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Improved techniques for high accuracy isotope ratio measurements of nuclear materials using thermal ionization mass spectrometry

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Abstract

A set of new techniques with significantly improved accuracy and precision has been developed and qualified for isotope ratio measurements of nuclear material using thermal ionization mass spectrometry (TIMS). First, we have modified the classical total evaporation technique to provide both high precision and high accuracy for a broader range of isotope ratios. This NBL-modified total evaporation technique acquires isotope ratio data until the entire sample is consumed, similar to the classical total evaporation technique, but also corrects the usually low abundances of isotopes such as ^{234}U and ^{236}U for peak tailing contributions originating from the isotope intensities of ^{235}U and ^{238}U. Using the NBL-modified total evaporation technique, we have analyzed a series of NIST/NBL certified reference materials (CRMs) and report new results. For the ^{235}U/^{238}U isotope ratio, the relative standard deviation (RSD) between sample turrets is below 0.01%, based on the analysis of 5–10 samples per sample turret.

As a second new development, the NBL-modified total evaporation technique is combined with a multi-dynamic measurement routine that further improves the accuracy of the ^{234}U/^{238}U and ^{236}U/^{238}U isotope ratio measurements. Multi-dynamic isotope ratio measurements combine the simultaneous detection of multiple isotopes with dynamic cycling of mass in two or more steps. This technique is applied on a new mass spectrometer equipped with a dispersion quadrupole, which for the first time allows the necessary fast switching of the ion beam dispersion during multi-dynamic measurements. The advantage of multi-dynamic compared to static measurements is that the dependence of the isotope ratio results on both the cup efficiencies and the current amplifier gains is eliminated. The result is a higher degree of accuracy for nuclear materials analyses.

The impact of the NBL-modified total evaporation and the multi-dynamic measurement techniques on several recent certification projects at NBL is demonstrated for uranium. These techniques have significantly improved reproducibility and accuracy for nuclear safeguards measurements and certification of nuclear materials. They have the potential to improve precision and accuracy for other mass spectrometric applications as well.

Keywords: Isotope ratios; Total evaporation; Multi-dynamic measurements; TIMS

1. Introduction

Isotopic measurements of uranium are performed on a broad range of samples, including bulk fuel or weapons materials with considerable quantities of actinides [1,2], environmental soils, biota, and water, and individual particles with picograms or less of analyte. The variation of the uranium isotopic composition between different samples as well as the dynamic range of the isotope ratios is large compared to most other elements. The naturally occurring isotopes ^{235}U and ^{238}U are usually considered as the major isotopes, whereas ^{234}U and ^{236}U are called minor isotopes because they are less abundant in most samples by a factor of 10^{-2} to 10^{-10}. The variety of sample compositions and especially the dynamic range of the ratios place considerable demands on the mass spectrometer, in particular, the need for high abundance sensitivity and ionization efficiency, low background and noise, and high linearity and efficiency of detectors.

It is generally recognized that there is no one single type of mass spectrometer that fulfils all of the requirements for measuring all varying sample types and compositions encountered in a laboratory. Accelerator mass spectrometers, for example, have very high abundance sensitivity and low background but low sample throughput and large sample

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requirements, whereas inductively coupled plasma mass spectrometers have high sample throughput, no need for extensive sample preparation and the potential for high precision but demonstrate different characteristics regarding mass bias and interferences. These different instrument types are best viewed as complementing each other in their analytical capabilities.

For certain types of analyses, such as the certification of isotopic reference materials or the age determination of geological samples, state-of-the-art technology presently favors thermal ionization mass spectrometry (TIMS). Sources of uncertainty in TIMS are relatively small and relatively well understood, making the instrument suitable for measurements with high precision and accuracy. But even with a state-of-the-art TIMS instrument, significant effort has to be spent in order to accurately correct for the effect of mass fractionation. Furthermore, the linearity of all detectors such as Faraday cups and secondary electron multipliers (SEMs) have to be checked and, if necessary, empirically corrected. If any kind of multi-detector system is used, inter-calibration procedures have to be developed and performed on a regular basis.

This article introduces a set of two new measurement techniques, designated the NBL-modified total evaporation and the multi-dynamic measurement technique, which were developed in order to improve precision and accuracy for uranium isotope ratio measurements on a state-of-the-art TIMS instrument.

The new methodological developments were accompanied by a series of basic instrumental tests such as linearity tests, amplifier signal decay tests, cup efficiency tests, etc., because measurement procedures can only be validated to provide high precision and accuracy if those tests have been performed. Linearity, efficiency, and amplifier signal decay characteristics of Faraday detectors have a significant influence on the accuracy of isotope ratio data obtained with a isotope mass spectrometer.

All the work described in this article was performed on a new TIMS instrument, the ThermoFinniganMAT Triton, which has been installed at the New Brunswick Laboratory (NBL), U.S. Department of Energy.

Within the following two sections, the two new techniques introduced by this paper, designated as the NBL-modified total evaporation technique and the multi-dynamic measurement technique, will be described.

1.1. The NBL-modified total evaporation technique

The NBL-modified total evaporation technique is a modification of the classical total evaporation technique, which has been previously described in references [3,4]. The basic principle of the classical total evaporation technique is briefly discussed here, followed by a description of the modifications we have developed.

The major challenge to the analyst for achieving high accuracy is the effect of mass dependent fractionation within the ion source of the mass spectrometer. This fractionation effect is best observed and corrected by using the $^{235}U/^{238}U$ ratio of a certified reference material (CRM) which typically has the lowest uncertainty. Additionally, the $^{235}U/^{238}U$ ratio is usually the ratio which can be measured with the highest precision.

Because the lighter isotopes of an element are evaporated from the filament preferentially, all isotope ratios vary or drift during the course of the measurement. During the evaporation, and total consumption of a uranium sample, the $^{235}U/^{238}U$ ratio varies by more than 0.7% relative to the true ratio. This effect is illustrated in Fig. 1. In order to measure this ratio with high accuracy, a reproducibility of about 0.02% or better is needed, which is of about 1/30 of the entire 0.7% range. Thus, an external sample-to-standard comparison to correct for fractionation has to be performed in a very precise and consistent manner.

Fig. 1 shows the fractionation histories of two samples of CRM U500 called TIMS-A and TIMS-B measured on the same TIMS instrument, in which data were collected until the uranium samples were totally evaporated from a rhenium filament. The measured $^{235}U/^{238}U$ ratio on the ordinate is plotted versus the percentage of sample analyzed or consumed on the abscissa, which is correlated with time. Percent of sample analyzed and time would be proportional if the ion currents were exactly constant in time. The experimental curves obtained in TIMS are compared with a theoretical curve, based on mass balance equations for all isotopes and the Rayleigh fractionation factor given by the square root of the mass ratio. In a gas-source mass spectrometer, the theoretical curve is a good approximation of observed behavior, because a gas sample in a large reservoir remains isotopically homogeneous throughout the analysis time. This is certainly not true for a solid sample loaded onto a filament in a TIMS instrument, where the degree of sample homogeneity and mass fractionation depends on the sample temperature and the way it is loaded onto the filament, and furthermore, on the chemical composition of the sample and its possible impurities. As shown by the examples called TIMS-A and TIMS-B in Fig. 1, the fractionation histories of samples in TIMS can vary significantly.

If only a fraction of the total sample evaporation history is measured and evaluated as in a conventional isotope ratio measurement procedure, this fraction has to be equivalent for sample and standard. Both sample and standard must have identical evaporation and fractionation histories in order to achieve an accurate mass fractionation correction. In practice, this is quite difficult to achieve with satisfactory precision. In the worst case, it is possible that repeated measurements of a sample consistently define a TIMS-A fractionation curve, whereas those of the standard look more like TIMS-B. Correction of the measured sample ratios using results of the standard would cause a biased correction for the sample, the difference reflecting the dependence on the way the samples were prepared and analyzed. In our experience, this can lead to significant deviations between

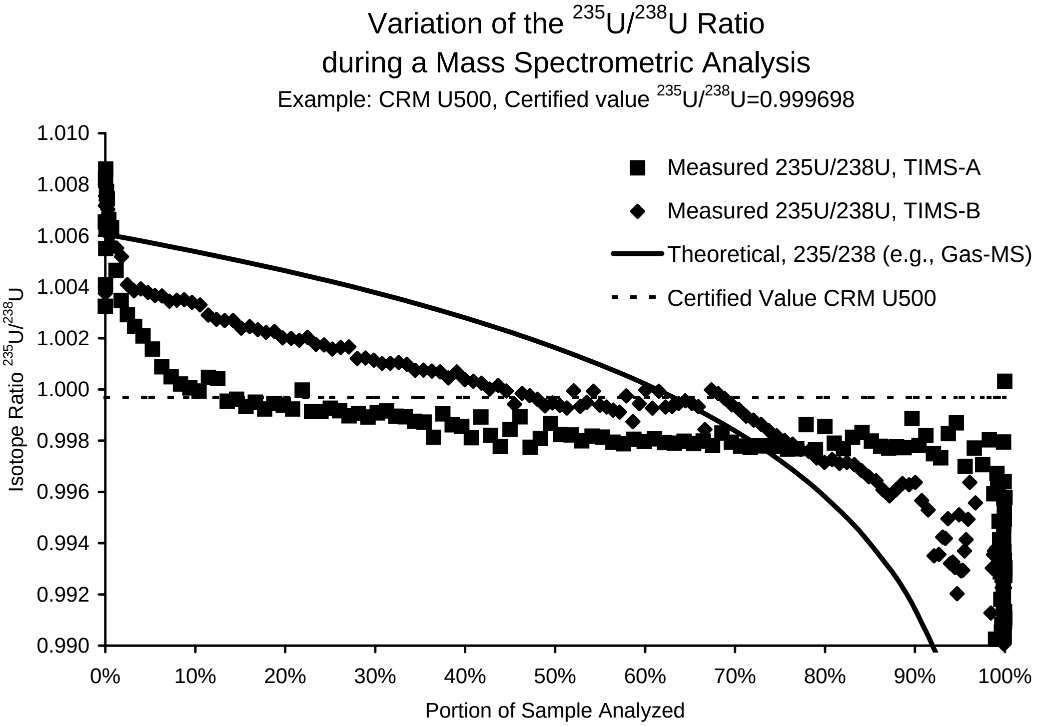

Fig. 1. Drift of the $^{235}U/^{238}U$ ratio during a mass spectrometric analysis of CRM U500, certified value $^{235}U/^{238}U = 0.999698$. TIMS-A and TIMS-B data obtained in total evaporation mode. Theoretical curve based on Rayleigh fractionation law and mass balance.

results obtained by different instrument operators and/or mass spectrometers.

It was determined [3,4] that the total evaporation method, in which the data acquisition is conducted continuously until the entire sample is consumed, is the most precise and reliable technique for major ratio measurements. This technique is considered to be relatively accurate because fractionation corrections are small and thus measurements can be performed without using a CRM as a reference comparator. However, as shown in many analyses of CRMs at our laboratory and at other nuclear facilities, this is not always true. The unavoidable time-dependant drift in the isotope ratios, in combination with simultaneous changes of the ionization efficiency and ion source transmission during the run can cause biases in total evaporation measurements. In measurements of CRMs, residual biases of up to +0.05% from the certified value for the $^{235}U/^{238}U$ ratio have been observed, and may occur with a high reproducibility of 0.02% or better. Isotope ratios measured in total evaporation mode for an unknown sample can be corrected for mass fractionation externally by means of a CRM as a reference comparator as long as it is measured in the same manner and with the same precision. Thus, the combined uncertainty of the corrected ratio would consist of two identical contributions arising from both the sample and comparator measurements. Therefore, the combined uncertainty would be a factor of about square root of two (=ca. 1.41) times the uncertainty of the uncorrected sample measurement, which does not cause a significant increase. The use of a comparator may appear to be a step back towards conventional measurements, because total evaporation measurements were originally expected to be accurate without correction. But the main advantage of the total evaporation method is the ability to achieve high precision for a broader range of sample matrices and sizes compared to conventional measurements, in which only a fraction of the sample life is measured and evaluated.

After reaffirming the advantage of the classical total evaporation versus the conventional measurement technique, the modifications to the classical total evaporation technique will be explained, which provide high accuracy and precision for both the major and minor ratios for the same sample measurement.

In order to analyze as much sample as possible during a classical total evaporation measurement, the integration of isotope intensities is usually performed directly without interruption until the sample is completely evaporated. Typically, only the electronic background is measured briefly at the beginning or the end of a sample run. One downside of this procedure is that the background at the minor isotopes ^{234}U and ^{236}U, generated by the peak tails of the major isotopes ^{235}U and ^{238}U, cannot be corrected accurately during the course of the run. The peak tails are caused by inelastic scattering of ions on their passage through the flight tube of the mass spectrometer. This background depends mainly on the ion beam intensities of the major isotopes ^{235}U and ^{238}U, but also on measurement conditions such as ion source vacuum, analyzer vacuum and ion source focussing, which may change during the course of the measurement run. The

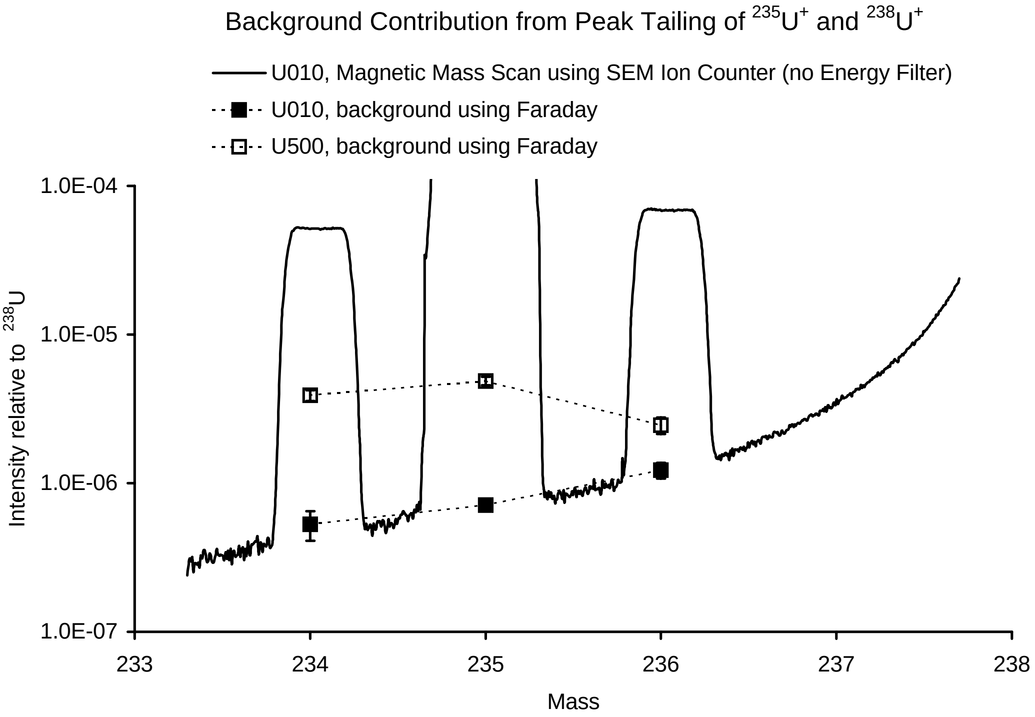

Fig. 2. Background contribution from peak tailing from ^{235}U and ^{238}U.

magnitude of this background at masses ^{234}U and ^{236}U can be significant compared to the true ion beam intensities, as shown in Fig. 2. As an example of this effect, the background of a sample of CRM U010 (234/235/236/238 = $5.5 \times 10^{-5}/1 \times 10^{-2}/6.9 \times 10^{-5}/1$) was measured in two ways. First, a magnetic mass scan was performed with an ion counter (without energy filter) and second, the background was measured using the Faraday multi-collector by switching the beam 0.5 mass units up and down and averaging the measured intensities. The results of both ways agree well, so the background can be accurately measured and corrected for using the Faraday multi-collector during the sample run of CRM U010. For the example shown in Fig. 2, the background intensity for the $^{234}\mathrm{U}/^{238}\mathrm{U}$ ratio is about 5.3×10^{-7}, which is about 1% of the ^{234}U intensity, and for ^{236}U the relative background contribution is almost 2%. The ion current intensities of ^{234}U and ^{236}U are large enough to measure the (uncorrected) $^{234}\mathrm{U}/^{238}\mathrm{U}$ and $^{236}\mathrm{U}/^{238}\mathrm{U}$ ratios with a precision of about 0.1%. This shows that the background contributions are clearly significant in this case and need to be corrected quite accurately. In the case of CRM U500, the pattern of the background contribution is different compared to CRM U010. Although the background to peak intensity ratio is much lower in the case of CRM U500, the background contribution is significant for U500 as well. As a conclusion, the background is sample-specific and should be measured and corrected online (using the sample itself) on a regular basis throughout the sample analysis.

In contrast to the classical total evaporation, for the NBL-modified total evaporation technique the data acquisition is interrupted on a regular time interval in order to perform background measurements. We have created an inter-block heating program (block = sequence of 10 mass cycles, duration ca. 10 min) to control all filament heating actions during the entire data acquisition process. Within the first few blocks the evaporation filament is heated on a block-by-block basis until the desired target intensity is reached, followed by inter-block heating until the sample is completely evaporated. Using this NBL-modified total evaporation technique, the $^{235}\mathrm{U}/^{238}\mathrm{U}$ ratio is evaluated by integrating the individual intensities for the entire measurement, as is done in any total evaporation measurement:

$$\left(\frac{^{235}\mathrm{U}}{^{238}\mathrm{U}}\right)_{\text{NBL-MOD TE}} = \frac{\sum_{\text{cycles}} {}^{235}\mathrm{U}}{\sum_{\text{cycles}} {}^{238}\mathrm{U}} = \frac{\sum_{\text{cycles}} ({}^{235}\mathrm{U}/{}^{238}\mathrm{U})_{\text{measured}} {}^{238}\mathrm{U}}{\sum_{\text{cycles}} {}^{238}\mathrm{U}}$$

Because of the discontinuous nature of the data acquisition using the NBL-modified total evaporation technique and due to observation of bias even using the classical total evaporation techniques, it is necessary to apply an external calibration using measurements from CRMs analyzed in a manner analogous to the samples.

In order to determine the advantage using the NBL-modified total evaporation technique compared to conventional analyses, every measurement performed by the NBL-modified total evaporation technique can be evaluated in the conventional manner by averaging the measured $^{235}\mathrm{U}/^{238}\mathrm{U}$ ratios for only part of the measurement time. The first two blocks of the NBL-modified total evaporation measurement represent the initial heating prior to a conventional non-total evaporation procedure, and therefore the data evaluation is started at block 3 and terminated after a fixed number of subsequent blocks, e.g., after 5 or 10 blocks. Measurements of the $^{235}U/^{238}U$ ratio for both the modified total evaporation and the conventional evaluation of the same samples are compared with regard to precision and accuracy in the Section 3.

Similarly to conventional analyses, in the NBL-modified total evaporation technique, the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios are usually measured in static mode (or multi-dynamic mode, see next section) using a Faraday multi-collector, simultaneously with measurement of the $^{235}U/^{238}U$ ratio. But in contrast, minor ratio data are evaluated only for those blocks where the intensity is sufficient for reasonable precision (e.g., at an intensity of at least 33% of the desired target intensity), which usually applies to all blocks from block 3 until the last block just before the intensity is declining rapidly.

If the $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios are not evaluated for the entire duration of the measurement then they are not evaluated for the same portion of the sample life as the major ratio. Thus, the mean for the $^{234}U/^{235}U$ ratio does not represent the same portion of the sample evaporation history as the mean for the $^{235}U/^{238}U$ ratio, and consequently the mean $^{234}U/^{235}U$ must not be corrected using the mean $^{235}U/^{238}U$. Consequently, the minor ratios can only be corrected *internally* using the “true” externally corrected $^{235}U/^{238}U$ ratio of the sample. For multi-dynamic measurements (see next section), the internal mass fractionation correction is already incorporated in the multi-dynamic algorithms.

The minor isotopes are corrected for background contributions from the major isotopes for each mass cycle. This is achieved by measuring background intensities at masses 233.5, 234.5, 235.5, and 236.5 and subtracting the average background calculated for masses 234 and 236 from the raw peak intensities at 234 and 236. Additionally, peak-centering, electronic baseline measurements and ion beam re-focussing actions are performed between blocks.

1.2. The multi-dynamic measurement technique

The multi-dynamic measurement technique provides improvements in accuracy by mitigating bias associated with detectors and electronics. A brief description of several sources of bias is provided, followed by a discussion of some benefits provided by multi-dynamic measurements.

A comprehensive analysis of significant sources of bias is important for a complete statement of uncertainties associated with a measurement. The sources of bias depend on the isotope ratio techniques, which in turn depend on the dynamic range of the ratio. Depending on the dynamic range of the isotope ratio to be measured, one or more different types of detectors may be required to detect extremely different sizes of ion currents in one experiment. For ratios from 10^{-4} to 10^{-10}, a combination of an SEM detector for the low abundance isotopes and a Faraday cup detector for the more abundant isotopes is used [5,6]. The precision and accuracy of this method is usually limited to 0.1–0.2% by uncertainty contributions arising from various sources, such as the detector inter-calibration between the SEM and the Faraday cup, the dead-time loss of the SEM counting system, the linearity correction required for the SEM [7] and counting statistics.

For ratios between $\sim 1 \times 10^{-4}$ and 1, the use of Faraday cups operated in peak-jumping mode or even a Faraday multi-collector array operated in static mode is usually preferred. But this type of measurement is also associated with several small sources of uncertainty, such as linearity of the Faraday amplifiers, cup efficiencies, and current amplifier gains [8,9]. These parameters can significantly influence the accuracy of a TIMS measurement, and certain measurement procedures are inherently more accurate than others. Measurement procedures have to be designed to minimize the influence of parameters that cause bias. For instance, the overall detector efficiency, which can be defined as the product of the cup efficiency factor and the gain factor of the current amplifier attached to each Faraday cup, are the most common parameters that cause bias in static isotope ratio measurements [8,9].

First, the cup efficiencies can change over a period of time by frequent application of high ion currents to the cups [8]. Cups are particularly influenced by frequent implantation of alkali ions such as Cs, Na, and K. Cup efficiency factors have been shown to depend on both the element analyzed and the experimental conditions [9], although they may also vary with respect to cup geometry, coating material, etc.

Second, the current amplifiers are usually inter-calibrated by applying a constant current sequentially to all current amplifiers of the multi-collector array. The stability of the current amplifier gains with time depends on the temperature stability of their environment and the quality of the electronic components.

If cup efficiencies and current amplifier gains are being determined experimentally ([8,9] and this study), the precision is usually about 0.005% for the cup efficiencies and about 0.0005% for the current amplifier gains.

One known way to overcome biases or uncertainties in cup efficiencies and current amplifier gains simultaneously is by the use of a multi-dynamic measurement technique. It was first used for precise Nd and Sr isotope ratio measurements for various geo-chemical and cosmo-chemical applications, based on algorithms such as those given in [10]. When all isotopes of interest are detected simultaneously by Faraday cups in each step of a dynamic mass cycle, the isotope ratios can be calculated in a way that cancels out detector efficiency differences. Mathematically, the procedure requires a priori knowledge of one isotope ratio, which is used to normalize for both the mass dependent fractionation and the detector efficiencies at the same time. In the case of uranium, the major $^{235}U/^{238}U$ ratio would be most suitable for this purpose, because it can be measured accurately using the NBL-modified total evaporation technique.

In general, multi-dynamic isotope ratio measurements should be possible for many elements, as long as ion beams are properly aligned within the centers of their respective Faraday cups. During a multi-dynamic analysis, the switching from one isotope mass step to another results in a slight change in ion beam dispersion. It is possible for some ion beams to strike off-center, causing slight biases in the detection efficiencies, depending on the change in dispersion and the mass difference to the center cup mass.

In principle, the change in dispersion could be compensated by moving the cups for each mass step. A much more practical way to achieve the necessary change in dispersion within a fraction of a second is with the use of a dispersion quadrupole located between the magnet and the multi-collector. It enables a fast change in dispersion as required for multi-dynamic measurements with fixed cup positions.

One new approach for alleviating bias due to the dependency of isotope ratios on the current amplifier gains, but not the cup efficiencies, is through the use of a "virtual amplifier." The "virtual amplifier" rotates the connection between Faraday cups and current amplifiers ("amplifier rotation"). In this case, the presence of a biased gain value in one of the amplifiers would not effect the average isotope ratios, because this biased gain value is being used in the numerator in one block of the measurement and in the denominator in another block and is therefore cancelled in the overall average.

In order to test the multi-dynamic technique, a ThermoFinnigan MAT Triton multi-collector TIMS equipped with a dispersion lens was used. First, a series of static and multi-dynamic neodymium isotope ratio measurements was performed. The (non-nuclear) element Nd was chosen for this purpose because it is an excellent element for testing the instrument at the ppm level of stability and precision and because the ^{146}Nd/^{144}Nd ratio is considered to be constant ($^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$), allowing other neodymium isotope ratios to be internally normalized.

The following three procedures have been used and compared to each other for neodymium isotope ratio measurements:

1. Nd multi-dynamic: This is the most accurate procedure, because it eliminates the dependence on both the current amplifier gains and the cup efficiencies (for algorithms, see [10]). The ability to adjust dispersion during the multi-dynamic mass cycle is an advantage.
2. Nd static: This is a conventional static neodymium procedure requiring the gains of the Faraday current amplifiers to be measured prior to each measurement.
3. Nd static amplifier rotation: This is a static neodymium procedure using the "virtual amplifier," in which the Faraday current amplifiers are switched cyclically to all Faraday cups, thus eliminating the dependence of the results on the current amplifier gains only.

Table 1
Standard multi-dynamic mass cycle, consisting of 5 mass steps

Step	Amplifier (cup)						
	2 (L3)	3 (L2)	4 (L1)	5 (C)	6 (H1)	7 (H2)	8 (H3)
1				234	235	236	
2			234	235	236		238
3		234	235	236		238	
4	234	235	236		238		
5		233.5	234.5	235.5	236.5	237.5	238.5

The integration and idle times are 8 s for each line. Step 5 is the background measurement step.

Neodymium isotope ratios can be measured very reproducibly due to the internal normalization, but unfortunately the measurements cannot be considered accurate due to the lack of certified Nd reference materials for use as comparators. This is not the case for uranium, where various gravimetrically prepared CRM's have been produced to provide accuracy assessment and traceability to SI. For the determination of minor uranium ratios, even well-established multi-collector and ion counting methods can generate systematic biases due to cup efficiencies, current amplifier gains, non-linearity effects in ion counters, etc. In order to overcome the two most significant sources of inaccuracy in the case of static multi-collector measurements, namely cup efficiencies and current amplifier gains, we adapted the multi-dynamic procedure to measure the ^{234}U/^{235}U and ^{236}U/^{235}U isotope ratios.

As in the case of neodymium, multi-dynamic uranium measurements require the accurate knowledge of one isotope ratio for normalization of cup efficiencies as well as mass dependent fractionation. Using an accurately known and previously determined ^{238}U/^{235}U ratio, a multi-dynamic uranium measurement has the potential of transferring the level of accuracy and traceability from the ^{238}U/^{235}U ratio to the ^{234}U/^{235}U and ^{236}U/^{235}U isotope ratios.

Table 1 shows the mass cycle for uranium isotopes in a multi-dynamic Faraday detector measurement. The positions of the moveable cups are adjusted relative to ^{235}U in the center Faraday cup in mass step 2. When another uranium isotope is switched into the center Faraday cup, a dispersion quadrupole was used to slightly change the ion beam dispersion in a way that the ion beams of all isotopes are centered simultaneously within their respective Faraday cups. Each mass cycle of the multi-dynamic procedure requires a unique setting of the dispersion quadrupole voltage.

The mathematical algorithms for multi-dynamic uranium measurements, reflecting the mass cycle shown in Table 1, are given as follows.

Using the definitions of $R(234/235)_n$ and $R(238/235)_n =$ ratios ^{234}U/^{235}U and ^{238}U/^{235}U, respectively, measured in line n (see Table 1), and $R(238/235)_n =$ true ("normalizing") ratio ^{238}U/^{235}U, obtained using the NBL-modified total evaporation technique, the result for the

Table 2
Modified multi-dynamic mass cycle to minimize amplifier memory

Step	Amplifier (cup)						
	2 (L3)	3 (L2)	4 (L1)	5 (C)	6 (H1)	7 (H2)	8 (H3)
2			234	235	236		238
4	234	235	236		238		
5		233.5	234.5	235.5	236.5	237.5	238.5
1				234	235	236	
3		234	235	236		238	

Integration time: 8 s for steps 1–4, 32 s for step 5. Idle time: 25 s prior to step 1, 8 s prior to steps 2, 3, and 4. The idle time prior to the background measurement step 5 is 32 s in order to avoid decay contributions of previous step 4 to the background measurement.

multi-dynamic ratio $R(234/235)_n$ is given by

$$R\left(\frac{234}{235}\right)_n = \sqrt[3]{\frac{R(234/235)_1 R(234/235)_2 R(234/235)_3 R(238/235)_4}{R(238/235)_n}}$$

which includes the linear fractionation correction. At the level of precision achieved for minor uranium isotope ratios (>0.002% RSD), no significant difference was observed between the different types of fractionation corrections, e.g., linear, Rayleigh law, exponential, power law, etc.

The multi-dynamic $^{236}\mathrm{U}/^{235}\mathrm{U}$ ratio is given by

$$R\left(\frac{236}{235}\right)_n = \sqrt[3]{\frac{R(236/235)_1 R(236/235)_2 R(236/235)_3 R(238/235)_n}{R(238/235)_3}}$$

using $R(238/235)_3$ in place of $R(238/235)_4$. While cup efficiencies and amplifier gains are mathematically eliminated for the minor ratios, they are not eliminated for the measurement of the $^{238}\mathrm{U}/^{235}\mathrm{U}$ ratio. If the $^{238}\mathrm{U}/^{235}\mathrm{U}$ ratio is not known from previous measurements, the bias on this ratio can be minimized by using a certified reference comparator.

To express $^{238}\mathrm{U}$ as the denominator isotope, the calculated multi-dynamic results for $R(^{234}\mathrm{U}/^{235}\mathrm{U})_n$ and $R(^{236}\mathrm{U}/^{235}\mathrm{U})_n$ are divided by the true (or corrected) value of the normalizing ratio $R(^{238}\mathrm{U}/^{235}\mathrm{U})_n$.

For multi-dynamic measurements, the time sequence of mass steps within the mass cycle has to be adjusted to minimize amplifier memory and thereby avoid mutual interferences between isotopes detected sequentially in the same cup. Faraday current amplifiers must be able to dissipate large signal intensities prior to measuring a much smaller signal. This is critical when elements with large differences in their isotope abundances are analyzed. An example for uranium is shown in Table 2. The idle times between the individual lines 1–4 are chosen as a function of ion beam intensities. However, a signal decay test should be performed on all current amplifiers to optimize the amplifier time-decay.

In addition, a linearity test can be performed using NBL CRM U500 or IRMM-072 series to establish the accuracy of minor ratio measurements for a large range of ion current intensities.

2. Experimental

For all measurements performed in this work, degassed zone-refined Re filaments were used. All uranium samples were loaded by drying a few microliters of $UO_2(NO_3)_2$ solution containing 1 μg/μl uranium on the evaporation filament. The typical sample loading amount was 5–10 μg. Isotope ratio measurements were performed on a Triton and a MAT261 TIMS manufactured by ThermoFinnigan MAT.

The Triton TIMS at NBL is equipped with a multi-collector with nine Faraday cups and one ion counter. The ion counter is combined with a RPQ retardation filter to improve the abundance sensitivity to about 10 ppb at mass 237. Construction details about the Triton TIMS can be found on the manufacturer's internet page (www.thermofinniganmat.de).

3. Results

3.1. $^{235}\mathrm{U}/^{238}\mathrm{U}$ data using the NBL-modified total evaporation technique

In order to test the NBL-modified total evaporation technique, a variety of NBL CRMs were analyzed, including U005A, U010, U030A, U050, U100, U200, U500, U750, and U900. Figs. 3 and 4 show the performance of the NBL-modified total evaporation technique using the Triton TIMS in comparison with the classical total evaporation method using the MAT261 TIMS at NBL.

Fig. 3 shows the relative deviation of measured $^{235}\mathrm{U}/^{238}\mathrm{U}$ ratios for nine CRMs, all normalized to U500 as the reference comparator. CRM U500 was chosen because it is considered to have one of the best known $^{235}\mathrm{U}/^{238}\mathrm{U}$ values. For both the Triton and the MAT261 TIMS, the RSD of $^{235}\mathrm{U}/^{238}\mathrm{U}$ ratios between individual samples on the same turret is about 0.015–0.030%, while the RSD between averages of sample turrets is better than 0.01%, based on the analysis of 5–10 samples per turret.

The results displayed in Fig. 3 show that the measured $^{235}\mathrm{U}/^{238}\mathrm{U}$ ratios of all analyzed reference materials are well within the 95% confidence interval derived from the certificates. However, if only the precision of the measurement is considered for the uncertainty, significant deviations from the certified $^{235}\mathrm{U}/^{238}\mathrm{U}$ ratios appear for some of the NIST/NBL series materials. We observed a deviation of about −0.05% for CRM U050, about −0.02% for U010, and about +0.035% for U005A. These deviations were found independently using both the NBL-modified total evaporation technique on the Triton and the classical total evaporation technique on the MAT261.

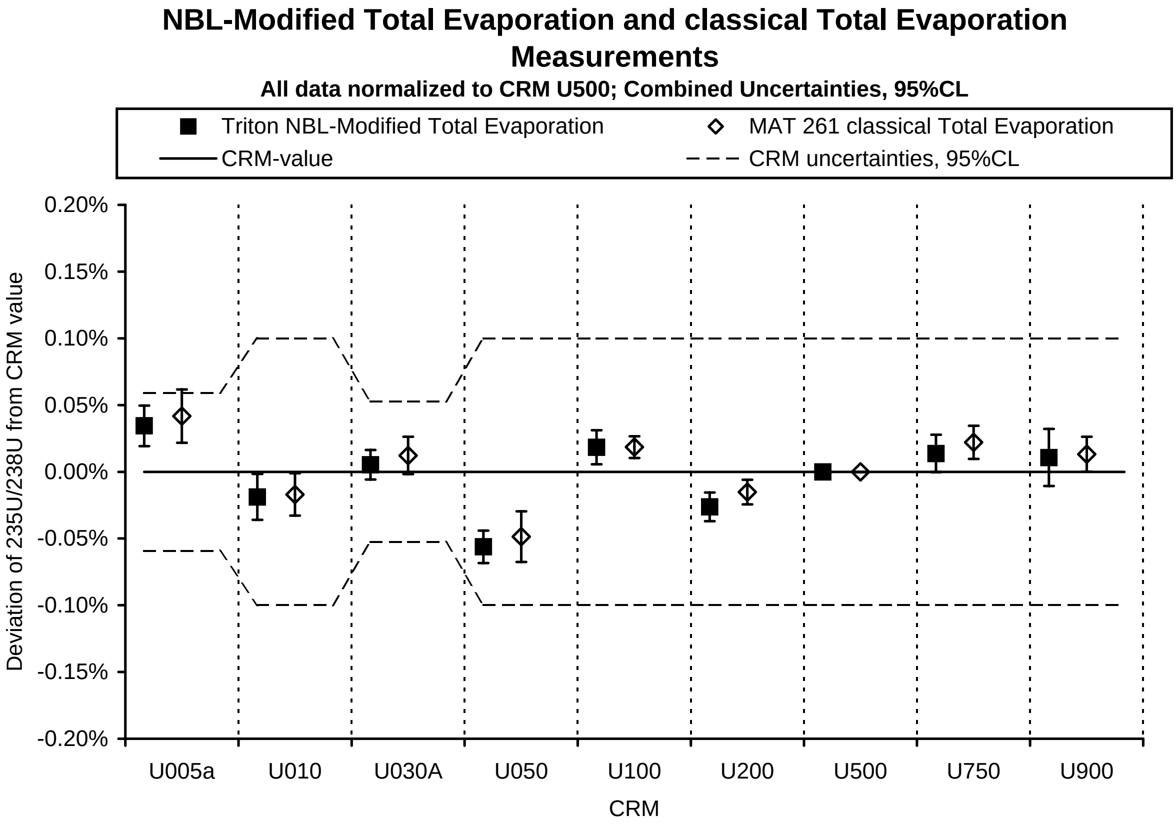

Fig. 3. Deviation of $^{235}U/^{238}U$ ratios for various CRMs measured using the NBL-modified total evaporation technique on the Triton and the classical total evaporation technique on a MAT261. All data are corrected using CRM U500 as comparator.

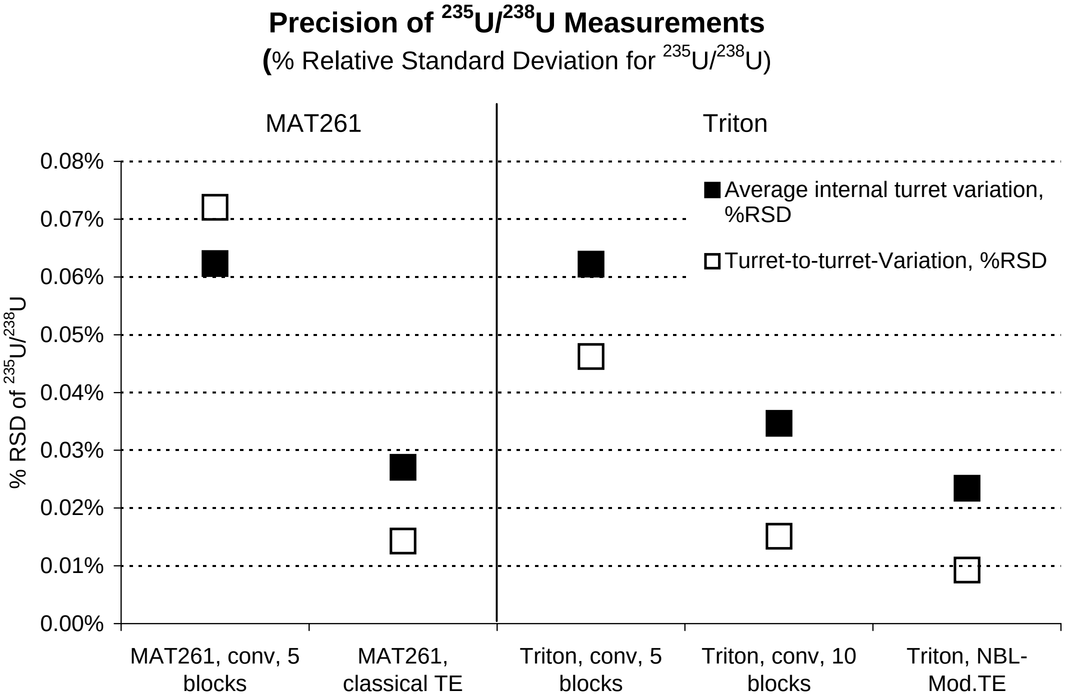

Fig. 4. Precision of measurements for CRM U050 using U030A as reference comparator. Results using the NBL-modified total evaporation technique are compared with conventional evaluation of the same samples (5 and 10 blocks), and with conventional data (5 blocks) and classical total evaporation data acquired on the MAT261.

Table 3
Results for major $^{235}U/^{238}U$ isotope ratio measurements of various NIST/NBL CRMs

CRM	$^{235}U/^{238}U$ CRM value	$^{235}U/^{238}U$ measured	Uncertainty (95% CL)	Relative uncertainty (95% CL)	Combined relative uncertainty[a] (95% CL)
U005A	0.00509001	0.00509194	0.00000065	0.013	0.101
U010	0.0101400	0.0101382	0.0000012	0.012	0.101
U030A	0.0313666	0.0313692	0.0000028	0.009	0.100
U050	0.0527841	0.0527564	0.0000060	0.011	0.101
U100	0.1135960	0.1136169	0.000014	0.013	0.101
U200	0.251259	0.2511930	0.000027	0.011	0.101
U500	0.999698				
U750	3.16613	3.16670	0.00030	0.009	0.100
U900	10.3757	10.3769	0.0013	0.013	0.101

Shown are results obtained using the NBL-modified total evaporation technique on the Triton. All measurements are reported relative to CRM U500 as the reference comparator.

[a] The combined relative uncertainty includes the uncertainty of the $^{235}U/^{238}U$ ratio of CRM U500 used as reference comparator.

Therefore, both instruments consistently record similar deviations.

In Table 3, the deviations of the measured ratios from the certified values are given for each of the CRM materials using the NBL-modified total evaporation technique. The data are based on a new set of measurements with significantly improved precision for some widely used NIST/NBL series materials. Uncertainty statements for these measurements also incorporate the large contribution of the reference comparator ($^{235}U/^{238}U$ for U500, known with an uncertainty of 0.1% based on a 95% confidence level). The new measurements show minor differences in the $^{235}U/^{238}U$ ratios compared to certified values for some materials. Several of these were certified more than 25 years ago, and demonstrate the need for more accurately certified nuclear reference materials. This work is in progress.

Fig. 4 shows that the NBL-modified total evaporation technique yields better precision than the classical total evaporation or the conventional measurement techniques. Data from the Triton are of CRM U050 using CRM U030A as reference comparator. The precision (%RSD) of total evaporation results is compared with the precision of conventional measurements of either 5 or 10 blocks of data. Also shown in Fig. 4 are conventional measurements using 5 blocks of data and the classical total evaporation measurements on the MAT261.

Measurements using the NBL-modified total evaporation technique on the Triton and the classical total evaporation technique on the MAT261 provide the best performance. The conventional method takes into account only a fraction of the sample evaporation history and is therefore less reproducible.

The average internal turret variation for the NBL-modified total evaporation technique is typically about 0.02% RSD. This is similar to classical total evaporation measurements as described in the literature [3,4]. Turret-to-turret variations are very low using this method, exhibiting RSDs of turret averages of about 0.01% or less.

The development of the new NBL-modified total evaporation technique has already provided a significant impact on two recent certifications of reference materials (CRM) at NBL:

First, CRM U630 (^{235}U isotopic abundance ca. 63%) was analyzed by classical total evaporation on a MAT261 and by NBL-modified total evaporation on the Triton, using both CRM U500 and U750 as reference comparators. The agreement between the results of the two instruments and methods is given by an overall standard deviation of 0.005%.

As a second example, CRMs 113B and U045 (^{235}U isotopic abundance ca. 4.5%), two reference materials with identical isotopic compositions but different chemical form, were measured and certified. These materials were analyzed by classical total evaporation on a MAT261 and by NBL-modified total evaporation on the Triton, using CRM U030A as comparator. CRM 113b, a UF_6 material, was additionally measured on a MAT281 gas mass spectrometer by the double standard method. TIMS analyses yield a RSD of about 0.003%, and if the MAT281 gas UF_6 results are included, the overall standard deviation is about 0.004%.

The agreement between the two methods and instruments for these two examples confirms the reliability of the new NBL-modified total evaporation technique for certification measurements. The average for a series of several turrets has uncertainties in the 0.003–0.005% range, which is about 10 times better than the uncertainties of the current NIST/NBL series of reference materials which were used as comparators. The improved level of precision and accuracy may also allow a better distinction between natural samples of different geological origin. Measurements are under way.

The main advantage of the modified compared to the classical total evaporation technique is observed in the results for the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios. Fig. 5 compares the results for the $^{236}U/^{238}U$ ratio of CRM 113b measured in three different ways: by classical total evaporation and by conventional static mode for both the Triton and the MAT261, and additionally using the NBL-modified total evaporation technique for the Triton. These results have been corrected by normalizing the measured major ratio to the known certified value.

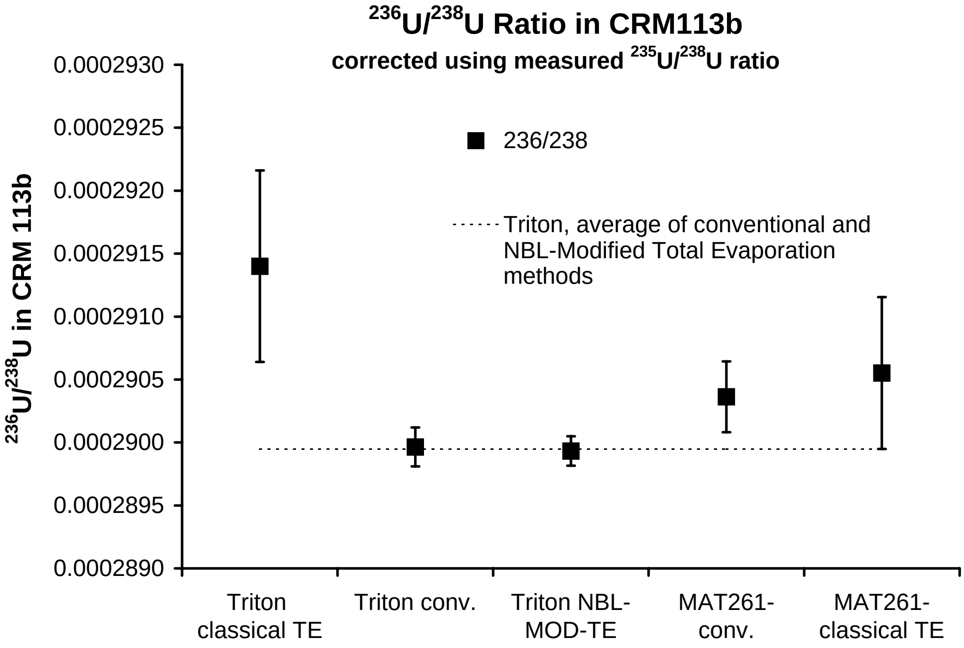

Fig. 5. Comparison of $^{236}U/^{235}U$ data for CRM 113b using different methods and instruments. The deviation of the results using classical total evaporation on both the Triton and the MAT261 is due to the lack of background correction. The error bars (1σ, 68% CL) do not include the comparator uncertainties.

The Triton results in conventional and NBL-modified total evaporation mode yield the most precise data (0.05% RSD) and agree very well with each other. In comparison, the results in classical total evaporation on both instruments, and also the conventional data on the MAT261, yield significantly higher $^{236}U/^{238}U$ values and show poorer precision. This is due mainly to the lack of a proper background correction. This comparison demonstrates the importance of proper background correction for the minor ratios and confirms the advantage of the NBL-modified total evaporation technique compared to classical total evaporation.

For both the classical total evaporation and the NBL-modified total evaporation technique, reference comparators were used to correct a residual bias of about 0.04–0.06% for the $^{235}U/^{238}U$ ratio due to mass fractionation effects. The overall uncertainty includes contributions from the measurement of sample and comparator and also from the certified uncertainty value of the comparator. The latter dominates the uncertainty budget, as shown in Table 4 for one turret of analyses. Further improvement in the precision of the measured $^{235}U/^{238}U$ will not reduce the overall uncertainty when the certified uncertainty value of the comparator is large.

Table 4
Uncertainty budget for CRM U630 measurements of $^{235}U/^{238}U$ using the NBL-modified total evaporation technique

Quantity	Standard uncertainty (%)	Relative contribution to combined uncertainty (%)
Reference comparator, certified value	0.050	91.7
Reference comparator, measured value	0.009	2.8
Sample, measured	0.011	4.6
Cup efficiency factor	<0.005	0.9
Linearity factor	<0.002	0.1

In order to remove this dominant contribution from the certified uncertainty value of the comparator, the residual bias of a measurement has to be effectively removed. Due to the flexibility of the NBL-modified total evaporation technique, it is possible to adjust the sample heating and evaporation process to avoid vigorous evaporation of the sample near the end of the measurement. By limiting temperature changes between subsequent measurement blocks, the residual deviation diminished below 0.01% for CRM U500. Although the $^{235}U/^{238}U$ ratio of CRM U500 is probably known better than the stated uncertainty limits (0.1% at 95% confidence level), some doubt is left whether residual bias has actually disappeared by this experimental change. More precise reference materials are needed to investigate the residual deviation. When the procedure is used with limited temperature changes the bias of an uncorrected ratio is diminished for measurements of CRM U500 and U030A, slight deviations from the certified values have been confirmed for measurements of CRM U005A and U050, in agreement with the results presented in Fig. 3 and Table 3.

In contrast to the NBL-modified total evaporation technique, the classical total evaporation on the MAT261 is programmed in a way that keeps the ion current intensity constant for the entire measurement time. The intensity is even kept constant towards the end of the sample life which causes the evaporation filament temperature to be increased rapidly during this stage of analysis. Strong evaporation of sample material from the filament may result in a decrease in ionization efficiency, leading to a relative loss of ^{238}U and

Table 5
Neodymium isotope ratio measurements of the La Jolla standard material, using multi-dynamic, static, and static with amplifier-rotation methods

	^{142}Nd/^{144}Nd	^{143}Nd/^{144}Nd	^{145}Nd/^{144}Nd
Neodymium isotope ratio measurements			
Nd multi-dynamic, 300 ng			
Mean (n = 14)	1.141836	0.5118452	0.3484042
S.D.	0.000017	0.0000031	0.0000013
RSD (ppm)	15.2	6.1	3.7
Specified RSD (ppm)		7	7
Nd static, 200 ng			
Mean (n = 12)	1.141775	0.5118510	0.3484030
S.D.	0.000015	0.0000036	0.0000017
RSD (ppm)	12.9	7.0	4.9
BIAS (ppm relative to multi-dynamic)	−53.1	11.3	−2.8
Nd static with amplifier rotation, 200 ng			
Mean (n = 14)	1.141830	0.5118453	0.3484045
S.D.	0.000012	0.0000022	0.0000011
RSD (ppm)	10.2	4.3	3.3
BIAS (ppm relative to multi-dynamic)	−4.6	0.2	1.9

All ratios normalized to ^{146}Nd/^{144}Nd = 0.7219; RSD is relative standard deviation.

a shift in the ^{235}U/^{238}U ratio creating a positive bias relative to the certified value. Keeping the ion beam intensity constant appears to have a disadvantage for minimizing the bias.

3.2. Multi-dynamic measurements

Because of the large dynamic range of uranium isotopic abundances encountered in nuclear materials, tests using CRMs were performed to evaluate the reproducibility and accuracy of multi-dynamic measurements. Because the linearity and signal decay characteristics of amplifiers influence the accuracy of these measurements, tests of these parameters are also presented using the Triton TIMS.

3.2.1. Multi-dynamic tests using neodymium isotope ratio measurements

Neodymium isotope ratio measurements were performed in multi-dynamic mode and in static mode, with and without the use of the amplifier-rotation technique that cyclically switches amplifier and Faradays during the course of a measurement. For each sample, 300 ng of the La Jolla Nd standard was loaded onto an evaporation filament and dried down with 1 μl of 0.5 molar phosphoric acid. Fourteen samples were measured in a double filament arrangement for each of the measurement modes. A typical ^{146}Nd ion current of 2.5×10^{-11} A was achieved for each sample run consisting of 18 blocks of data, with each block consisting of 10 integrations of 16-s duration. For the Nd static amplifier-rotation mode, the cyclical amplifier switching was done on a block-by-block basis. All neodymium results are shown in Table 5.

The multi-dynamic neodymium measurements met the limit of 7 ppm for ^{143}Nd/^{144}Nd and ^{145}Nd/^{144}Nd for the RSD specified for the instrument. The mean ^{143}Nd/^{144}Nd ratio of 0.511845(3) is about 25 ppm below the original value of 0.511858(7) reported for the La Jolla standard [12], but is well within the range of 0.51183–0.51188 found in a recent investigation using 12 TIMS instruments in 11 laboratories [13]. The bias of our result to the original (non-certified) value [12], and also the quite large data spread of about 100 ppm found in [13], may be caused in part by cup efficiency and amplifier gain inaccuracies in these measurements. It will be interesting to observe whether the spread of Nd isotope ratio data for the La Jolla Nd standard becomes smaller when instruments equipped with the advanced multi-dynamic capabilities such as a dispersion quadrupole are more commonly used for Nd isotope measurements. Although very precise Nd isotope ratio data with external reproducibilities in the lower ppm range can be obtained in multi-dynamic mode even without the use of a dispersion quadrupole [11], in those measurements the beam is not striking the center of the cups for all sub-configurations or dynamic steps. It is these non-alignment conditions that are thought to cause systematic deviations.

There is excellent agreement of static ^{142}Nd/^{144}Nd, ^{143}Nd/^{144}Nd, and ^{145}Nd/^{144}Nd measurements using the amplifier rotation with data obtained in the multi-dynamic mode (Table 5). This shows that, at least for those Faraday cups involved in the multi-dynamic measurement, the cup efficiencies agree to each other on a level of a few ppm. Comparing results of these two modes of Nd measurements is therefore a very powerful new method to measure relative cup efficiencies with a precision in the low ppm range. If cup efficiency tests are performed in the conventional way by switching a single constant ion beam into different cups, the precision is usually limited to significantly higher values of about 0.005% or 50 ppm. Although this study has to be extended to all remaining Faraday cups, these experiments demonstrate the level of precision and stability of the new multi-collector detection system.

Comparing the conventional static neodymium measurements with those performed in multi-dynamic mode shows significant deviations for $^{142}Nd/^{144}Nd$ and $^{143}Nd/^{144}Nd$ (Table 5). These deviations may be caused by variation or drift of the current amplifier gains on the level of few ppm. In order to investigate this problem, additional tests were performed to evaluate the statistical variation of current amplifier gain measurements. These tests showed a typical standard deviation of about 5 ppm for a series of 100 measurements for all relative current amplifier gains (relative to one reference amplifier). Therefore, the uncertainty of the current amplifier gain measurement is largely responsible for the limited precision and accuracy of pure static Nd isotope ratio measurements. The results of this study show that the amplifier rotation can be used to overcome the statistical variation of the current amplifier gains and to obtain reliable results with a precision at the several ppm level.

This precision for Nd is more than one order of magnitude better than presently achievable for uranium. Amplifier rotation may not be an improvement for uranium unless an internal normalization technique (double standard) is used. The multi-dynamic technique however, is valuable for achieving higher accuracy for uranium isotope ratio measurements because detector efficiency bias can be nearly eliminated.

3.2.2. *Decay of large signals at the current amplifier*

In contrast to neodymium, the isotope ratios of uranium exhibit quite a large dynamic range. Faraday detector systems of state-of-the-art TIMS instruments can be used over a range of more than four orders of magnitude, allowing static or multi-dynamic measurements of minor ratios below 10^{-4}. However, if one Faraday detector is used to measure a large ion current signal and then is subsequently used to measure an extremely small signal within a time period of a few seconds, as is the case for multi-dynamic or peak-jumping measurements, the amplifier circuitry must be able to dissipate the larger signal fast enough to avoid any contribution to the smaller signal. For this reason, the decay characteristics should be determined for each current amplifier. In peak-jumping or multi-dynamic isotope ratio measurements, idle times between the detection of extremely different ion currents have to accommodate the pre-determined decay characteristics.

An amplifier decay test is usually performed by switching an artificial current to the amplifier for a few seconds. After the current is switched off, the decay of the signal is recorded for about 33 s. This has to be done repeatedly in order to achieve statistically relevant decay characteristics. The decay characteristics of the Triton current amplifiers show a very fast initial decay, reaching a level below 5 ppm within the first few seconds, but the intensity seems to stay at the 1 ppm level for about 10–15 more seconds. When relative uncertainties of isotope ratios in the ppm range are required, or even when an extremely small signal has to be detected after a large one, the influence of the decay can be significant.

The sequence of the dynamic mass steps (see Table 1) within a multi-dynamic measurement has been arranged so

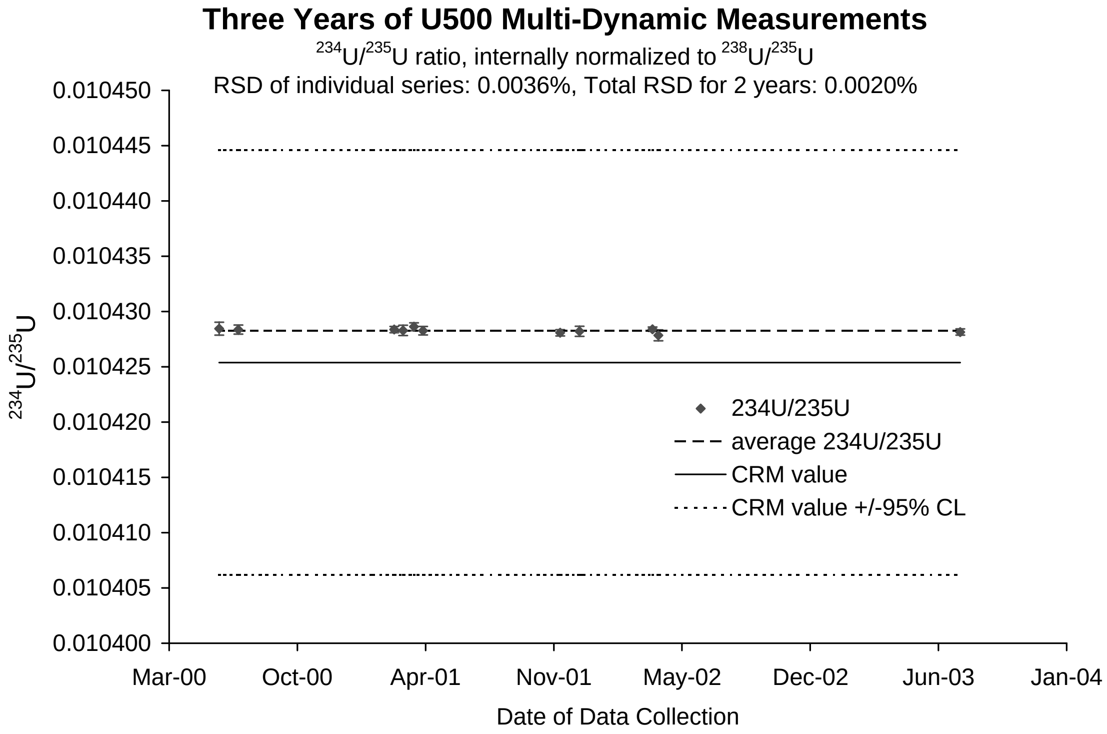

Fig. 6. Results of normalized $^{234}U/^{235}U$ ratios for CRM U500 measured in multi-dynamic mode, plotted versus the date of the data collection. The error bars (2σ, 95% CL) only reflect the reproducibility within each measurement series performed at the given dates. The certified values are indicated with a 95% confidence limit.

Table 6
Results for minor isotope ratio measurements of various NBL CRMs using the Faraday multi-collector

CRM	^{234}U/^{238}U measured	%RSE[a] (95% CL)	%Uc[b] (95% CL)	^{234}U/^{238}U CRM value	%Uc of CRM	Relative difference (%)
U005A	0.000034140	0.70	0.71	0.00003417	2.06	−0.09
U010	0.000054483	0.075	0.155	0.00005466	0.92	−0.32
U030A	0.00028717	0.054	0.144	0.0002866	0.22	0.20
U050	0.00029408	0.051	0.142	0.0002939	0.36	0.06
U100	0.00075513	0.030	0.136	0.0007536	0.30	0.20
U200	0.00156605	0.016	0.134	0.0015643	0.24	0.11
U500	0.01042521	0.008	0.133	0.010422	0.18	0.03
U750	0.0249021	0.007	0.133	0.024886	0.18	0.06
U900	0.089492	0.010	0.133	0.089463	0.21	0.03
CRM	^{236}U/^{238}U measured	%RSE[a] (95% CL)	%Uc[b] (95% CL)	^{236}U/^{238}U CRM value	%Uc of CRM	Relative difference (%)
U005A	0.000011799	1.92	1.921	0.00001186	0.85	−0.51
U010	0.000069287	0.24	0.249	0.00006880	1.03	0.71
U030A	0.00000615	2.50	2.501	0.00000619	0.84	−0.65
U050	0.00050728	0.030	0.074	0.0005057	0.42	0.31
U100	0.00042327	0.068	0.096	0.00042250	0.26	0.18
U200	0.00265491	0.026	0.073	0.0026566	0.28	−0.06
U500	0.00152334	0.028	0.073	0.0015195	0.41	0.25
U750	0.0105100	0.023	0.072	0.010500	0.34	0.10
U900	0.038263	0.021	0.071	0.038272	0.31	−0.02

CRMs U005A, U010, and U030A were measured in static mode; CRMs U050, U200, U500, U750, and U900 were measured in multi-dynamic mode. All minor ratios were normalized to the certified ^{235}U/^{238}U ratios.

[a] %RSE (relative standard error) represents the precision of the mean of repeated measurements; the number of replicates is not the same for every material.

[b] %Uc represents the combined uncertainty, which includes the certified uncertainty value of the ^{235}U/^{238}U ratio used for normalization.

that none of the minor ^{234}U or ^{236}U isotopes is measured in the same cup directly after a major isotope of ^{235}U or ^{238}U. Nevertheless, a lower limit of about 0.0003 for the ^{234}U/^{238}U and ^{236}U/^{238}U ratios has been established for multi-dynamic measurements.

3.2.3. Linearity tests

In order to perform a linearity check, suitable CRMs are chosen that have multiple isotopes differing in relative abundances by several orders of magnitude. An additional requirement is to have two isotopes whose ratio is close to unity, which can be used for mass fractionation correction. Any non-linearity effect on this particular ratio could then be nullified by ratioing isotopes of comparable ion currents. NBL CRM U500 and the IRMM-072 series fulfil both requirements.

A linearity check covering a range of almost five orders of magnitude using the IRMM-072 series was performed on the Triton Faraday detectors and the results showed no significant deviation from the certified values. The upper limit for the deviation was 0.006%, the uncertainty being dominated by the (combined) uncertainty of the certified values of about 0.019%. Therefore, no linearity correction is required for this multi-collector detection system.

NBL CRM U500 can also be used very effectively for assessing linearity. The isotopic composition of CRM U500 is characterized by a ^{238}U/^{235}U ratio that is close to unity and by a range of minor isotopic ratios from about ^{234}U/^{235}U $= 0.01$ to ^{236}U/^{235}U $= 0.0015$. Measurements of CRM U500 were performed within a range of two orders of magnitude for the ion current intensities for ^{235}U and ^{238}U, which effectively provided a linearity test covering

Table 7
Results for minor isotope ratio measurements of various NBL CRMs

CRM	^{234}U/^{238}U measured	%RSE[a] (95% CL)	%Uc[b] (95% CL)	^{234}U/^{238}U CRM value	%Uc of CRM	Relative difference (%)
U005A	0.000034189	0.029	0.136	0.00003417	2.06	0.06
U010	0.000054484	0.050	0.142	0.00005466	0.92	−0.31
CRM	^{236}U/^{238}U measured	%RSE[a] (95% CL)	%Uc[b] (95% CL)	^{236}U/^{238}U CRM value	%Uc of CRM	Relative difference (%)
U005A	0.000011977	0.049	0.083	0.00001186	0.85	0.99
U010	0.000069242	0.049	0.083	0.00006880	1.03	0.64

CRMs U005A and U010 were measured in ion counting mode. All minor ratios were normalized to the certified ^{235}U/^{238}U ratios.

[a] %RSE (relative standard error) represents the precision of the mean of repeated measurements; the number of replicates is not the same for every material.

[b] %Uc represents the combined uncertainty, which includes the certified uncertainty value of the ^{235}U/^{238}U ratio used for normalization.

an overall range of almost five orders of magnitude, similar to the linearity test using IRMM-072. Within the next two sections, results with high accuracy and precision obtained in multi-dynamic mode for the minor isotopic ratios of CRM U500 are discussed.

3.2.4. Multi-dynamic measurements of $^{234}U/^{238}U$ and $^{236}U/^{238}U$

As explained before, multi-dynamic measurements should provide more accurate results compared to static measurements because the inter-calibration of the multi-collector

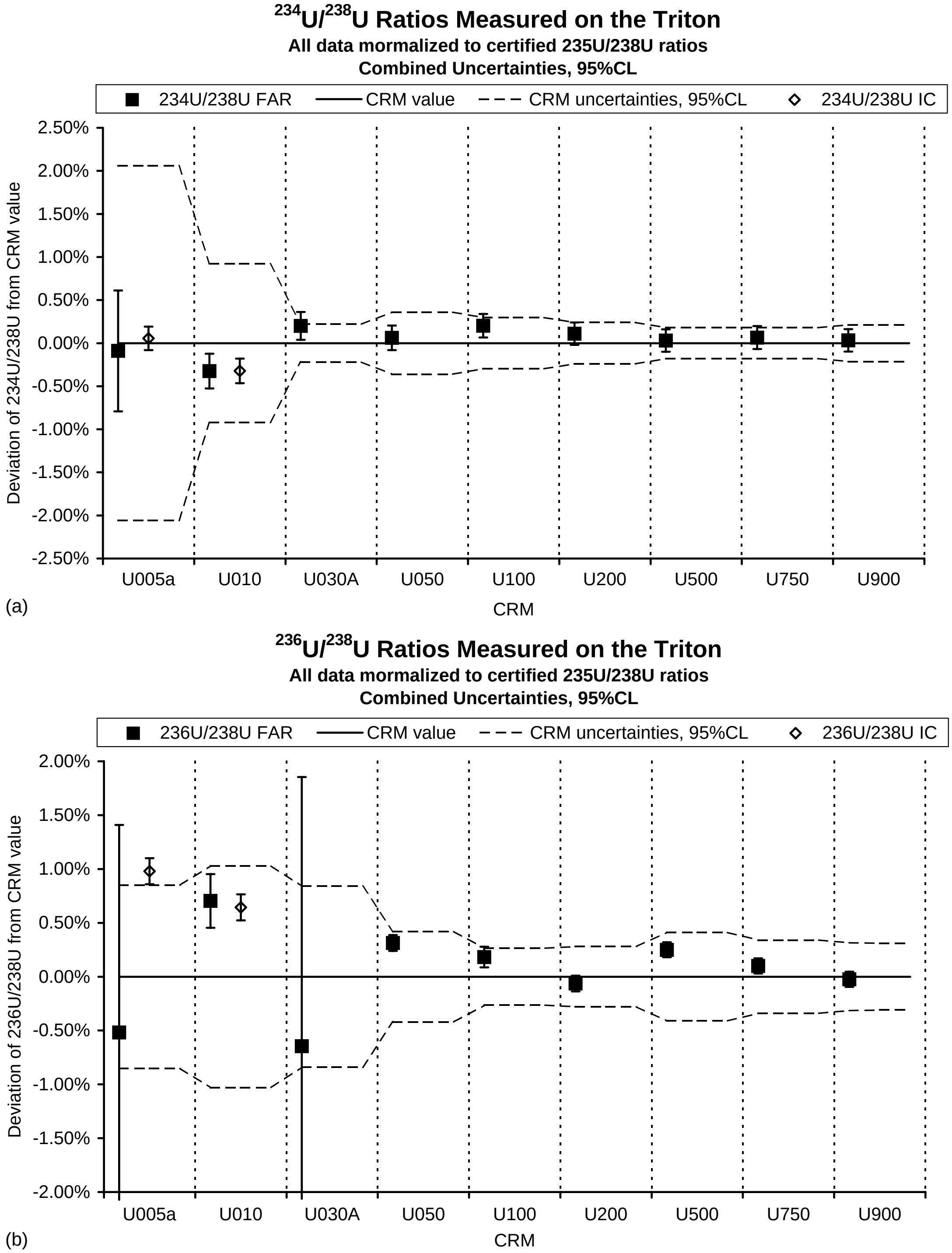

Fig. 7. (a) Results of measurements for $^{234}U/^{238}U$ ratios, relative deviation of the measured ratios from certified values, internally corrected using certified $^{235}U/^{238}U$ ratio. Error bars represent full uncertainties (95% CL), including measurement precision (%RSE) and the contributions from the normalization using the $^{235}U/^{238}U$ ratio. (b) Results of measurements for $^{236}U/^{238}U$ ratios, relative deviation of the measured ratios from certified values, internally corrected using certified $^{235}U/^{238}U$ ratio. Error bars represent full uncertainties (95% CL), including measurement precision (%RSE) and the contributions from the normalization using the $^{235}U/^{238}U$ ratio.

is circumvented. For a new Faraday detector system, with initial agreement of all cup efficiencies, static measurements might be as accurate as multi-dynamic ones. But it is recognized that cup efficiencies change over time, and these changes can bias measured ratios [8,9]. Therefore, the advantage of multi-dynamic measurements becomes more significant within the lifetime of a Faraday detector.

Fig. 6 shows the long-term reproducibility of the $^{234}\mathrm{U}/^{235}\mathrm{U}$ ratio. The error bars reflect the reproducibility (standard deviation) within a series of at least six sample runs on a single turret. For both $^{234}\mathrm{U}/^{235}\mathrm{U}$ and $^{236}\mathrm{U}/^{235}\mathrm{U}$ ratios (similar, not shown), the results are well within the 95% confidence limit of the certified CRM U500 values (±0.18% for $^{234}\mathrm{U}/^{235}\mathrm{U}$ and ±0.41% for $^{236}\mathrm{U}/^{235}\mathrm{U}$).

The data show an excellent consistency for the entire 3-year period from June 2000 until August 2003. The overall standard deviation is about 0.002% for $^{234}\mathrm{U}/^{235}\mathrm{U}$ and 0.015% for $^{236}\mathrm{U}/^{235}\mathrm{U}$, which is below the internal standard uncertainties of individual series (0.004 and 0.022%, respectively). This shows excellent long-term reproducibility for multi-dynamic measurements of minor uranium ratios.

3.2.5. Collection of minor isotope ratio measurements for various NIST/NBL CRMs

In Table 6 and Fig. 7a and b, results for Triton multi-collector measurements of the minor $^{234}\mathrm{U}/^{238}\mathrm{U}$ and $^{236}\mathrm{U}/^{238}\mathrm{U}$ isotope ratios are given.

Data are corrected for background at regular intervals during the course of a measurement by switching the magnetic field ±0.5 mass units from the minor isotope peaks, averaging the measured background intensities and subtracting those averages from the isotope peak intensities. The isotope ratio data are further corrected for mass fractionation using internal normalization to the known $^{235}\mathrm{U}/^{238}\mathrm{U}$ ratio. In Table 6, uncertainties for the minor isotope ratio measurements are given with and without the contribution from the mass fractionation correction using the $^{235}\mathrm{U}/^{238}\mathrm{U}$ ratio. For the Triton multi-collector, this contribution is the dominant source of uncertainty for minor ratios greater than about 0.0001.

From Fig. 7a and b, it can be seen that all measured minor isotope ratios agree with the certified values within their uncertainties derived from the certificates. But due to these large uncertainties of the certified values, this agreement is not particularly meaningful. If only uncertainties from the measurements would be considered, some significant differences between measured and certified minor ratios appear for both $^{234}\mathrm{U}/^{238}\mathrm{U}$ (e.g., U010, U030A) and $^{236}\mathrm{U}/^{238}\mathrm{U}$ (e.g., U010, U050, U500), similar to the case of the major ratios.

Ion counting data for minor isotopes are also given in Fig. 7a and b and Table 7 for CRMs U005A and U010. The ion counting data are corrected for linearity according to the procedure described in [7], and corrected for background contributions at $^{234}\mathrm{U}$ and $^{236}\mathrm{U}$ using an RPQ energy filter. Inter-calibrations between Faraday detectors and ion counter were performed throughout the course of the measurements using a $^{235}\mathrm{U}$ ion beam intensity of about 5×10^{-14} A.

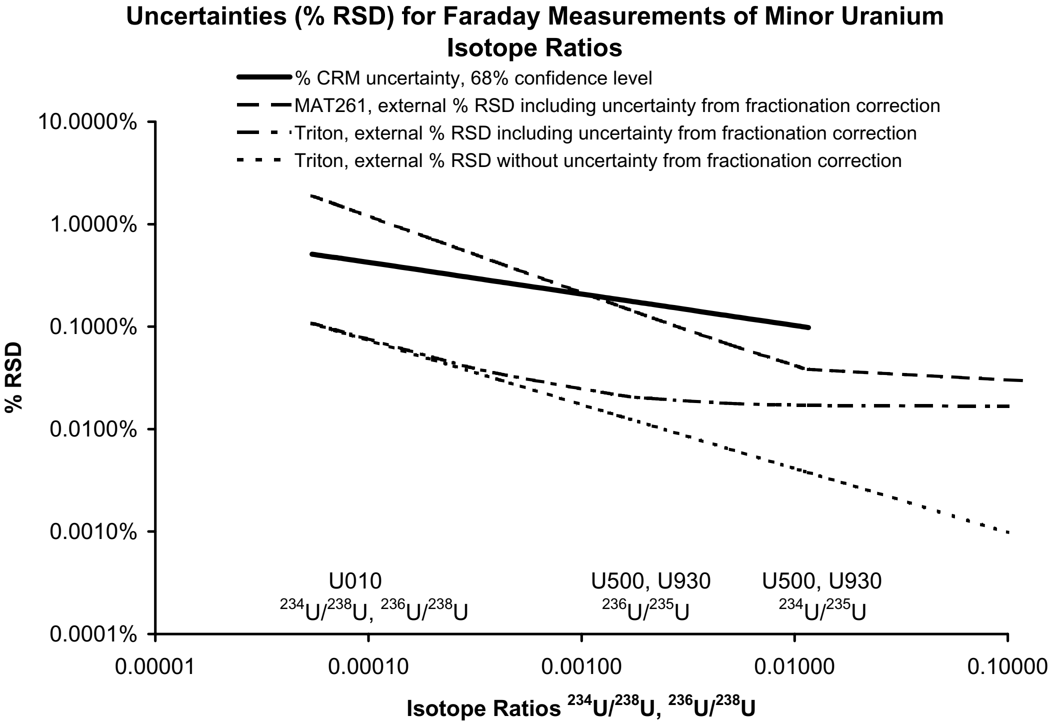

Fig. 8. Uncertainties for Faraday detector measurements of minor uranium isotope ratios, given as external relative standard deviation (%RSD). The uncertainty of the certified values is given using a 68% confidence limit (1σ) for consistency.

For CRM U010, minor ratio data by ion counting agree very well with data obtained using the Faraday multi-collector. This agreement confirms the accuracy of the linearity correction [7] applied to the ion counting data, which is significant (0.4%) in this case. The minor ratio values of CRM U010 (5.5×10^{-5} and 6.9×10^{-5}) establish a practical lower limit for measurements using the Faraday multi-collector. At an intensity level of about 1 mV for the minor isotope beams, the uncertainty of the amplifier baseline becomes a limiting factor.

The most accurate method for minor isotope measurements depends on the isotope intensities and ratios, on the sensitivity and precision of the mass spectrometric equipment. For the Triton, minor ratios above 3×10^{-4} can be measured with highest precision and accuracy using the Faraday multi-collector and the multi-dynamic technique. For ratio values between 5×10^{-5} and 3×10^{-4} use of the Faraday multi-collector in static mode would be the best choice. Ratios below 5×10^{-5} are best measured in ion counting mode. For instruments with a smaller Faraday dynamic range, ion counting measurements might be preferred for ratios below 3×10^{-4}.

A graphical summary of the uncertainty contributions for measurements of minor uranium isotopes using the Faraday multi-collector is given in Fig. 8. The %RSD curves represent regressions calculated from uncertainties encountered in the actual measurements. The external repeatability (dotted line) is the RSD of multiple sample measurements. When the uncertainty caused by the normalization to the certified major ratio is taken into account, the uncertainty approaches a lower limit with increasing minor ratio value. This limit is 0.017% for $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios, which is 1/3 of the 0.05% uncertainty in the U500 major ratio.

This contribution has to be taken into account for a complete uncertainty calculation, but even in this case the total uncertainties achieved in this study are about one order of magnitude smaller than those given by the certificates, which are shown as a 68% confidence limit (1σ) in Fig. 8 for consistency. The uncertainties achieved using the MAT261 are significantly larger compared to the Triton, and in case of U010 they are even larger than the CRM uncertainties.

4. Conclusions

A set of two new techniques for the measurement of major and minor isotope ratios of uranium with improved precision and accuracy has been introduced.

First, the NBL-modified total evaporation technique provides measurements with improved precision and accuracy for the $^{235}U/^{238}U$ ratio. A reproducibility of 0.02% RSD can be achieved in automated measurement sequences on a routine basis. Averages between turrets of at least five replicate samples even from different instruments can be determined with a reproducibility of 0.005% RSD. This precision is similar to the level achieved by UF_6 gas isotope ratio measurements.

A series of NIST/NBL CRMs has been analyzed using CRM U500 with a $^{235}U/^{238}U$ ratio of almost unity as a reference comparator. For some CRMs, e.g., U005A, U010 and U050 deviations by up to ±0.05% from the certified $^{235}U/^{238}U$ ratios have been found. The deviations are still within the 95% confidence interval derived from the certificates, but the extent of the deviations seems to be significant in the view of state-of-the-art measurement precision.

Second, the NBL-modified total evaporation technique was combined with the multi-dynamic measurement technique for uranium in order to improve the accuracy of the minor isotope ratio measurements. This technique obviates the need for the inter-calibration of the multi-collector, which has been observed to cause additional uncertainties and even bias in static measurements. Multi-dynamic measurements for uranium have been shown to exhibit very high reproducibility within time periods in the order of several years, in which cup efficiencies can change and cause significant bias in static data.

Within this work, new data for the minor isotope ratios $^{234}U/^{235}U$ and $^{236}U/^{235}U$ for various NIST/NBL CRMs are presented. Using the multi-dynamic measurement technique, these new results exhibit an improved level of accuracy and traceability for minor isotope ratio measurements. This can be justified for the following reasons:

1. The multi-dynamic measurement procedure is independent on the inter-calibration between Faraday cups and current amplifiers and therefore provides a higher level of accuracy compared to static measurements. Compared to the peak-jumping mode, multi-dynamic measurements are also more accurate because no drift correction for the signal intensity versus time is required.
2. Linearity tests using the IRMM-072 series and NIST/NBL CRM U500 performed in this study provide a proof of linearity within the entire dynamic range of the Faraday multi-collector.
3. The measured $^{234}U/^{235}U$ and $^{236}U/^{235}U$ isotope ratios were normalized to the certified major ratios $^{235}U/^{238}U$, which have an uncertainty of 0.1% (95% CL) for most CRMs of the NIST/NBL U-series. Due to this normalization, the certified uncertainty value of the major ratio contributes significantly to the uncertainty budget of the corrected minor ratios $^{234}U/^{238}U$ and $^{236}U/^{238}U$. This contribution causes a lower limit to the combined uncertainties of 0.13 or 0.67%, respectively, for the corrected $^{234}U/^{235}U$ and $^{236}U/^{235}U$ isotope ratios. As a consequence the normalization using a certified isotope ratio leads to an increase of the uncertainty of the minor ratios. On the other hand, even this normalization provides the traceability of the measured minor isotope ratios to the SI system.

Due to the high level of accuracy and traceability, the new techniques presented here may also be used for the certification of isotope reference materials for other elements, including low mass elements whose isotope ratios measurements are significantly affected by mass fractionation. The modified total evaporation technique might be a valuable alternative for those cases where no double spike is available for the mass fractionation correction.

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