical tail correction, expressed in ppm, as generated by linear and exponential interpolations of half-mass zeroes for a mono-isotopic peak, and (2) the differences (Δ) between these corrections and the actual tail contribution. Our results confirm the previous work done by Thirlwall (2001), in that the total contribution for a given peak is significantly lower than the average of half-mass zeroes. However, the tail shape as a whole is not identical to Thirlwall's, especially at -5 and -4 amu. This may be due to the specific methods in which Thirlwall and we determined our profiles.

Table 2a

Tail profile for a mono isotopic uranium peak in the range of -5.5 to -0.5 amu from the central peak, as estimated in this study on the GEOTOP IsoProbe™ instrument

Test/analysis period	Intensity (V)	Tail contribution (ppm) from central peak										
		$Z_{-5.5}$	Z_{-5}	$Z_{-4.5}$	Z_{-4}	$Z_{-3.5}$	Z_{-3}	$Z_{-2.5}$	Z_{-2}	$Z_{-1.5}$	Z_{-1}	$Z_{-0.5}$
Royal Holloway IsoProbe (Thirlwall, 2001)												
^{238}U solution	~ 8	–	–	1.2	2.3	3.5	4.7	6.8	8.5	13.5	27	370
$\pm$ 2S.E.				0.3	0.7	1.0	0.7	0.9	0.6	0.6	1.4	35.8
GEOTOP IsoProbe (this study)												
Test ^{233}U July 2001												
Solution 1	~ 25	1.70	1.77	1.65	2.41	2.36	4.07	4.65	8.41	11.20	27	173
Solution 2	~ 85	1.27	1.48	1.98	2.52	3.06	4.13	5.84	8.46	13.41	27	226
Solution 3	~ 100	1.27	1.59	1.89	2.41	3.02	4.35	5.67	8.70	13.07	27	211
Mean July		1.27	1.53	1.93	2.47	3.04	4.24	5.75	8.58	13.24	27	218
Test ^{233}U November 2001												
Solution 4 Run #1	~ 140	1.39	1.69	1.98	2.46	3.01	4.34	5.24	8.51	12.86	27	326
Solution 4 Run #2	~ 140	1.39	1.71	1.95	2.49	3.08	4.14	5.47	8.40	13.18	27	287
Solution 4 Run #3	~ 140	1.48	1.73	2.04	2.57	3.17	4.15	5.54	8.37	13.35	27	271
Mean November		1.42	1.71	1.99	2.50	3.09	4.21	5.41	8.43	13.13	27	295
Mean study		1.36	1.64	1.97	2.49	3.07	4.22	5.55	8.49	13.17	27	264
$\pm 2\sigma$		0.09	0.11	0.06	0.06	0.06	0.11	0.22	0.13	0.22		47
Half-mass zero mean			1.66		2.52		4.31		9.36		139	
Δ_{mean}			0.02		0.03		0.09		0.88		112	
Half-mass zero log-mean			1.64		2.46		4.13		8.55		59	
$\Delta_{log-mean}$			0.00		-0.03		-0.09		0.06		32	

The tail profile as determined by Thirlwall (2001) on the Royal Holloway IsoProbe™ for ^{238}U, is also given.

The theoretical tail correction (in ppm) for a mono-isotopic peak (estimated by the linear or the exponential interpolation of half-mass zeroes), and the differences (Δ) between these corrections and the effective tail contribution, are calculated.

Table 2b

Tail profile for a mono isotopic uranium peak in the range of $+0.5$ to $+3.5$ amu from the central peak, as estimated in this study on the GEOTOP IsoProbe™ instrument

Test/analysis period	Intensity (V)	Tail contribution (ppm) from central peak								
		Z_{-1}	$Z_{-0.5}$	$Z_{+0.5}$	Z_{+1}	$Z_{+1.5}$	Z_{+2}	$Z_{+2.5}$	Z_{+3}	$Z_{+3.5}$
Royal Holloway IsoProbe (Thirlwall, 2001)										
^{238}U solution	~ 8	27		30.2	12.6	6.6	3.8	2.5	1.3	0.3
± 2S.E.		1.4		3.5	0.8	1.0	0.4	0.6	0.5	0.5
GEOTOP IsoProbe (this study)										
Test ^{232}Th July 2001										
Solution 1	~ 4.1	27	261	35.2	16.9	8.0	5.3	3.1	3.2	0.9
Solution 2	~ 6.7	27	248	33.9	15.0	7.8	5.2	2.6	3.7	0.6
Mean July		27	255	34.6	15.9	7.9	5.2	2.9	3.4	0.7
Test ^{238}U November 2001										
Solution 1	~ 7.4	27	260	32.4	14.2	6.0	6.6	2.7	4.5	2.1
Solution 2	~ 8.4	27	294	35.6	16.4	7.6	7.1	3.3	5.3	2.0
Mean November		27	277	34.0	15.3	6.8	6.9	3.0	4.9	2.1
Mean study		27	266	34.3	15.6	7.3	6.0	2.9	4.2	1.4
± 2σ				1.4	1.3	0.9	1.0	0.3	0.9	0.8
Final values for this study		27		34.3	15.6	7.3	*4.6*	2.9	*2.0*	1.4

The tail profile, as determined by Thirlwall (2001) on the Royal Holloway IsoProbe™ for ^{238}U, is also given.

Values in italic correspond to log-mean estimations. The measured Z_i values for these masses are certainly affected by interferences or contamination.

For exponential tail correction, the difference between the log-mean calculations and the effective contributions is negligible, at -5, -4, -3 and $+3$ amu. However, this exponential interpolation significantly overestimates the real tail contribution near the peak between -2 and $+2$ amu (see Tables 2a and 2b). Thus, for uranium isotopic analysis, the exponential estimation cannot optimize the tail correction
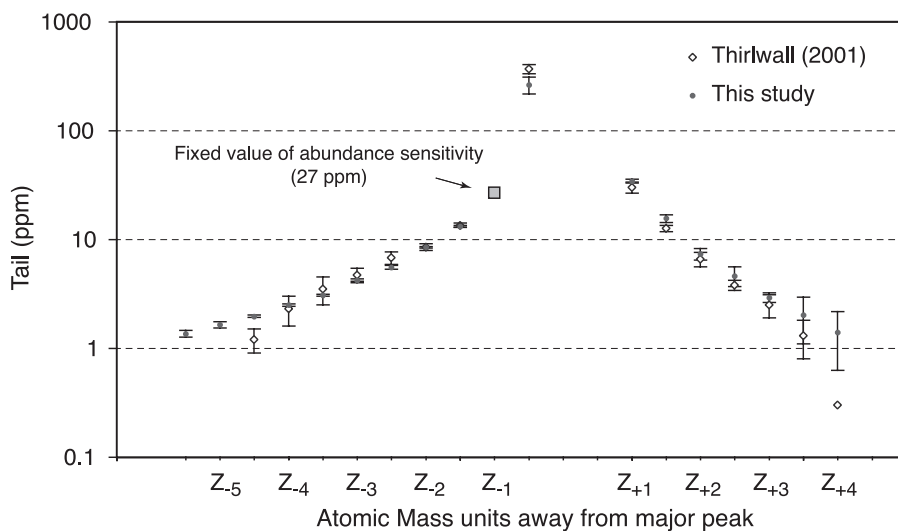

Fig. 2. Tail shape between -5.5 and $+3$ amu, as determined for uranium on the GEOTOP IsoProbe™ instrument (filled circles; data from Tables 2a and 2b). Also reported are the results obtained by Thirlwall (2001) on the Royal Holloway IsoProbe™ instrument (open diamonds). For comparison purposes, the tail profile observed on the GEOTOP instrument was normalized to the average abundance sensitivity value observed on the Royal Holloway IsoProbe™ (27 ppm).

around the major ^{235}U peak. In this mass range, the juxtaposed ^{235}U and ^{238}U tails do not display an exponential shape. This implies that, for our Iso-Probe™ instrument, exponential tail correction onto the ^{236}U beam and onto the ^{234}U beam is inappropriate (see Tables 2a and 2b and Fig. 2).

4.4. Time fluctuation of the abundance sensitivity

During a U isotope analysis, abundance sensitivity can be estimated online by means of intensity monitoring on mass 237 (H5). In fact, considering the dynamic of such an analysis, the tail contribution of the minor peaks integrated onto mass 237 is negligible compared with that of the ^{238}U peak. Since the intensity measured on H5 is essentially associated with the tail contribution of the ^{238}U peak, the proportion of the ^{235}U peak contribution is only of the order of 0.1%, for example (see Table 2b). Therefore, I_{237} provides an online approximation of the abundance sensitivity, via:

$$Z_{-1} = I^{237}/I^{238}_{\text{Estimate}}$$

where $I^{238}_{\text{Estimate}}$ is determined in the same way as in Section 4.2., by means of an average linear discrimination bias, ε.

While estimating abundance sensitivity in this way, we observed variations from 23 to 32 ppm (mean ∼ 25 ppm) in the course of this study. These variations might be due to the irreproducibility of the cup alignment or pressure fluctuation within the analyzer from one day to the next. However, we also observed significant variations in abundance sensitivity in the course of a single day (usually a decrease of a few ppm). This phenomenon cannot be caused by the irreproducibility of the Faraday cup alignment. Fluctuations in the vacuum within the analyzer in the course of the day could account for it. Nevertheless, we are not able to clearly explain such variations at this time.

These abundance sensitivity variations were taken into account for the tail correction. In each analysis, we used the Z_{-1} value determined online, and the Z_i parameters were normalized to this value (see Section 4.3). This way, the daily reproducibility obtained on the HU-1 standard is significantly improved (see Section 6.1) in comparison with the consideration of a daily mean value for the abundance sensitivity. This dem-

onstrates that (i) the interference measured on mass 237 during the OPZ monitoring is constant at the time scale of an analysis (see Section 3.2) and (ii) that its measurement is sufficiently accurate to properly determine the abundance sensitivity and its fluctuations.

4.5. Linearity of the system

An inherent condition for using the tail profile correction method described above is that the system must behave linearly. This means that:

(i) Tail shape is independent of the peak considered. First, we could consider this assumption to be true at a first order over the mass range of the element analyzed (here, 233 to 238). It must be observed that this is not the case over a broader mass spectrum (see for example, the tail shape difference for ^{238}U and ^{209}Bi, as shown by Thirlwall, 2001).

(ii) The tail shape remains independent of the peak height over the range of beam intensities monitored during analysis: a few mV for ^{234}U to 200 V for ^{238}U. It is clear that for uranium isotopic analysis this assumption has to be essentially verified over the entire range of beam intensities of the two largest peaks (^{238}U and ^{235}U) monitored during an analysis, since the tail contributions of the minor peaks (^{233}U, ^{234}U and ^{236}U) are negligible.

The ^{233}U tests carried out to determine the tail shape provide the first clue that the second assumption is true, since the results we obtained over a wide range of ^{233}U signals are reproducible (Tables 2a and 2b).

To obtain further confirmation of this assumption, we analyzed, over a 1-day period, seven unspiked HU-1 solutions over a wide range of intensities. By monitoring the total tail contribution at each half-mass and at U-free unit mass, we were able to test the constancy of tail shape over the mass spectrum of uranium over a period of time (1 day) at different intensities. The results, which are illustrated in Fig. 3, are expressed in the form of (I_{233}/I_{237}), ($I_{233.5}/I_{237}$), ($I_{234.5}/I_{237}$), ($I_{235.5}/I_{237}$), (I_{236}/I_{237}) ratios as a function of the I_{238} intensity, as estimated according to I_{235} intensity. These values represent the total tail contribution of ^{238}U, ^{235}U and ^{234}U peaks at mass (237 − i), normalized to the tail contribution monitored at mass 237. This normaliza-
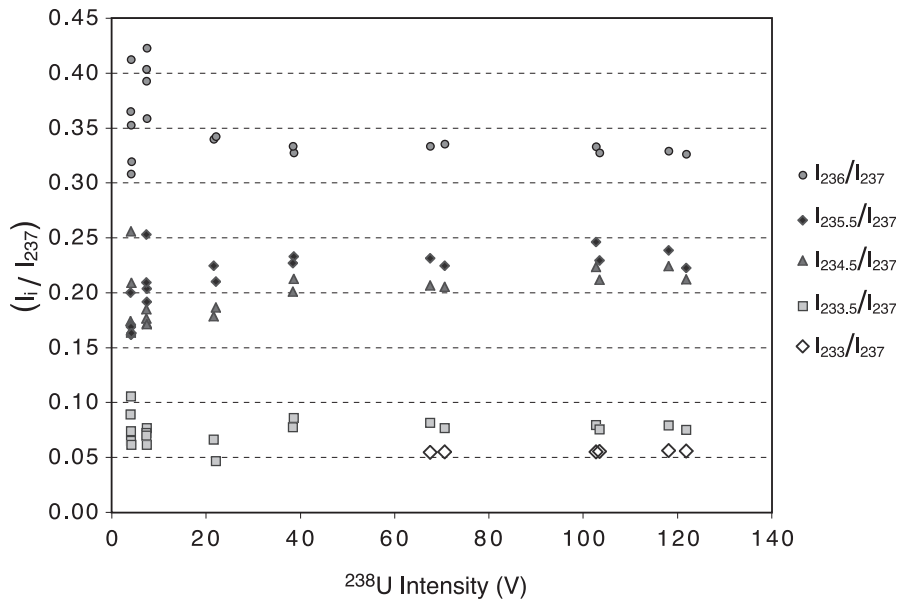
Fig. 3. Linearity of the tailing effect. Total tail contributions at half-mass and at U-free unit mass were monitored during successive analyses of seven unspiked HU-1 solutions covering a wide range of intensities. Results are expressed in the form of (I_{233}/I_{237}), $(I_{233.5}/I_{237})$, $(I_{234.5}/I_{237})$, $(I_{235.5}/I_{237})$, (I_{236}/I_{237}) ratios as a function of I_{238} intensity. The good reproducibility that can be observed for each ratio demonstrates the constancy of the tail shape, in the course of a day, over (1) the mass spectrum of uranium; and (2) different intensity scales.

tion makes it possible to take into account variations in abundance sensitivity observed in the course of the day (see above). The (I_{237-i}/I_{237}) ratios remained constant (see Fig. 3); the greater irreproducibility is observed in analyses carried out at low ^{238}U intensities and is due to the very low intensities monitored at half-masses and at U-free unit masses for these analyses.

These experiments confirm that the integrated tail contribution of ^{238}U, ^{235}U and ^{234}U peaks onto a given mass is constant over a wide range of intensities in the course of a single day. Therefore, if one assumes that tail shape is independent of the peak considered, these tests demonstrate that tail shape, characterized by the (Z_{-i}/Z_{-1}) ratios, is independent of peak height.

5. Correction for mass discrimination

5.1. Spike calibration

The $^{236}U-^{233}U$ double spike used to monitor and correct for mass discrimination was prepared from pure ^{236}U and ^{233}U solutions. To calibrate it, we developed a method similar to that proposed for Pb

double/triple-spike calibration against the NIST SRM-982 reference standard (Hamelin et al., 1985; Galer, 1999). The spike composition is calibrated in reference to natural uranium with the accepted nominal value of 137.88 for the $^{238}U/^{235}U$ ratio (see Cowan and Adler, 1976; Cheng et al., 2000). In practice, we used a solution of the natural uraninite HU-1 in much the same way as NIST SRM-982 is used for Pb double/triple-spike calibration. The true isotopic composition of the spike is determined by considering the mathematical system built by: (i) analysis of the spike alone, and (ii) analysis of a mixed solution of spike and natural uranium (HU-1) (see Hofmann, 1971).

To our knowledge, this approach is new for the U–Th community. In the past, $^{236}U-^{233}U$ double spikes have been calibrated by using a certified reference material, the CRM U-500 (Chen and Wasserburg, 1981; Chen et al., 1986; Edwards et al., 1987; Cheng et al., 2000). In this case, the isotopic composition of the spike is determined by analyzing a mixed solution of the spike and this standard. This provides the absolute $^{236}U/^{233}U$ ratio of the spike, normalized for mass discrimination to the reference $^{238}U/^{235}U$ value of U-500 (Cheng et al., 2000). The abundance of trace

isotopes in the spike (^{234}U, ^{235}U, ^{238}U) is then determined by another analysis (Cheng et al., 2000).

The double-spike calibration method we propose here has certain advantages. First, the precise determination of the $^{236}U/^{233}U$ ratio is done relative to a natural uranium solution (HU-1), which avoids having to take into account the trace impurities contained in standard reference materials such as U-500 (essentially ^{236}U for this standard) and their associated errors. Second, this spike calibration protocol takes into account only the widely accepted and used reference value of natural uranium ($^{238}U/^{235}U = 137.88$). For instance, for mono spike techniques, correction for mass discrimination is performed by normalizing the measured $^{238}U/^{235}U$ ratio against the nominal value of 137.88 (e.g. Bard et al., 1990; Luo et al., 1997; Delanghe et al., 2002; Robinson et al., 2002). For double-spike techniques, the $^{234}U/^{238}U$ ratio is calculated by dividing the calculated $^{234}U/^{235}U$ ratio by the natural $^{238}U/^{235}U$ value of 137.88 when the ^{238}U is not monitored (e.g. Chen et al., 1986; Ludwig et al., 1992; Cheng et al., 2000; Shen et al., 2002 or this study). Since this is the only reference value we take into account throughout our protocol (including spike calibration and analysis procedures), we avoid accumulating systematic errors associated with both the $^{238}U/^{235}U$ of the U-500 standard and the nominal value of natural uranium in determining the total error propagation in a $^{234}U/^{238}U$ analysis. Moreover, we can disregard the error associated with the nominal value of natural uranium as is often done, in practice, with $^{234}U/^{238}U$ isotopic analysis on geological samples.

5.2. Mass discrimination correction models

Unlike in TIMS, the mass discrimination effect in a plasma source can be considered independent of time during the analysis and is characterized by the preferential transport of heavier isotopes of a given element into the mass analyzer. Various mass fractionation laws, namely linear, power and exponential laws, are commonly used to correct for this mass bias. It should be observed that, for the "exponential" law, different mathematical forms are described in the literature. Taylor et al. (1995) have evaluated these three mass discrimination correction models and have shown that, for their Plasma-54 MC-ICP-MS, the power and exponential functions result in the best correction for uranium analysis.
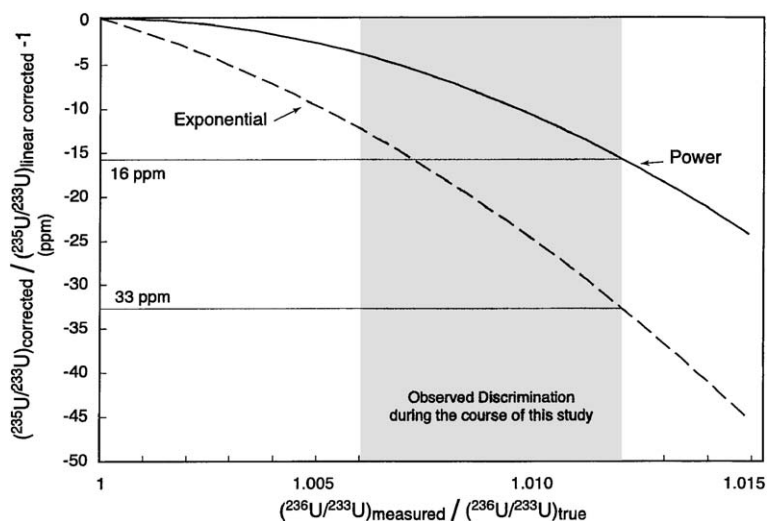

Fig. 4. Simulation of the difference between the "exponential" or the "power" law mass discrimination corrections and the linear law correction for the $^{235}U/^{233}U$ ratio as a function of the measured spike reference ratio ($^{236}U/^{233}U$). The mass discrimination, expressed by the ratio ($^{236}U/^{233}U$)$_{measured}$/($^{236}U/^{233}U$)$_{true}$, varied from 1.006 to 1.012 in the course of this study. Within this range of variation, the error induced on corrected $^{235}U/^{233}U$ ratios does not exceed 33 ppm, irrespective of the mass discrimination law used. This error is insignificant relative to the total error of a $^{234}U/^{238}U$ analysis (~ 1‰).

In our opinion, the linear law corrects with sufficient accuracy at the level of precision we need for our experiments. In fact, in the course of this study, the GEOTOP IsoProbe™ displayed a bias factor of 0.2–0.4% per amu in the mass range of U isotopes. Since this bias is low, unlike the bias observed on the Plasma 54 (~ 1%) by Taylor et al. (1995) (see also Luo et al., 1997), the difference between the linear mass bias correction and the power or exponential corrections is negligible in comparison to the total analytical precision. This is illustrated in Fig. 4, which shows the simulated difference between the exponential and power corrections of the $^{235}U/^{233}U$ ratio relative to the linear correction as a function of the measured reference ratio ($^{236}U/^{233}U$), varying over the mass bias range observed in the course of this study. This difference does not exceed 33 ppm for the $^{235}U/^{233}U$ ratio (Fig. 4) and is of the same order for the $^{234}U/^{233}U$ ratio (not shown).

There are two main advantages in using the linear law. The error-correlation calculations and error propagations in mass discrimination correction are made easier. In the same way, resolution of the double-spike system (Hofmann, 1971; Hamelin et al., 1985; Galer, 1999), as described above for uranium, becomes simpler with the linear mass discrimination model than with any other one.

6. Precision and accuracy

6.1. HU-1 uraninite

The HU-1 uraninite is commonly assumed and used as a secular equilibrium standard (Ludwig et al., 1992). This was recently proved by Cheng et al. (2000) for the $^{238}U–^{234}U$ series. In fact, these authors have shown that this uraninite solution exhibits a $^{234}U/^{238}U$ atomic ratio that is highly consistent with geological materials that were likely to have behaved as closed systems and to have reached the secular equilibrium state. These results enabled Cheng et al. (2000) to precisely re-determine the half-life of ^{234}U. For the remainder of the text, all the results are presented in the form of activity ratios using the ^{234}U half-life value calculated by these authors ($T_{1/2}$ = 245,250 ± 490 years). However, the error associated with this value is not propagated.

The HU-1 uraninite was analyzed according to the method described in Section 3.1. Fig. 1 compares the results of 20 analyses measured over a 3-day period with the results obtained for the same analysis using linear and exponential tail correction (see Section 4.1). Several conclusions can be drawn from this figure.

First, besides having greater analytical precision, our ''tail form correction'' model dramatically improves external reproducibility over the other two tail correction models (~ 1%, 2σ). This significant irreproducibility is due to imprecise measurement of the signal monitored at half-masses. In fact, since the half-mass correction of tail represents up to ~ 4% of the signal measured at mass 234 (for a sample at secular equilibrium), a precise estimate of the baseline is required. This entails a sufficient integration time for these signals. For the analyses presented in Fig. 1, the time acquisition of a half-mass signal consists of 12 scan cycles with a 5-s integration time per cycle. This 1-min integration time is certainly insufficient to measure this signal accurately. Moreover, because the half-mass sequence is monitored before the main analytical sequence, the signal measured at half-mass position is not necessarily representative of the true signal monitored during the main sequence. More particularly, it does not take into account any signal fluctuations that can occur during the analysis. Since the tail correction model we propose obviates the need to measure the half-mass baselines, the external reproducibility obtained by this method is improved to around 0.1% (2σ) for each analysis day (see Fig. 1).

Second, although our procedure improves analytical precision significantly, it systematically induces an offset of ~ 0.3% (see Fig. 1). Although the reasons for this gap are not fully understood, this bias might result from the way we determine the tail shape (see Section 4.3). For this determination, we conserved the Faraday cup alignment, even though they were optimized for uranium isotope analysis (H1: mass 233 to H5: mass 237), and assumed that the tail shape produced by a ^{233}U beam (i.e. Z_i parameters) was equivalent to the tail shape produced by the ^{238}U peak. This assumption may not be completely valid, and may result in a distortion in our tail estimates with respect to the actual tail shape of the ^{238}U peak. Since this model leads to a result lower than the expected value, the estimated tail

Table 3

Comparison between ^{234}U/^{238}U measurements for the NBL-112a standard (formerly NIST NBS-960) on the GEOTOP MicroMass IsoProbe™ MC-ICP-MS and TIMS or ICP-MS compiled values given by other laboratories

Method	Analysis	^{234}U/^{238}U Atomic ratio	δ^{234}U(‰)[a]
MC-ICP-MS			
This study			
Day #1	#1	0.00005287 ± 3	− 36.7 ± 0.6
Day #1	#2	0.00005291 ± 3	− 35.9 ± 0.6
Day #1	#3	0.00005288 ± 3	− 36.5 ± 0.5
Day #1	#4	0.00005287 ± 2	− 36.7 ± 0.4
Day #1	#5	0.00005284 ± 3	− 37.3 ± 0.5
Day #2	#6	0.00005288 ± 3	− 36.5 ± 0.5
Day #2	#7	0.00005291 ± 2	− 35.9 ± 0.4
Day #2	#8	0.00005291 ± 2	− 36.0 ± 0.4
Day #2	#9	0.00005286 ± 2	− 37.0 ± 0.3
Day #2	#10	0.00005290 ± 2	− 36.1 ± 0.3
Day #2	#11	0.00005289 ± 2	− 36.4 ± 0.4
Day #2	#12	0.00005285 ± 3	− 37.1 ± 0.5
Day #2	#13	0.00005289 ± 3	− 36.3 ± 0.5
Day #2	#14	0.00005290 ± 2	− 36.2 ± 0.3
Day #2	#15	0.00005290 ± 3	− 36.2 ± 0.6
Day #3	#16	0.00005292 ± 2	− 35.8 ± 0.5
Day #3	#17	0.00005289 ± 2	− 36.5 ± 0.4
Day #4	#18	0.00005289 ± 2	− 36.4 ± 0.4
Day #4	#19	0.00005289 ± 2	− 36.4 ± 0.4
	Mean (± 2σ, n = 19)	0.00005289 ± 4	− 36.42 ± 0.80 n = 19
	2σ (%)	0.08%	
Luo et al. (1997)	(1)	0.00005286 ± 6	− 36.9 ± 1.1 n = 8
Shen et al. (2002)	(2)	0.00005285 ± 7	− 37.1 ± 1.2 n = 10
Robinson et al. (2002)	(3)	0.00005287 ± 9	− 36.7 ± 1.7 n = 8
TIMS			
Chen et al. (1986) I	(4)	0.00005267 ± 11	− 40.4 ± 2.0 n = 6
Chen et al. (1986) II	(5)	0.00005266 ± 16	− 40.6 ± 2.9 n = 4
Banner et al. (1990)	(6)	0.00005277 ± 10	− 38.6 ± 1.8 n = 4
Stein et al. (1991)	(7)	0.00005267 ± 15	− 40.4 ± 2.7 n = 9
Edwards et al. (1993)	(8)	0.00005285 ± 7	− 37.0 ± 1.2 n = 8
Gariépy et al. (1994)	(9)	0.00005277 ± 13	− 38.6 ± 2.4 n = 12
Stirling et al. (1995)	(10)	0.00005288 ± 9	− 36.6 ± 1.6 n = 6
Bard et al. (1996a,b)	(11)	0.00005288 ± 19	− 36.6 ± 3.5 n = 6

Table 3 (*continued*)

Method	Analysis	^{234}U/^{238}U Atomic ratio	δ^{234}U(‰)[a]
TIMS			
Luo et al. (1997)	(12)	0.00005284 ± 16	− 37.3 ± 2.9 n = 15
Israelson and Wohlfarth (1999)	(13)	0.00005290 ± 31	− 36.2 ± 5.6 n = 7
McCulloch and Esat (2000)	(14)	0.00005277	− 38.6 n = 5
Cheng et al. (2000)	(15)	0.00005286 ± 10	− 36.9 ± 1.7 n = 21
Delanghe et al. (2002)	(16)	0.00005283 ± 10	− 37.6 ± 1.9 n = 33
NBS Certification			
Delanghe et al. (2002)		0.00005290 ± 20	− 36.2 ± 3.6

[a] δ^{234}U=[(^{234}U/^{238}U) − 1] × 1000, where (^{234}U/^{238}U) is the activity ratio. All the δ^{234}U values are calculated using the half-life values given by Cheng et al. (2000).

shape and, more specifically, the most sensitive parameter Z_{-4} are overestimated. Moreover, small variations in the daily mean of HU-1 analyses are observed from day to day (from 0.996 to 0.999). We think that this variation is caused by the irreproducibility of the Faraday cup alignment, especially the H5 cup that monitors mass 237.

To deal with these two problems, we applied a correction coefficient, θ, to the Z_{-4} parameter for each day of analysis. This coefficient, calculated from more than 10 days of analyses, spread over a 6-month period, varies from 0.91 to 0.98, which represents a decrease of 2% to 9% below the expected value of Z_{-4}. This pragmatic approach translates the results so that the daily mean of HU-1 analyses is set to 1 (see Fig. 1).

In practice, we analyzed at least six spiked HU-1 samples per day. This enabled us to determine the θ correction coefficient, which was then applied to the other analyses carried out during the day. This implies that, in much the same way as Robinson et al. (2002) and Shen et al. (2002), the analyses are done with reference to the accepted value of a standard material (here HU-1).

6.2. NBL-112a standard

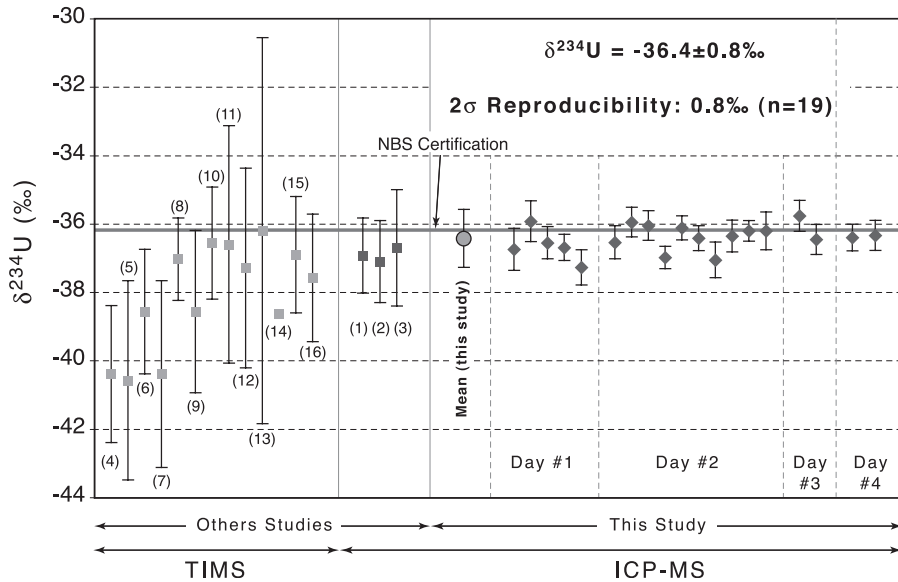The New Brunswick Laboratory Certified Reference Material 112a (NBL-112a standard, also called

Fig. 5. Assessment of the ^{234}U/^{238}U external reproducibility (expressed as δ^{234}U values) with the NBL-112a standard solution (formerly NIST NBS-960). For comparison purposes, previously published results (squares) are also reported. Numbers in brackets refer to the reference column in Table 3. All δ^{234}U values were re-calculated using half-life values from Cheng et al. (2000). Mean δ^{234}U value (present study): -36.42 ± 0.80‰ (2σ, $n = 19$). All error bars refer to 2σ analytical precision. Within-run 2σ analytical precision typically ranges from 0.3‰ to 0.6‰.

CRM-145—formerly NBS SRM-960) was analyzed to assess the validity of our approach. Corrected ^{234}U/^{238}U isotope ratios are listed in Table 3 and shown in Fig. 5. Between 200 and 800 ng of uranium were consumed per analysis. Analyses were performed on 4 different days, with at least 1-week intervals between each day of analysis. The results yield a mean δ^{234}U value of -36.42 ± 0.80‰ (2σ, $n = 19$). This is consistent with values previously reported by other laboratories and determined on MC-ICP-MS, as well as on TIMS (see compiled values in Table 3). Two major conclusions can be drawn from these results. First, the pragmatic approach that consists in applying a correction coefficient θ (estimated from HU-1 analyses) to the Z_{-4} parameter for each day of analysis is validated. Second, these results confirm that the HU-1 and the NBL-112a admitted values are consistent within error, and therefore, that the HU-1 uraninite is indeed in secular equilibrium for the ^{238}U–^{234}U series.

The use of this second standard allows us to assess our external analytical reproducibility, which was 0.8‰ (2σ, $n = 19$) when measured on 4 different days. This is consistent with the error anticipated according to Faraday cup irreproducibility.

6.3. Experiments with natural samples

In order to assess our total long-term reproducibility (chemical and analytical combined) on natural samples, replicated measurements of carbonate samples were performed during the study. Two types of carbonates were analyzed: one coral from the Rendez-Vous Hill, Barbados (5a isotope stage), and a sedimentary carbonate rock core sample taken from a borehole at a depth of 470 m in the Mesozoic sedimentary rocks of the eastern Paris basin. These two kinds of material were chosen because they are representative of two major applications of the U–Th systematics in the Earth sciences, which have a growing need for high precision and accuracy:

(1) Absolute dating of marine carbonates such as corals, used for paleo-sea level studies (Stirling et al., 2001; Gallup et al., 2002) and paleo-reconstitution of (^{234}U/^{238}U) seawater (Henderson, 2002), for instance.

(2) Studies of radionuclide migration in deep geological formations conducted to assess the safety of radioactive waste disposal in such environ-

ments (see, for example, Schwarcz et al., 1982; Smellie and Stuckless, 1985; Gascoyne and Schwarcz, 1986; Smellie et al., 1986; Gascoyne and Cramer, 1987; Ivanovich et al., 1992; Griffault et al., 1993).

The second application is primarily concerned with determining whether a geological system is at secular equilibrium or not. Most of the studies in this field were conducted by means of α-counting techniques. The results obtained by this analytical method generally do not have a precision better than $4-5\%$ (2σ), based on counting statistics. Excluding highly altered and/or fractured zones, this is not accurate enough for host-

Table 4
Replicate δ^{234}U and [U] measurements of two in-house standards on the GEOTOP VG Sector TIMS and MicroMass IsoProbe™ MC-ICP-MS

Method	Sub-sample	^{238}U (ppb)	δ^{234}U (‰)[a]
Rendez-Vous Hill Coral (Barbados)			
TIMS			
GEOTOP	#1	3163.2 ± 15.3	116.2 ± 10.2
	#2	3130.1 ± 18.6	111.1 ± 9.4
	#3	3152.9 ± 15.6	109.7 ± 8.0
	#4	3146.5 ± 18.2	116.7 ± 9.9
	#5	3179.8 ± 17.3	115.3 ± 9.6
	#6	3184.7 ± 13.0	114.3 ± 3.4
	#7	3181.0 ± 14.0	120.6 ± 5.7
	#8	3204.4 ± 14.7	109.9 ± 7.0
	#9	3210.8 ± 16.4	111.8 ± 12.3
	#10	3208.7 ± 8.4	109.5 ± 12.9
	Mean	3194.9 ± 29.1	113.5 ± 7.4
	($\pm 2\sigma$, $n = 10$)		
	2σ (%)	0.91%	0.67%
MC-ICP-MS			
GEOTOP	#1	3209.2 ± 2.9	116.8 ± 0.5
	#2	3205.9 ± 2.4	118.5 ± 0.8
	#3	3204.8 ± 2.4	118.3 ± 0.5
	#4	3207.4 ± 2.4	117.6 ± 0.4
	#5	3201.6 ± 2.4	117.1 ± 0.6
	#6	3211.0 ± 3.3	118.0 ± 0.5
	#7	3200.9 ± 4.6	117.9 ± 0.5
	#8	3203.3 ± 2.4	118.6 ± 0.4
	#9	3220.6 ± 3.1	119.1 ± 0.4
	#10	3216.8 ± 4.9	117.1 ± 0.5
	#11	3202.5 ± 2.4	118.2 ± 0.4
	Mean	3208.1 ± 12.9	117.9 ± 1.4
	($\pm 2\sigma$, $n = 11$)		
	2σ (%)	0.40%	0.13%
Oxford University (Henderson and Robinson, pers. com)			116.9 ± 0.8

Table 4 (*continued*)

Method	Sub-sample	^{238}U (ppb)	δ^{234}U (‰)[a]
Carbonate Rock Sample (HTM-02924 A #1, ANDRA)			
MC-ICP-MS			
	#1	526.7 ± 0.4	9.6 ± 0.8
	#1 bis#	527.0 ± 0.4	10.6 ± 1.0
	#2	524.0 ± 0.5	10.3 ± 0.9
	#2 bis	524.3 ± 0.5	11.2 ± 0.7
	#3	527.9 ± 0.4	9.5 ± 1.0
	#3 bis	528.2 ± 0.4	11.3 ± 0.4
	#4	526.4 ± 0.4	11.5 ± 1.0
	#5	528.4 ± 0.5	9.8 ± 1.3
	#5 bis	528.1 ± 0.5	11.1 ± 0.8
	#6	528.4 ± 0.5	11.0 ± 1.1
	#7	528.0 ± 0.5	9.9 ± 1.2
	#7 bis	527.6 ± 0.5	11.1 ± 1.3
	#8	526.4 ± 0.5	10.6 ± 0.6
	#9	527.7 ± 0.5	10.2 ± 0.7
	Mean	527.1 ± 2.9	10.5 ± 1.4
	($\pm 2\sigma$, $n = 14$)		
	2σ (%)	0.54%	0.13%
	Mean	527.1 ± 2.8	10.3 ± 1.3
	($\pm 2\sigma$, $n = 9$)		
	2σ (%)	0.54%	0.13%

#: The suffix "bis" indicates a duplicated measurement of the sample solution.

[a] δ^{234}U $= [(^{234}$U$/^{238}$U$) - 1] \times 1000$, where (^{234}U$/^{238}$U) is the activity ratio. The δ^{234}U values are calculated using the half-life values given by Cheng et al. (2000).

rock studies, in which disequilibria should not be significant. The application of advanced analytical techniques, such as MC-ICP-MS, should open up new perspectives in this field.

6.3.1. Rendez-Vous Hill coral sample (Barbados)

About 100 g of the coral were finely ground to ensure homogeneity of the sample. The coral sub-samples weighed from 100 to 400 mg. After addition of the ^{236}U–^{233}U spike, the sub-samples were dissolved in HNO_3. U and Th were then co-precipitated with Fe carrier. Finally, the samples were processed through anion exchange columns in order to separate and purify the uranium fraction, using a procedure similar to that reported by Edwards et al. (1987).

We prepared 11 samples over three distinct series. The MC-ICP-MS analyses were performed in the course of 5 days of analysis spread over a 5-month period. The results are listed in Table 4 and presented in Fig. 6. The external reproducibility on this in-house
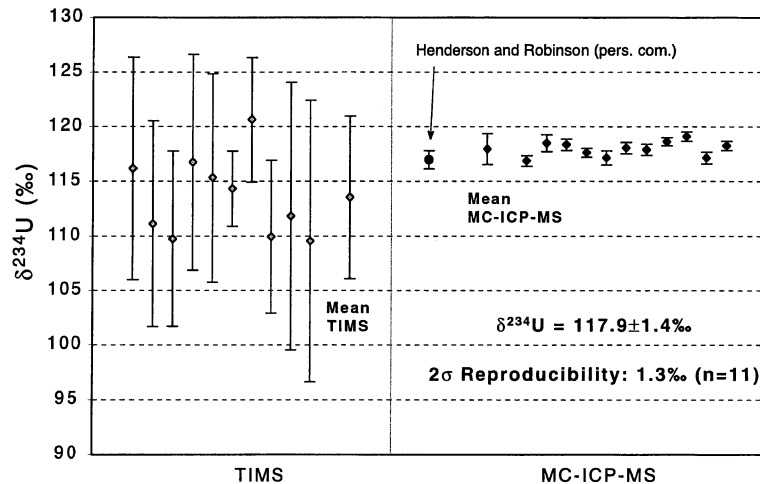
Fig. 6. External reproducibility of the $^{234}U/^{238}U$ ratio (expressed as $\delta^{234}U$ values) determined by replicate analyses of a coral sample (Barbados). Data are listed in Table 4. MC-ICP-MS results are compared with TIMS measurements also obtained at GEOTOP on a VG Sector™ mass spectrometer equipped with a 10-cm electrostatic analyzer and a pulse-counting Daly detector. Also reported is the analysis performed by Henderson and Robinson (pers. com.) on a Nu™ MC-ICP-MS at Oxford University (filled circle). All $\delta^{234}U$ values are calculated using the half-life values determined by Cheng et al. (2000). Error bars represent 2σ analytical precision. The MC-ICP-MS total external reproducibility is estimated to be $\pm 1.3‰$ (2σ, $n = 11$).

standard is 1.3‰ (2σ, $n = 11$) and the results are consistent within error with (i) our TIMS measurements and (ii) an external analysis of this sample carried out by Henderson and Robinson (pers. com.) at Oxford University on a NU™ MC-ICP-MS (see Table 4 and Fig. 6). Moreover, the measurements were taken over a range of ^{234}U intensities from 5 to 22 mV, indicating that the tail contribution can be modelled as a linear system.

6.3.2. Carbonate rock sample

The sedimentary carbonate sample we used here as another in-house standard is part of a study in relation to investigations conducted by ANDRA (Agence nationale pour la gestion des déchets radio-actifs—the French agency for nuclear waste management) into the feasibility of high-level-waste repository in a deep clayey environment. ANDRA is building a scientific Underground Research Laboratory at a depth of 450 m in a deep Jurassic clay layer of the Paris basin (Callovo-Oxfordian argilites). Borehole core samples from the target formation and its bounding limestone formations were analyzed for their uranium content and isotopic composition in order (i) to document the mobility of this element in

such deposits, and (ii) to constrain the time scale of the geological phenomena responsible for an eventual remobilization.

The sample (HTM 02924 A #1) we chose as an internal standard belongs to a transect performed perpendicular to a major sub-horizontal stylolitic joint located in the Bathonian limestone, near the interface with the Callovo-Oxfordian formation (Deschamps et al., 2002). The chemical procedure developed for these types of carbonates is quite different from the usual chemical procedure, as described above, because of the large amount of clay and organic impurities in the matrix. This chemical protocol will be described more precisely elsewhere.

The sample was finely powdered. Nine sub-samples, weighed from 0.8 to 1.9 g, were then chemically prepared over six distinct series. The MC-ICP-MS analyses were performed in the course of 7 days of analysis spread over an 8-month period. The results are listed in Table 4 and illustrated in Fig. 7. The results of some sub-sample solutions that were analyzed twice on 2 different days of analysis are also given. These duplicate measurements are consistent, within error, with previous analyses. Con-
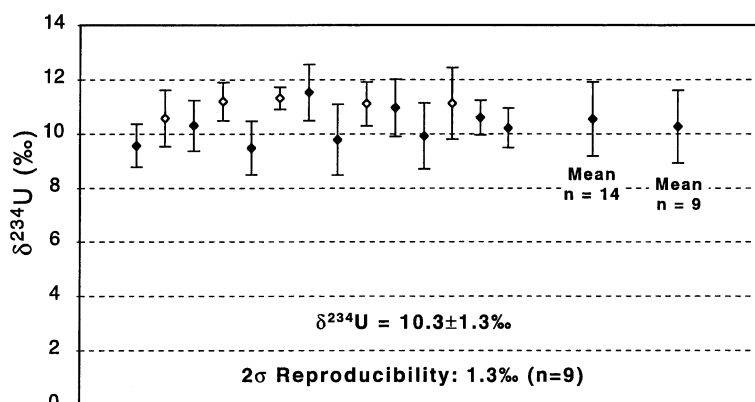
Fig. 7. $\delta^{234}U$ (‰) replicate analyses of the HTM 02924 A #1 carbonate rock sample using the GEOTOP IsoProbe™ instrument. Data are from Table 4. Filled diamonds: single measurements; open diamonds: duplicate measurement of the previous sub-sample solution. $\delta^{234}U$ values are calculated using the half-life values determined by Cheng et al. (2000). Error bars indicate 2σ analytical precision. The total external reproducibility is estimated to be ± 1.3‰ (2σ, $n=9$).

sidering only the first MC-ICP-MS analysis of each sub-sample, the total reproducibility on this internal standard is about 1.3‰ (2σ, $n=9$). This is of the same order as the reproducibility obtained from the coral standard, indicating that the heavy chemical protocol does not induce significant drift in the results.

This sample displays a significant disequilibrium ($\delta^{234}U=+10.3 \pm 1.3$‰), as do all the transect samples (see Deschamps et al., 2002), indicating that U remobilization has occurred in the system within a period of 1 Ma. These results highlight the importance of using highly precise and accurate techniques, such as MC-ICP-MS, as opposed to α-counting spectrometry, in studies on natural radionuclide migration over recent geologic time in host-rock formations.

amu of each peak. This model can be of great relevance to the precise, accurate analysis of isotopic ratios with a wide dynamic range, such as those in the U–Th series, on instruments with relatively poor abundance sensitivity.

Our external analytical precision and reproducibility, as determined on replicate analyses of the NBL-112a standard solution, is 0.8‰ at the 95% confidence level. On natural carbonate samples, the external reproducibility (combined chemical separations plus spectrometric measurements) is about 1.3‰. The technique we developed on the GEOTOP IsoProbe™ is therefore a robust tool for U isotopic studies, especially when very high precision data are required and large amounts of uranium (at least 200 ng) are available, such as in radionuclide migration studies on radioactive waste repository safety.

7. Conclusion

In this paper, we have shown that precise, accurate $^{234}U/^{238}U$ measurements can be achieved using Faraday collectors only. However, the problem caused by the poor abundance sensitivity of the GEOTOP IsoProbe™ instrumentation needed to be fully addressed. The tail correction method we developed enabled us to correct for the large offset observed in the results obtained with the usual linear or exponential interpolation of baseline measurement monitored at ± 0.5

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