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Characterisation of secondary electron multiplier nonlinearity using MC-ICPMS

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Abstract

We have investigated the signal response characteristics of a commonly used (ETP) secondary electron multiplier (SEM) using a ThermoFinnigan Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) over a range of applied beam intensities from 10 to 5×10^5 counts per second (cps). Sample switching while maintaining the same tuning parameters allows a "static" SEM–Faraday cup assessment of nonlinearity by MC-ICPMS, rather than a peak-switching approach as recently reported using thermal ionisation mass spectrometry (TIMS) [S. Richter, S.A. Goldberg, P.B. Mason, A.J. Traina, J.B. Schwieters, Int. J. Mass Spectrom. 206 (2001) 105]. For two SEMs of the same type (ETP) we find a count rate nonlinearity of 0.3 and 1.1% per decade of ion beam intensity variation for intensities of less than about 3×10^4 and 10^5 cps, respectively. Above a nominal threshold of 3×10^4 and 10^5 cps there is a more pronounced nonlinearity effect with an additional 0.4 and 1.6% per decade. A previous TIMS study on the same type of multiplier [S. Richter, S.A. Goldberg, P.B. Mason, A.J. Traina, J.B. Schwieters, Int. J. Mass Spectrom. 206 (2001) 105] found evidence of nonlinearity at the higher intensity range only. Although the SEM we have most rigorously tested may display an anomalously high degree of nonlinearity, we suggest that the form of behaviour is general and must be well-calibrated prior to routine high precision sample analysis.

Additional tests show that after a high intensity beam was measured on the SEM of the MC-ICPMS system, the SEM yield is elevated for at least 15–20 s, which can be envisaged as a memory effect related to the intensity of previously measured signals. Therefore, it is impossible to see the nonlinearity effect at low count rates using a peak jumping routine on the ICPMS because of intervening high intensity beams (e.g., ^{235}U and ^{238}U) applied to the SEM. This "memory" effect has important implications for MC-ICPMS measurement protocols that use multi-static or peak jump routines.

Keywords: Secondary electron multiplier; Linearity; ICPMS; Isotope ratio mass spectrometry

1. Introduction

Many applications in fields such as environmental monitoring, the nuclear industry, geochemistry, archaeometry, cosmochemistry and geochronology require the measurement of isotope systems with extremely high dynamic ranges, where low intensity beams are measured on a discrete-dynode detector such as a secondary electron multiplier (SEM) or Daly detector. Technological developments in the past decade have resulted in the potential for higher measurement precision, e.g., [2], which puts greater demands on the accuracy of the detector systems. Critically, ion-counting systems need to be well-characterised for the full range of applied beam intensities. For example, we are specifically interested in the use of uranium-series disequilibrium as a chronological tool for geological samples that preserve past climate information [3]. Precise and accurate determination of events is necessary if we are to understand the timing and rates of past environmental change. High accuracy is also required in order that

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chronologies developed using one dating system can be reliably compared with those from other laboratories using the same or other systems. A specific advantage of developing MC-ICPMS techniques compared with the more established high precision TIMS measurement techniques for U-series isotopes is higher sensitivity and, therefore, reduced sample size required for a given precision [2]. However, comparison of U–Th dating results on standard carbonate samples measured at different laboratories shows age differences of 10% on a 30,000-year-old sample, measured with typical analytical precisions of better than 1% for MC-ICPMS and 4% for TIMS data [4]. This highlights the fact that analytical accuracy needs to be improved significantly to exploit effectively the increased precision of new techniques.

SEMs are essential for the measurement of low abundant isotopes, but it is well known that the detected count rate response of an SEM to varying applied ion beam intensities is not linear [1,5], and this ultimately limits the accuracy of measurements. The nonlinear behaviour of an SEM can be conveniently attributed to two effects, the dead time – often dominated by the electronic counting system [1,6] – and other nonlinear behaviour determined by the physical characteristics of the SEM itself. The dead time can be considered simply as the temporal resolution of the ion counting system, i.e., the interval of time between the detection of one ion and the system being ready to detect the next, resulting in coincidence losses which can be corrected for provided the dead time is known (e.g., [1,6]). The dead time can be measured electronically and, at permil precisions, the error resulting from uncertainty in the dead time corrected measurements typically becomes significant only for count rates $>10^5$ cps. Less well understood, however, is the nonlinear response of almost all SEMs, which usually results in relatively more pulses counted at higher beam intensities. Unlike many instrumental biases SEM nonlinearity cannot be calibrated electronically, but requires careful experimental determination.

A method to measure SEM nonlinearity using a TIMS SEM peak jump routine with a certified reference material, such as NIST U500, was suggested by Richter et al. [1]. They noted apparently linear behaviour to applied beam intensities of 1×10^4 to 3×10^4 cps, and thereafter a nonlinearity of several permil per decade variation in applied ion beam intensity. However, the ion beam intensity of an ICPMS typically fluctuates more than that of a TIMS over measured timescales and so the peak jump method suggested by Richter et al. [1] cannot be readily used. Thus, an alternative experimental design for nonlinearity characterisation is needed. We have developed a method for nonlinearity characterisation suitable for MC-ICPMS employing a "static" SEM–Faraday cup ratio measurement mainly using the $^{234}U/^{238}U$ ratio of Harwell URAN 84.5 (HU), a secular equilibrium uraninite standard [7]. Using this method, we demonstrate an additional nonlinearity effect for count rates below 10^4 cps for one of the multiplier types used by Richter et al. [1] (ETP multiplier, manufactured by ETP-SGE). We also report a memory effect that has not previously been recognised, but has significant implications for the design of isotope measurement protocols using MC-ICPMS.

2. Methods

2.1. Instrumental

We have conducted experiments on SEM linearity by measuring U-series isotopes on two ThermoFinnigan Neptune high resolution MC-ICPMS (Neptune I and II) and a ThermoFinnigan Triton TIMS at the Bristol Isotope Group laboratory. The collector system of the mass spectrometers consists of eight moveable Faraday cups and a fixed center cup or SEM. The axial beam can be deflected either into the central Faraday cup or the SEM. The cup configuration used for U and Th measurements in our laboratory is shown in Table 1.

The mass spectrometers are all equipped with ETP multipliers which are located behind an energy and angular filtering device (Retarding Potential Quadrupole—RPQ) to improve the abundance sensitivity. The RPQ filter, however, strongly influences the SEM peakshape. The applied voltage for Faraday cup to SEM deflection together with suppressor and decelerator potentials within the RPQ are routinely tuned to obtain optimal peakshape prior to a measurement sequence.

The sample introduction system on Neptune I and II incorporates a Cetac Aridus nebulizer with a nominal uptake rate of 50 μl/min. We usually obtain a UH^+/U^+ ratio smaller than 10^{-7}. The ICPMS gas flows are set to obtain a stable ion beam with a good intensity and consistently low UO^+/U^+ ratio $<10^{-3}$. Typically, we obtain ~100 pA intensity of ^{238}U using a 30 ppb solution and 50 μl/min uptake rate. Typical instrument parameters are given in Table 2.

The Faraday cup amplifiers are internally "gain calibrated" using a highly stable current generator, but compared to possible nonlinearity effects of the SEM, the Faraday cup intercalibration and baseline uncertainty are generally insignificant. For our study on SEM nonlinearity, we used ETP AF180H discrete dynode type SEM with Al-based dynode surfaces and an acceleration potential of about 2000 V. This design is

Table 1
Cup configuration used for ThermoFinnigan Neptune I and II U–Th measurements

	Low 1	Center (SEM)	High 1	High 2	High 3
Uranium 1		^{234}U			^{238}U
Uranium 2	^{235}U	^{236}U	^{238}U		
Uranium 3[a]		^{235}U		^{238}U	
Thorium 1		^{229}Th		^{232}Th	
Thorium 2		^{230}Th	^{232}Th		
Thorium 3[b]		^{232}Th			

[a] Uranium 3 is only used for nonlinearity experiments and not part of our routine U–Th measurements.

[b] ^{232}Th on the SEM is only needed for low ^{232}Th concentration peak jump method which is not used for the data shown in this study.

Table 2
MC-ICP-MS operating parameter settings for ThermoFinnigan Neptune and Cetac Aridus nebuliser

RF power	1200 W
Cool gas	16 l/min
Auxillary gas	0.7–0.8 l/min
Sample gas	0.9 l/min
Aridus sweep gas	4–5 l/min
Aridus N_2	0.2 ml/min
Sample uptake rate	50 μl/min
Extraction voltage	2000 V

used widely in commercial ICPMS and offers the advantage of low darknoise (typically less than 1 count per minute (cpm) for a new ETP multiplier), a good dynamic range, stable yield and a well-formed and stable peak shape.

2.2. Dead time

One non-linear response of SEMs can be attributed to the dead time of the ion detection and counting system. The counting system consists of a high-bandwidth pulse amplifier, a discriminator to reject pulses that do not exceed a specified amplitude, and an electronic counter. A perfect counting system would count every current pulse from the SEM's final dynode not rejected by the discriminator. In practice, two closely spaced pulses cannot be distinguished as separate events and are counted as a single pulse. The dead time is the time after one electron pulse event during which subsequent pulses cannot be detected. There are two contributors to the dead time: (1) the inherent SEM dead time, i.e., the duration of the current pulse delivered by the SEM, typically less than 10 ns and (2) the limitations of the counting system. In most cases, the latter is the major contribution to the effective dead time; indeed it is often the case that the counting system's dead time is fixed electronically so that it is well-known and stable over time. Whether electronically determined or not, the dead time can be characterised empirically as described in Richter et al. [1] and a correction is then possible according to:

$$C_{\text{corr}} = \frac{C_{\text{meas}}}{1 - \tau C_{\text{meas}}} \quad (1)$$

where τ is dead time, typically $\tau = 10$–50 ns [1,7].

The dead time of the counting system in our Neptune MC-ICPMS was determined by means of replacing the signal from the SEM by a pulse generator (HP8082A) and accurately measuring the double-pulse resolution giving 20.6 ± 0.8 ns (full range). For our system the impact of dead time uncertainty becomes significant only for count rates bigger than 10^5 cps. The dead time correction is conducted online for all measurements made in this study. The pulse generator was also used to measure the linearity of the counting system from 1 kcps to 1.6 Mcps. The results indicate that the counting system nonlinearity is less 30 ppm, limited by the frequency stability of the pulse generator.

2.3. Sample preparation

For our SEM linearity study we used a solution of uraninite (URAN 84.5, provided by UKAEA Harwell in 1990), and a Table Mountain Latite (TML) sample, which are both secular equilibrium standards [4,7,8]. This means that the $^{234}U/^{238}U$ ratio should simply be the ratio of the activity constants of the nuclides. In this study, we use the ^{234}U and ^{230}Th activity constants given by Cheng et al. [7], which yield $^{234}U/^{238}U = 5.4887 \times 10^{-5}$ for secular equilibrium. Both samples were spiked with a mixed $^{229}Th/^{236}U$ spike, U and Th were then separated following a widely used chemical separation and purification procedure (e.g., [9]) and analysed separately in 2% HCl solution. A spike was added because we decided to adopt the same procedures for standards as used for all samples analysed for U–Th to ensure comparability of the methods and results. Furthermore, the added spike potentially enables investigation of both the $^{234}U/^{238}U$ and the $^{230}Th/^{238}U$ ratios of the secular equilibrium samples. Procedual chemistry blank values were typically less than 0.01 ng ^{238}U, 0.1 pg ^{235}U, 1 fg ^{234}U, 0.01 ng ^{232}Th and 1 fg ^{230}Th, respectively.

2.4. MC-ICPMS procedures

We adopted a sample–standard bracketing procedure to derive corrections for mass fractionation and Faraday cup to SEM gain. For U measurement we used New Brunswick Laboratories NBL-112a (CRM-112a, formerly NBS SRM 960) as our standard. Thorium measurements were bracketed with an in-house ^{229}Th–^{230}Th–^{232}Th Th-standard (TEDDi). This standard has a $^{229}Th/^{232}Th$ ratio of 2.96×10^{-3} and a $^{230}Th/^{232}Th$ ratio of 4.48×10^{-3}. These values were characterised by MC-ICPMS measurements of TEDDi versus IRMM-035 and the Santa Cruz Th-A standard, using the average $^{230}Th/^{232}Th = 5.856 \times 10^{-6}$ value for Santa Cruz Th-A compiled in [10], and by TIMS measurements of TEDDi alone.

2.4.1. Faraday cup to SEM gain

Theoretically, a beam of 6.24×10^7 ions per second applied to a Faraday cup with 10^{11} Ω resistor should generate a potential difference of 1 V. In practice, the count rate response of Faraday cups and SEMs depends on various parameters, and the two detection systems have to be experimentally cross-calibrated to derive Faraday cup to SEM gain (also called "yield"). In TIMS measurements, the yield is commonly determined by switching a beam of appropriate intensity (5–10 mV) between the SEM and a Faraday cup. However, static measurement routines should be used for MC-ICPMS because of pronounced fluctuations in beam intensity within typical time spans of seconds to minutes due to the nebulizer system. Therefore, two isotopes with high dynamic range and a known ratio (such as ^{234}U and ^{238}U) were simultaneously measured on the SEM and a Faraday cup. The $^{234}U/^{238}U$ ratio of NBL-112a, characterised by

Cheng et al. [7] to $5.286 \times 10^{-5} \pm 0.0025 \times 10^{-5}$, was used for yield calculation for uranium. Our NBL-112a standard solution has a ^{238}U concentration of 30 ppb and it was measured before and after each U-analysis. Since Th and U can have different yields [11], the Th-standard (TEDDi) was used to derive the Faraday cup to SEM gain for Th measurements using static measurements of ^{230}Th/^{232}Th.

2.4.2. Mass fractionation

The natural ^{235}U/^{238}U ratio of 7.2526×10^{-3} [12], measured statically on two Faraday cups using NBL-112a, was used for mass fractionation correction of uranium isotopes. Because U and Th could have different mass fractionation correction factors [8], Th mass fractionation was obtained using multi-static measurement of ^{229}Th/^{232}Th and ^{230}Th^{232}Th of the Th-standard (TEDDi). For both, U and Th, the mass fractionation correction was applied using the exponential law [13,14].

2.4.3. Abundance sensitivity

The ratio of tail (at $m/z = 236$) to ^{238}U-intensity of NBL-112a, simultaneously measured with the ^{235}U/^{238}U ratio, was used to derive the abundance sensitivity at two atomic mass units from ^{238}U. The ^{238}U tailing effect on ^{234}U, which was checked by prior measurements at halfmasses 234.5 and 233.5, is negligible.

Abundance sensitivity for samples with high ^{232}Th/^{230}Th ratios (e.g., TML) was measured using the Th-samples themselves with tail measurements of beam intensities at atomic masses of 231.5, 231, 230.5, 229.5 and 228.5. The tail to the ^{232}Th-intensity ratios were interpolated to masses 230 and 229 to correct the measured ratios of ^{230}Th/^{232}Th and ^{229}Th/^{232}Th. We currently have an abundance sensitivity of 45–50 ppb of the ^{232}Th intensity on mass 230.

2.4.4. Background

After every sample or standard, we ran a wash procedure that starts with a short pre-wash (1 min 2% HCl solution). After the pre-wash, 0.05N HF–2% HCl wash solution was used for 5 min to reduce intensities, especially of Th. After that 2% HCl blank wash solution was used for another 10 min and the intensities of all the relevant isotopes were measured. These values were then used as the blank solution background correction for subsequent sample or standard measurements. Typical values of such solution blanks were ^{234}U < 1 cps, ^{235}U < 100 cps, ^{236}U < 1 cps, ^{238}U ~ 20,000 cps, ^{229}Th < 10 cps, ^{230}Th < 1 cps, ^{232}Th < 1000 cps. The wash procedure effectively reduces the intensities by at least 4–5 orders of magnitude. The uncertainties of the background intensities are typically 20%. SEM darknoise and the baseline of the Faraday cups were characterised before each set of measurements.

2.5. Experimental design

To measure nonlinearity effects, we prepared different dilutions of a spiked HU uranium stock solution with ^{238}U intensities between 4×10^{-3} and 40 V to be measured on the Faraday cup. Static measurements of ^{234}U/^{238}U ratios were then carried out for ^{234}U intensities between 10 and 10^5 cps. Using the ^{234}U/^{238}U ratio of uraninite was limited to a maximum of 10^5 cps because the maximum ^{238}U intensity on the Faraday cup must not exceed 50 V. Therefore, we used the ^{235}U/^{238}U ratio with the ^{235}U beam on the SEM to measure nonlinearity at count rates >10^5 cps. Similar experiments were done using Th isotopes of a spiked TML sample. Table 3 illustrates the relevant isotopic ratios of samples used in this study. The secular equilibrium samples were run as "unknowns" between bracketing measurements of U- and Th-standards (NBL-112a or TEDDi), respectively. The bracketing standards were always measured at the same intensity as each other for a given experiment to make sure that any potential nonlinearity contribution to the yield determination was constant.

Table 3
Values of isotopic ratios of samples used for the nonlinearity study

	HU uranium	U500	TML thorium
^{234}U/^{238}U	5.4887×10^{-5}	0.010422	
^{235}U/^{238}U	7.2526×10^{-3}	0.999698	
^{236}U/^{238}U	3.59×10^{-5} [a]	0.001519	
^{229}Th/^{232}Th			3.964×10^{-5} [a]
^{230}Th/^{232}Th			5.7878×10^{-6}

[a] Ratio is result of added spike.

Although not specifically designed for MC-ICPMS measurements, we also attempted to characterise the Neptune I SEM for nonlinearity using the protocols suggested by Richter et al. [1] for TIMS measurements which incorporate ^{234}U/^{235}U and ^{236}U/^{235}U measurements of U500 with a peak jump routine. For mass fractionation correction we bracketed the U500 measurements with NBL-112a.

Apart from dead time, SEM darknoise and the Faraday cup gain and baseline corrections, all corrections and data reduction was conducted offline. All calculated errors quoted in this study are based on Monte Carlo variation of all initial uncertainties. Errors are given at 95% confidence level.

3. Results

3.1. SEM yield

The change of yield between two bracketing standard measurements must be small in order to make reliable nonlinearity measurements. We observed that the yield of the ETP SEM was very stable, it typically varied less than 0.5% during a 12 h period. Fig. 1 shows the SEM yield of a sequence determined using NBL-112a measurements, measured with a near constant ^{234}U intensity of about 2×10^4 cps.

3.2. Nonlinearity characterisation using a peak jump method

Fig. 2 shows the ^{234}U/^{235}U ratios derived by the peak jump routine on the SEM using U500 according to Richter et al.

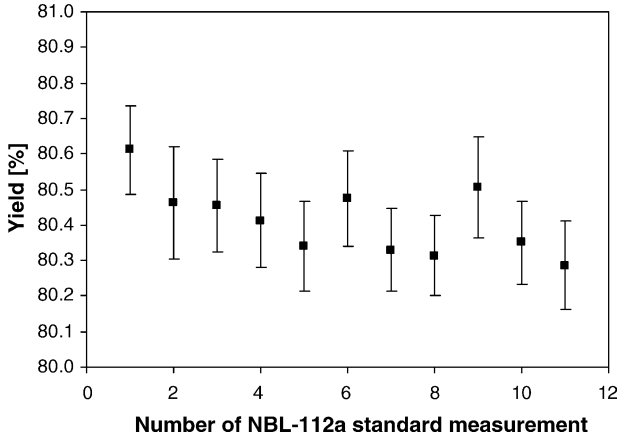

Fig. 1. SEM–Faraday cup gain ("yield") variation over a period of about 12 h derived by NBL-112a measurements. The ETP multiplier displays a very stable yield with variations of usually less than 0.2% per hour. All errors quoted in this manuscript and in all figures are at 95% confidence level (2 sigma).

[1]. Precision is influenced by instabilities in beam intensity on time scales of seconds to minutes. We observe regular intensity variations of more than 10% at about 0.01 Hz frequency, probably due to droplet building at the nebulizer tip. The influence is pronounced at low count rates as long integration times are needed for reasonable counting statistics. Thus, pronounced changes of the beam intensities in time scales of tens of seconds have a distinct effect on the precision of ratios measured with a peak jump routine. Therefore, this method is not useful for precise characterisation of SEM nonlinearity in ICPMS. However, no obvious nonlinearity effect can be seen for count rates less than 10^5 cps, whereas for ^{235}U intensities greater than 10^5 cps there is a significant nonlinearity of about 3% per decade. It has been argued that the ^{234}U intensity (numerator) in such experiments is below a nominal threshold ($\sim 10^4$ cps) of nonlinear behaviour [1].

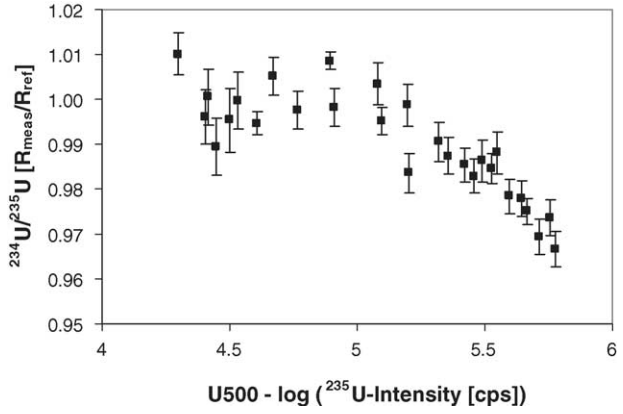

Fig. 2. Nonlinearity characterisation of the SEM Neptune I using a peak jump routine with U500 according to Richter et al. [1]. Short-term intensity variation results in large uncertainties of the ^{234}U/^{235}U ratios shown in this diagram. However, no obvious nonlinearity can be observed for ^{235}U count rates smaller than 10^5 cps, a nonlinearity of 3% is obtained for count rates exceeding 10^5 cps.

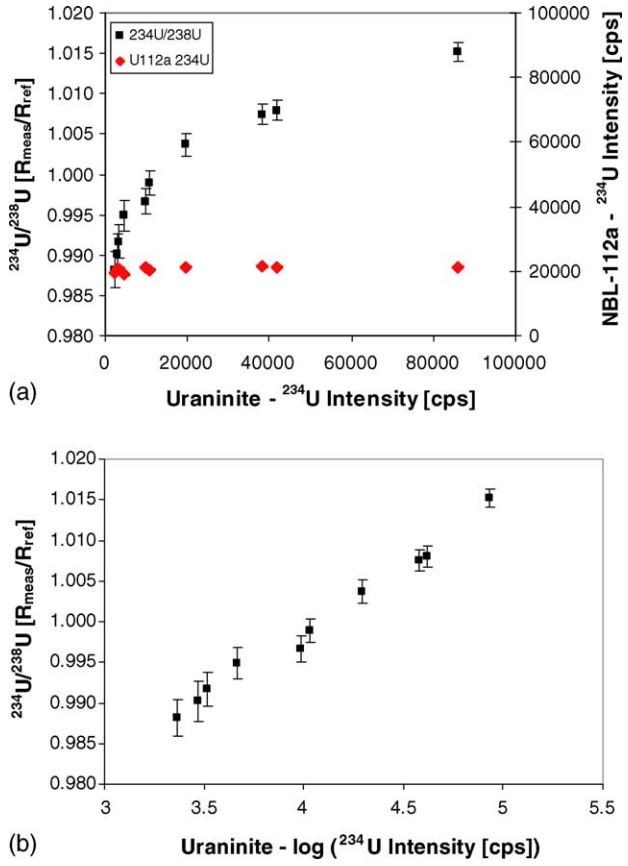

Fig. 3. (a) A sequence of HU measurements at different concentrations (^{234}U intensities), measured using Neptune I. The bracketing NBL-112a solution was run at a near constant intensity of 2×10^4 cps. The HU ^{234}U/^{238}U ratio, shown as measured ratio divided by the reference value, clearly increases with ^{234}U intensity applied to the SEM. ^{238}U is always measured on the Faraday cup, therefore the ^{234}U nonlinearity results in increasing ^{234}U/^{238}U ratios as the numerator relatively increases. For both, the bracketing NBL-112a and the HU samples, ^{234}U/^{238}U and ^{236}U/^{238}U were measured with a multi-static routine. ^{235}U/^{238}U was exclusively measured statically on two Faraday cups, no ^{235}U was therefore applied to the SEM. See text for details. (b) Log-scaled plot of normalised ^{234}U/^{238}U ratios shown in (a). In log space the ratios show a linear increase with increasing ^{234}U-intensity.

Therefore changes of the ^{234}U/^{235}U ratio with ^{235}U intensity as denominator should only be affected by nonlinearity in response to the ^{235}U intensity. In Fig. 2, a relative increase of the ^{235}U intensity results in a decrease of the ^{234}U/^{235}U-ratio.

3.3. Nonlinearity characterisation using multi-static measurements: uranium

We subsequently tested the same SEM using our alternative, static method. Ten different dilutions of the spiked HU uranium were measured, bracketed by NBL-112a with a near constant intensity of about 2×10^4 cps for ^{234}U (Fig. 3a). Note that both the standard and the samples were measured in a "multi-static" mode, i.e. ^{234}U/^{238}U and ^{236}U/^{238}U were measured alternately. Uranium-238 and ^{235}U were exclusively measured on Faraday cups and therefore are not influenced by nonlinearity effects.

In contrast to the results reported in Fig. 2, the multi-static approach clearly reveals a nonlinearity for the $^{234}U/^{238}U$ ratio for count rates of ^{234}U between 2000 and 80,000 cps. The SEM yield during this sequence (Fig. 1) is stable within 0.5% over 12 h and could not have been responsible for the effect. The general form of the relationship between intensity and the measured $^{234}U/^{238}U$ ratio is exponential (Fig. 3b), and there is no obvious lower threshold to the nonlinearity in the data. The correct value for the $^{234}U/^{238}U$ ratio of the uraninite is obtained at a ^{234}U intensity between 1×10^4 and 2×10^4 cps. We observed that a sample ^{234}U-intensity of 2×10^4 cps – which is the same as the bracketing standard ^{234}U-intensity – yields a $^{234}U/^{238}U$ ratio elevated by 0.3%. This discrepancy will be addressed in the discussion below.

To extend the graph of Fig. 3b to higher and lower intensities, additional measurements were made using both $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios of HU. Fig. 4 shows the stacked intensity bias graph with the $^{234}U/^{238}U$ and $^{235}U/^{238}U$ results. Overall, the nonlinearity starts without an obvious threshold at count rates of 10–100 cps and becomes significantly steeper for count rates exceeding 10^5 cps. The data in Fig. 4 can be conveniently described by two linear functions in log-linear space. We calculate a nonlinearity effect for the Neptune I ETP multiplier that starts nominally at $C_{lim,1} = 10$ cps with a slope of $m_1 = 0.011 \pm 0.0008$ and a change in slope at $C_{lim,2} = 10^5$ cps to $m_2 = 0.027 \pm 0.0015$. The quoted thresholds are not sharp limits because the SEM characteristics do not suddenly change. In reality the change in SEM response is likely to vary smoothly with ion beam intensity, but this response can be conveniently modeled using discrete nominal thresholds [1].

The nonlinearity of the SEM in Neptune I illustrated in Figs. 2–4 is unusually large. Therefore, we also undertook similar measurements on the SEM in Neptune II to determine if this was a general or a specific problem with the multiplier in Neptune I. The results for Neptune II, shown in Fig. 5, are qualitatively similar to those for Neptune I but they have

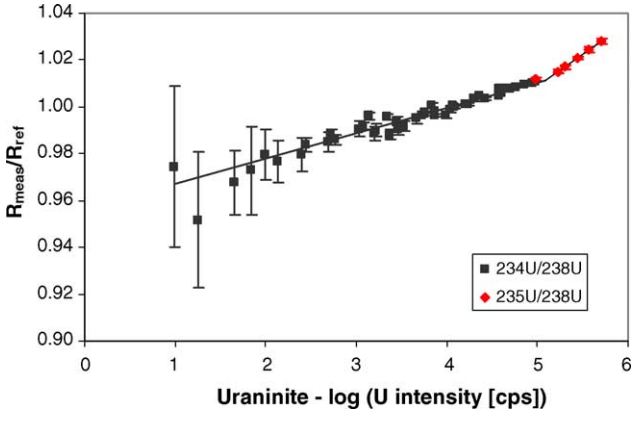

Fig. 4. Neptune I SEM nonlinearity characterisation: plot of normalised $^{234}U/^{238}U$ (R_{meas}/R_{ref}) for HU for the full range of applied log-scaled intensities from 10 to 5×10^5 cps. Nonlinearity effects start at the lowest intensity without any obvious threshold, different slopes are obtained for count rates below and above a threshold of 10^5 cps.

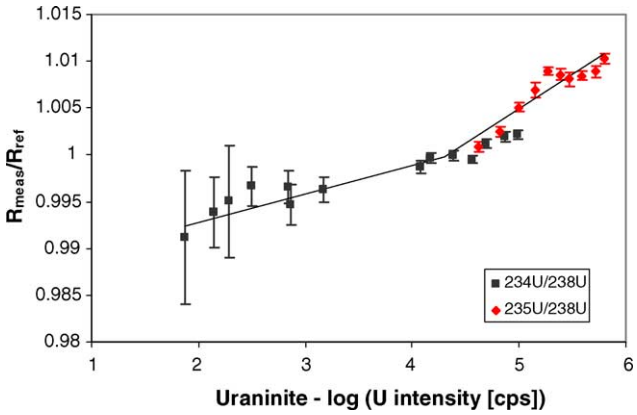

Fig. 5. Plot of normalised $^{234}U/^{238}U$ (R_{meas}/R_{ref}) for HU for the full range of applied log-scaled intensities for the Neptune II SEM. The general nonlinearity is similar to Neptune I (Fig. 4) with shallower slopes and a different threshold for the slope change.

different slopes, and a different threshold for the onset of the higher slope m_2. For count rates smaller than 3×10^4 cps we find a nonlinearity with $m_1 = 0.003 \pm 0.0006$. We model the change in nonlinearity to $m_2 = 0.0074 \pm 0.002$ at intensities above $C_{lim,2} = 3 \times 10^4$ cps.

3.4. Nonlinearity characterisation using multi-static measurements: thorium

To check for any elemental dependency on nonlinearity, a similar experiment was conducted for thorium isotopes on Neptune I using a spiked Table Mountain Latite (TML) thorium solution (Table 3). The ^{230}Th intensity was varied between 10^2 and 10^4 cps, and the ^{229}Th intensity between 10^3 and 10^5 cps, so that we only obtained the nonlinearity slope of the Neptune I SEM for count rates below 10^5 cps. Fig. 6 shows that the nonlinearity effects are the same for measurements of both the $^{229}Th/^{232}Th$ and $^{230}Th/^{232}Th$ ratios. We observe no significant difference between the nonlinearity characterised by U and Th (Figs. 4 and 6). The slope determined using TML and Th isotopes ($m = 0.011 \pm 0.0018$) is identical to that

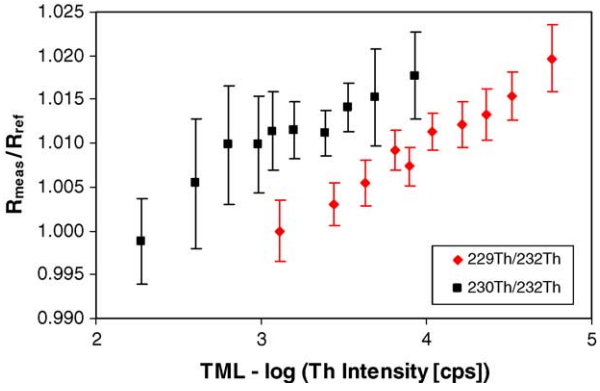

Fig. 6. Linearity characterisation of Neptune I SEM using a TML thorium solution. The $^{229}Th/^{232}Th$ ratios are normalised to the first value. $^{229}Th/^{232}Th$ and $^{230}Th/^{232}Th$ yield the same nonlinearity slope.

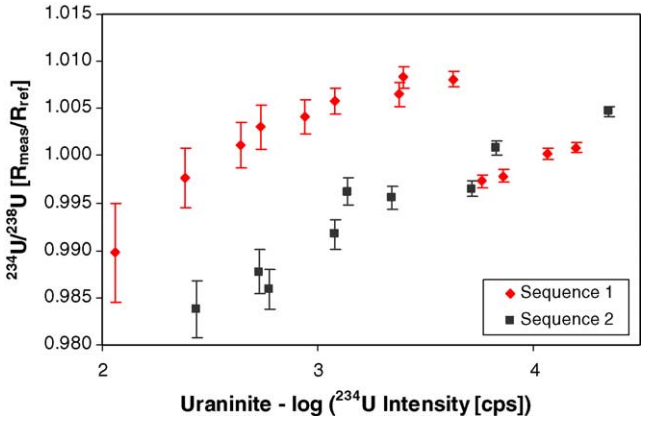

Fig. 7. $^{234}U/^{238}U$ ratios of HU with and without jump on ^{235}U, Neptune 1. The first nine measurements of sequence 1 included multi-static $^{235}U/^{238}U$ measurements with ^{235}U on the SEM, whilst ^{235}U was not measured on the SEM for the last four measurements. Clearly the ^{235}U beam interveningly applied to the SEM increases the measured $^{234}U/^{238}U$ ratio. In sequence 2, $^{234}U/^{238}U$ was remeasured over the same range of ^{234}U intensities without ^{235}U on SEM.

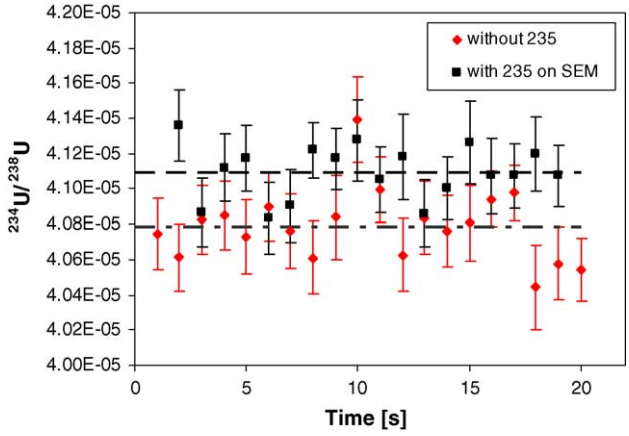

Fig. 8. $^{234}U/^{238}U$ ratio determined through time for two scenarios: static measurements of $^{234}U/^{238}U$ ratio only (without 235, mean is chained line) and after a high intensity (^{235}U) beam was applied to the SEM for 2 s (with 235 on SEM, mean is dashed line), measured using Neptune II. The $^{234}U/^{238}U$ ratio after applying ^{235}U to the SEM continues to be elevated by 0.8% for at least 20 s.

determined using HU and U isotopes ($m = 0.011 \pm 0.0008$). A nonlinearity correction should therefore be the same for both U and Th.

3.5. *Effects of prior beam intensities*

As a complication to the consistent pattern of nonlinearity that emerges from the data discussed so far, we found a significant difference of the measured $^{234}U/^{238}U$ ratio depending on whether or not ^{235}U was also measured on the SEM (Fig. 7). It can be seen that the $^{234}U/^{238}U$ ratios of different dilutions of HU show a significant (~1.5%) and systematic jump within a sequence when ^{235}U is interveningly measured on the SEM as part of the method. This effect is eliminated if ^{235}U is no longer measured on the SEM during a sequence. We can exclude the RPQ or the Faraday cup as a cause of this effect because collecting the ^{235}U beam on the SEM for 2 s is the only difference between the measurement sets in Fig. 7. It is also unlikely that it is related to the electronics of the counting system. The effect must therefore be related to the high intensity of ^{235}U measured on the SEM, which is about 130 times that of the ^{234}U beam.

We further explored this phenomenon by measuring the variation of the $^{234}U/^{238}U$ ratios over 20 s directly after applying a high intensity ^{235}U beam for 2 s on the SEM. The first $^{234}U/^{238}U$ ratio measured directly after the jump from ^{235}U to ^{234}U (with no stabilisation time) differed widely (10%) from the others. This effect can be explained by the time needed to equilibrate the charge of the Faraday cup. However, after this anomalously high first value, measured $^{234}U/^{238}U$ ratios continued to be 0.8% too high for at least 15–20 s using the SEM of Neptune II (i.e., $4.109 \times 10^{-5} \pm 7.2 \times 10^{-8}$ compared to $4.079 \times 10^{-5} \pm 9 \times 10^{-8}$, Fig. 8). A similar result was obtained using Neptune I ($4.537 \times 10^{-5} \pm 9 \times 10^{-8}$ with a jump on ^{235}U and $4.499 \times 10^{-5} \pm 1 \times 10^{-7}$ without a jump on ^{235}U). Note also that there is no significant decline in the elevated ratio during the 20 s measurement interval, suggesting that the lifetime of this effect is substantial. The same experiment on the TIMS showed the short-term effect due to the charging of the Faraday cup, but the continuing effect on $^{234}U/^{238}U$ was not detected ($5.377 \times 10^{-5} \pm 7 \times 10^{-8}$ with a jump on ^{235}U and $5.385 \times 10^{-5} \pm 1 \times 10^{-7}$ without a jump on ^{235}U, Fig. 9).

We further tested the effect of prior measurement of high intensities for $^{229}Th/^{232}Th$ and $^{230}Th/^{232}Th$ ratios using a spiked TML thorium solution in three experiments: (1) measuring only $^{230}Th/^{232}Th$, (2) alternate measurement of $^{229}Th/^{232}Th$ and $^{230}Th/^{232}Th$ within one multi-static method, and (3) measuring only $^{229}Th/^{232}Th$. The multi-static method (experiment 2) is typical of that used for routine collection of thorium isotope ratios in MC-ICPMS and TIMS. The

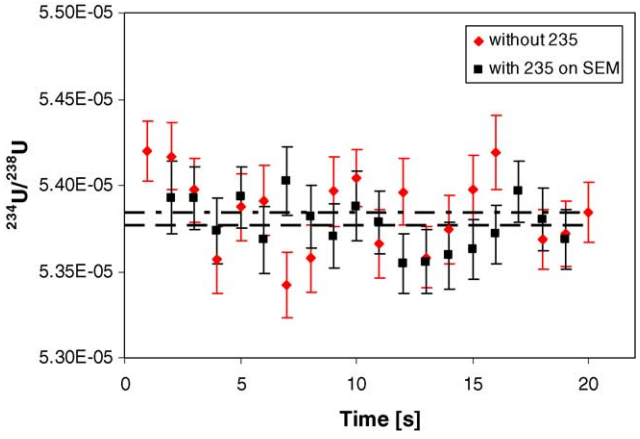

Fig. 9. The same experiment as Fig. 8 but using a Triton TIMS. No elevated $^{234}U/^{238}U$ ratios can be observed after applying a high intensity (^{235}U) beam to the SEM (mean values indicated by dashed line (with ^{235}U) and chained line (without ^{235}U)).

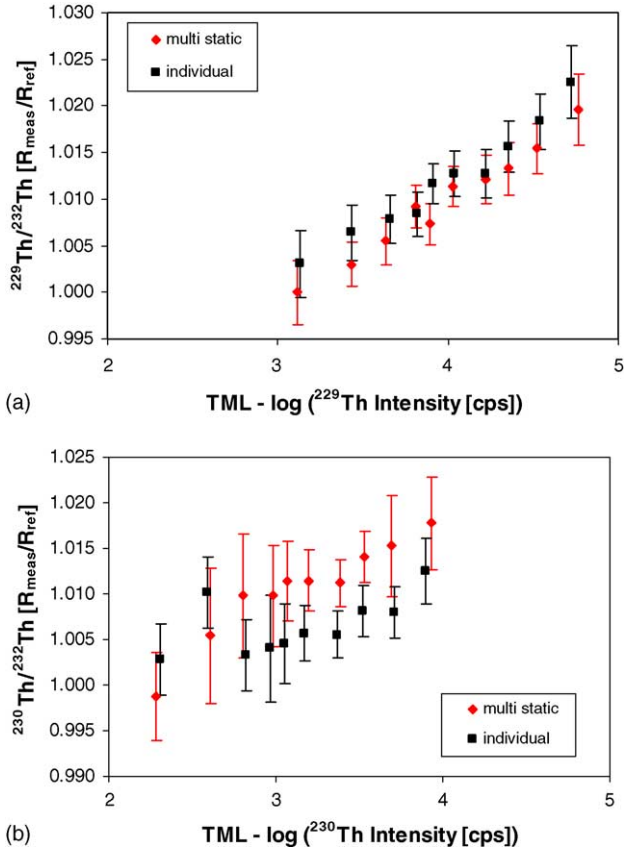

Fig. 10. (a) ^{229}Th/^{232}Th ratios of TML thorium solution measured on Neptune I with ("multi-static") and without ("individual") jump on ^{230}Th. The individual ratios show slightly (0.3%) higher values than the ones derived by multi-static measurements, but within the uncertainty they are almost the same. (b) ^{230}Th/^{232}Th ratios of TML measured on Neptune I with ("multi-static") and without ("individual") jump on ^{229}Th. The individual ratios are about 0.5% smaller than the multi-static results.

intensity of ^{229}Th was about seven times the ^{230}Th intensity. This caused an offset of about five permil between the ^{230}Th/^{232}Th ratio measured on its own and in conjunction with ^{229}Th/^{232}Th (Fig. 10). There was not such an obvious difference in the measured ^{229}Th/^{232}Th ratio when measured in conjunction with the ^{230}Th/^{232}Th ratio, but the ^{229}Th/^{232}Th ratio measured on its own seems to be about 0.3% higher.

3.6. Nonlinearity characterisation using multi-static measurements and TIMS

Finally, we tried to identify possible SEM nonlinearity at small count rates by TIMS. These experiments were performed using a ThermoFinnigan Triton MC-TIMS equipped with the same type of ETP multiplier. Unfortunately, one cannot adopt the same experimental setup of using external standard measurements at constant intensity for yield and mass fractionation correction for TIMS because switching between different samples on a TIMS is not rapid and requires filament heating, new focussing and tuning which influences the actual yield. Experimental details on how we performed this TIMS experiment are given in the Appendix. Our preliminary results indicate that within the uncertainties, the ^{234}U/^{238}U ratios of uraninite derived at two different low ^{234}U intensities of 45 and 560 cps are the same ($5.3060 \times 10^{-5} \pm 2.9 \times 10^{-7}$ and $5.3185 \times 10^{-5} \pm 1.2 \times 10^{-7}$, respectively). However, the ^{234}U/^{238}U ratio of 5.3185×10^{-5} for the ^{234}U intensity of 560 cps is significantly lower than the known value for secular equilibrium. This could be explained by the yield determination made using a beam intensity of 2.3×10^5 cps. The offset of 2.8% to the reference value could either suggest something like 1% nonlinearity per decade, or that the yield characterisation is not accurate for other reasons such as changing of the focus position between calibration and measurement. Our results are thus equivocal, so far we have no clear evidence for the nonlinearity effect at low count rates using TIMS. Obviously, further work on TIMS is necessary.

4. Discussion

4.1. Nonlinearity effects

Our observations strongly suggest that nonlinearity of commonly used SEMs using MC-ICPMS extends to much lower beam intensities than suggested by Richter et al. [1] for TIMS. The observed nonlinearity starts at count rates as low as 10 cps (here called first component of nonlinearity), and above count rates of 10^4 to 10^5 cps an additional degree of nonlinearity is observed (here called second component of nonlinearity). To our knowledge, the first component of nonlinearity starting without an obvious threshold, has not previously been reported. The second component of nonlinearity seems to equate with that observed by Richter et al. [1]. Both the threshold for the onset of the second component of nonlinearity and the magnitude of the effect vary between individual multipliers, as also reported by Richter et al. [1]. The observed nonlinearity effects are more pronounced for the Neptune I SEM compared to that of Neptune II, but the general form of the effects is similar, suggesting the problem is general rather than being associated with one specific multiplier.

We exclude dead time as the cause for the effects documented for the SEMs of Neptune I and II. We can envisage two scenarios in which the dead time could influence the observations: the actual dead time of the SEM could exceed the electronic dead time resulting in a greater total dead time, or our electronically measured dead time is not accurate and it is less than 20 ns. If the real dead time was less than 20 ns, our dead time correction would contribute to the measured nonlinearity at high count rates. However, this effect is less than 0.2% for 10^5 cps and less than 2% even for 10^6 cps. Thus, the nonlinearity effects we found, especially at low count rates, cannot be attributed to an underestimated dead time. If the real dead time was greater than the electronic dead time, one would expect an opposite effect to that observed as dead time reduces the effective count rate response of the SEM.

The causes of SEM nonlinearity are not well understood, and Richter et al. [1] discuss possible explanations for what we have recognised as a second component of nonlinearity. The dynodes, especially the final one, are exposed to high electron avalanche pulses which can lead to charging effects because electrons can be captured in traps in the crystal lattice and on the surface. The residence time of electrons in most traps is quite short (in the order of ns), and the charge decays exponentially. Thus, after each electron pulse there is an exponentially decaying electron current due to detrapping electrons. If a new electron pulse occurs at the final dynode before the charge has decayed, the new pulse is superimposed and the current therefore increased. The magnitude of this increase in pulse size depends on the time between two pulses. The closer they are, the more the succeeding one is increased. As a result, the magnitude of small pulses which should be below the count discriminator level, can be sufficiently increased to exceed the threshold and hence be counted. This leads to relatively more counts at higher count rates and conveniently explains the second component of nonlinearity with a threshold of 10^4 to 10^5 cps.

It is difficult to determine a reason for the newly reported first component of nonlinearity. It could be a charging effect, but thermal effects may also be important because the SEM is heated by ion impact (converting dyonode) and the electron avalanches (especially the last dynodes). Trapped electrons have a characteristic lifetime τ which is a function of the temperature. The probability, w, of thermal fading at temperature T is proportional to $\exp(-E_a/kT)$, where E_a is the energy difference between the trap energy level and the conduction band, k is the Boltzmann constant and T the (absolute) temperature (e.g., [15]). The decay of trapped electrons can be described by

$$S(t) = S_0 \exp\left(\frac{-t}{\tau}\right) \quad (2)$$

where S is number of trapped electrons and $\tau = 1/w$.

It is possible that the dynodes have traps with temperature dependent lifetimes in the range of ms. Heating may therefore decrease the lifetime of trapped electrons, increasing the rate of release of electrons and thus the residual current. Although a small effect, heating may also add kinetic energy to the released secondary electrons which could increase the final pulse height above discrimination level. Such thermal effects may explain the dependence of count rate on the prior beam intensity we have observed experimentally, as cooling of the dynodes will take relatively long in the internal vacuum. Thus, thermal effects might be responsible for the nonlinearity at low count rates and may explain why there is no threshold to this nonlinearity effect.

4.2. Memory effects

Our uraninite experiments using Neptune I show a significant difference between $^{234}U/^{238}U$ derived measured with and without ^{235}U applied to the SEM. Whilst a short (2 s) jump on ^{235}U generates $^{234}U/^{238}U$ ratios elevated by 0.8% thereafter (Fig. 8), a ^{235}U beam regularly applied to the SEM during a multi-static $^{234}U/^{238}U$ and $^{235}U/^{238}U$ measurement results in a $^{234}U/^{238}U$ ratio elevated by 1.5% on Neptune 1 (Fig. 7). Therefore both the high intensity of ^{235}U and the time the beam was applied to the SEM seem to have an effect on the ^{234}U measurements. If only the ^{235}U intensity was responsible for the nonlinearity effect for both, ^{234}U and ^{235}U, one would expect a more than 2% elevated $^{234}U/^{238}U$ ratio as the ^{235}U intensity is 132 times greater than the ^{234}U intensity. We suggest that some combination of two different intensities, alternately applied to the SEM result in an "effective" intensity which determines the nonlinearity behaviour. A possible reason for the effective intensity could be a heating effect which depends on the beam intensities. The beam intensity and the time the beam is applied to the SEM result in a temperature T. Thus, two different beam intensities alternately applied to the SEM result in a mean temperature. Therefore, with two different intensities C_1 and C_2 applied to the SEM, the effective intensity could be described by

$$C_{eff} = aC_1 + bC_2 \quad (3)$$

where $a + b = 1$ and $0 \leq a,b \leq 1$.

For similar integration times of C_1 and C_2, $a = b = 0.5$ seems to be an adequate assumption.

The memory effect described above also explains the finding that for a bracketing NBL-112a ^{234}U intensity of 2×10^4 cps, the $^{234}U/^{238}U$ ratio derived at the same ^{234}U intensity of HU is 0.3% too high (Fig. 3). The data on both sample and standard were obtained using a multi-static routine with an intervening ^{236}U beam and so again the effective intensity is dependent on all intensities alternately applied to the SEM (Eq. (3)). For the HU sample with 2×10^4 cps of ^{234}U and 1.4×10^4 cps of ^{236}U, we derive an effective intensity of about 1.7×10^4 cps, whereas the bracketing NBL-112a has 2×10^4 cps of ^{234}U but no ^{236}U (the abundance sensitivity is monitored at this mass) and so has a lower C_{eff} of 1×10^4 cps. Given a nonlinearity starting at 10 cps and a slope of 1.1% per decade, the $^{234}U/^{238}U$ ratio of the HU sample is expected to be elevated by 0.25% relative to 10^4 cps effective intensity of NBL-112a which was used for yield calculation.

Our results also potentially explain why the nonlinearity characterisation according to Richter et al. [1] using a peak jump routine with U500 did not show the low intensity effects. As discussed previously, the peak jump routine on an ICPMS with low intensities results in large uncertainties due to short-term instabilities of the beam intensity. Thus, it is not useful for precise characterisation of ICPMS nonlinearity, but the effect of a prior high beam intensity applied to the SEM may also mask the nonlinearity. For U500, an offset between measured and known $^{234}U/^{235}U$ ratio would be expected because the ^{235}U intensity of U500 is about 100 times greater than the ^{234}U intensity. For Neptune I, with a first nonlinearity of 1.1% per decade of beam intensity, a two

orders of magnitude difference of intensity would lead to a relative yield difference of 2.2% and thus an underestimation of the $^{234}U/^{235}U$ ratio by 2.2%. This is sufficiently large that it should be measurable even at low precision, but no obvious nonlinearity effects can be seen in our data (Fig. 2) for count rates less than 10^5 cps. The reason for not observing the nonlinearity at low count rates may be that the peak jump routine also collects ^{235}U (and ^{238}U) in the SEM, and so these high intensity beams affect the subsequent measurement of the low intensity ^{234}U (and ^{236}U) beams. If the effective count rate was an average of the different ^{234}U, ^{235}U, ^{236}U and ^{238}U intensities, this would lead to a similar nonlinearity for all isotopes. Consequently, the nonlinearity effect at low count rates is masked and cannot be identified using the $^{234}U/^{235}U$ ratio derived by peak jumping.

4.3. Implications for other common ICPMS protocols

At present there is no single, commonly agreed MC-ICPMS method for U-series measurements, instead a number of slightly different methods are used by different laboratories, as described in Goldstein and Stirling [2]. For MC-ICPMS isotope ratio measurements using an SEM, both the mass fractionation factor and the SEM–Faraday cup yield need to be determined. Therefore, either an external standard solution with known isotopic ratios must be measured before and after the sample, or a known internal isotope ratio such as the natural $^{235}U/^{238}U$ is used. Note that every yield measurement includes the SEM nonlinearity effect specific for the particular count rate. Therefore, nonlinearity effects can be hidden if similar count rates are used for the sample measurement and the external standard yield determination. This can be demonstrated by measurements with matching intensities of samples and standard on Neptune I (Fig. 11). Because ^{234}U count rates for NBL-112a match those of ^{234}U of uraninite, no intensity dependency of the $^{234}U/^{238}U$ ratio can be observed, although this SEM is known to be strongly nonlinear. However, we observe a $^{234}U/^{238}U$ ratio that is about 0.5% too high. This can be explained by the multi-static routine used to obtain the data. As discussed above the ^{234}U intensity of the bracketing NBL-112a was matched to the sample intensity, but the effective intensity was smaller because NBL-112a does not contain ^{236}U. The matching intensities procedure is one of the possible external correction techniques that can be used for isotope measurements using ICPMS, but it is inherently unsuitable for our applications.

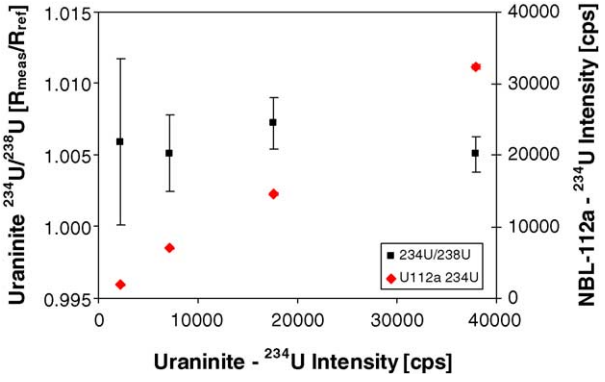

Fig. 11. HU $^{234}U/^{238}U$ measurements with matching ^{234}U intensity of bracketing NBL-112a standard and sample. Using this protocol no nonlinearity effect can be observed, although the SEM in Neptune I is known to be highly nonlinear. A 0.5% overestimation of $^{234}U/^{238}U$ is probably due to an effective intensity of NBL-U112a which does not match the effective intensity of HU. See text for details.

For peak jump or multi-static routines the nonlinearity effect is found to be complex and dependent on the various intensities applied to the SEM. Therefore, the nonlinearity effect may not be observed in measured ratios using multi-static protocols that rely on an "internal" $^{235}U/^{238}U$ ratio to correct for SEM yield. This approach can yield relatively good results but lead to the erroneous conclusion that a multiplier behaves linearly even up to count rates of about 10^6 cps.

5. Recommended protocols

5.1. Nonlinearity characterisation

SEM nonlinearity characterisation for MC-ICPMS must be done using a method similar to the one described above in order to derive the slopes and nominal thresholds of the two possible effects. We therefore suggest a protocol including the following key aspects.

(a) A stock solution with an isotopic composition of high dynamic range (e.g., natural uranium or HU) is required. This guarantees that all dilutions made from the stock have the same isotopic composition and the ratio can be statically measured on SEM and Faraday cup.
(b) Different dilutions of the stock must be prepared, the low abundant isotope is to be measured on the SEM, and the high abundant isotope must be measured on a Faraday cup for static measurements.
(c) An external standard for mass fractionation and yield determination is needed (e.g., NBL-112a). This should be measured alternately with the samples, and the intensity of the bracketing standard should not be varied.
(d) The measured ratios of the samples at different intensities show relative deviations from the yield derived by the bracketing standard, allowing calculation of the nonlinearity slope(s) in log-linear space.

5.2. U and Th isotope measurements using MC-ICPMS

As a result of our findings we propose a protocol for reliable U-series isotopes measurements by MC-ICPMS. This protocol is currently the standard method used by the Bristol Isotope Group and it is designed to avoid multi-static use of the SEM.

The protocol for U samples is divided into two parts:

1. collect only ^{236}U in the SEM to derive the ^{236}U/^{238}U ratio, while the ^{235}U/^{238}U ratio is measured simultaneously on two Faraday cups, and
2. collect only ^{234}U in the SEM to derive the ^{234}U/^{238}U ratio.

The same sample solution is therefore used twice with a short (2 min) break between the two measurements. To minimise potential memory effects it is recommended that one starts with the lower intensity applied to the SEM. The measurement of the bracketing U-standard is divided in the same way as for the samples.

For Th, the method depends on the ^{232}Th concentration. For high ^{232}Th concentrations, ^{232}Th must be measured on the Faraday cup whereas for low concentrations it is measured on the SEM. The "thorium Faraday" method (^{232}Th on Faraday cup) is split into two static measurements:

1. collect only ^{229}Th in the SEM for ^{229}Th/^{232}Th ratio, and
2. collect only ^{230}Th in the SEM for ^{230}Th/^{232}Th ratio.

This method is also applied for the bracketing Th-standard (TEDDi). Low ^{232}Th intensities require a peak jump routine for Th measurements. Collecting ion beams of different intensities in the SEM using a peak jump routine complicates a nonlinearity correction. However, the "thorium SEM" method (^{232}Th on SEM) is divided into two measurements using peak jump routines:

1. collect ^{230}Th and ^{229}Th alternately in the SEM for ^{230}Th/^{229}Th, and
2. collect ^{232}Th and ^{229}Th alternately in the SEM for ^{232}Th/^{229}Th.

In this case the potential effect of the different beam intensities on the measured ratio must be considered, and an effective countrate has to be used for nonlinearity correction.

5.3. Nonlinearity correction

Given a nonlinearity slope m in log-linear space and a nominal threshold C_{lim}, Richter et al. [1] suggest a nonlinearity correction in case of $C_{\mathrm{meas}} > C_{\mathrm{lim}}$ according to

$$C_{\mathrm{corr}} = C_{\mathrm{meas}} \left\{ 1 - m \log \left[\frac{C_{\mathrm{meas}}}{C_{\mathrm{lim}}} \right] \right\} \quad (4)$$

where C_{corr} and C_{meas} are corrected and measured count rate, respectively, m nonlinearity slope per decade of count rate intensity and C_{lim} nonlinearity threshold.

In case of two components of nonlinearity, as found in our study, we suggest a modified nonlinearity correction. Splitting the measurement methods as suggested above, corrections using two different slopes can be usefully applied. For $C_{\mathrm{meas}} > C_{\mathrm{lim},1}$

$$C_{\mathrm{corr},1} = C_{\mathrm{meas}} \left\{ 1 - m_1 \log \left[\frac{C_{\mathrm{meas}}}{C_{\mathrm{lim},1}} \right] \right\} \quad (5)$$

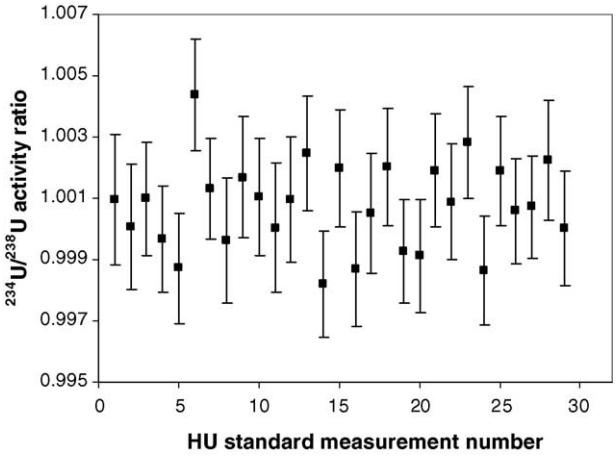

Fig. 12. Reproducibility of ^{234}U/^{238}U ratio of HU (n = 29). Eight differently spiked HU samples were used.

and if $C_{\mathrm{meas}} > C_{\mathrm{lim},2}$

$$C_{\mathrm{corr},2} = C_{\mathrm{corr},1} \left\{ 1 - (m_2 - m_1) \log \left[\frac{C_{\mathrm{meas}}}{C_{\mathrm{lim},2}} \right] \right\} \quad (6)$$

Here, the difference between the two total nonlinearity slopes, $m_2 - m_1$, is equivalent to the nonlinearity slope m found by Richter et al. [1]. If an SEM did not show the first component of nonlinearity (i.e., $m_1 = 0$), the correction would become that of Richter et al. [1] (Eq. (4)). If all isotopes are to be measured on the SEM in the same routine, and again in case of $C_{\mathrm{meas}} > C_{\mathrm{lim},1}$, we recommend a correction for nonlinearity according to Eqs. (7) and (6).

$$C_{\mathrm{corr},1} = C_{\mathrm{meas}} \left\{ 1 - m_1 \log \left[\frac{C_{\mathrm{eff}}}{C_{\mathrm{lim},1}} \right] \right\} \quad (7)$$

with C_{eff} according to Eq. (3).

Unlike corrections for dead time, which can be precisely calibrated and thus corrected online, the nonlinearity corrections described above are best conducted offline, because the origin of the nonlinearity effects is poorly known, and the parameters for the empirical correction function have to be determined experimentally. However, the complex dependency on an effective beam intensity for nonlinearity effects and the intrinsic instability of the plasma means that it makes sense to inspect and check the data before a routine correction is applied.

Our current reproducibility of the ^{234}U/^{238}U activity ratio of HU is based on 29 uranium measurements since our new protocol was established (Fig. 12). The data consist of measurements of eight aliquots of HU spiked with ^{236}U to give ^{234}U/^{236}U concentration ratios between 1.35 and 23.4. We currently have a reproducibility of ^{234}U/^{238}U = 1.0007 ± 0.0028 (2σ).

6. Conclusions

SEMs are essential components of mass spectrometers used for high-precision determination of isotopic ratios at low abundance, however, almost every SEM is nonlinear. We have developed protocols to investigate thoroughly the properties of SEMs using static SEM–Faraday cup sequences on MC-ICPMS. As a result of our studies on SEM nonlinearity we have found three effects:

- nonlinearity starting at low count rates of 10 cps, which has not been reported previously,
- a second component of nonlinearity with a threshold of 10^4 to 10^5 cps, which probably equates the nonlinearity described by Richter et al. [1], and
- a memory effect with an elevated SEM yield after a high intensity beam is applied to the multiplier.

It may be that the extent of nonlinearity for the ETP multiplier currently installed on our instrument Neptune I is anomalously large, but the results on Neptune II confirm the findings albeit with smaller overall effects. These findings have important implications for the accurate measurement of high dynamic isotope ratios at low abundance in a wide variety of fields including geology, nuclear industry, archaeometry and cosmochemistry.

A simple protocol is described for routine investigation of such effects that uses static measurements of a known isotopic ratio such as $^{234}U/^{238}U$ of a solution of uraninite at secular equilibrium, with different ^{234}U intensities applied to the SEM. The correction factors for mass fractionation and SEM–Faraday cup yield are based on interpolated values for an external standard of NBL-112a, natural uranium with well-established $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios.

It is difficult to identify the reason for the nonlinearity starting at low count rates, but it could be either a thermal or a charging effect. More data for different SEMs is desirable as well as further analogous work on TIMS.

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Appendix A. TIMS analytical protocol

The sample separation and purification for TIMS is basically the same as for ICPMS. Uranium is separated from an unspiked uraninite solution, then dried down and taken up in a drop of HNO_3. The U-samples are loaded on Re-filaments and the $^{234}U/^{238}U$ ratio is measured using a double filament technique.

For our linearity tests different amounts of uranium were loaded on several filaments. The yield characterisation must be done individually using each sample itself. Usually a beam with an appropriate intensity is switched between SEM and Faraday cup to obtain the SEM to Faraday cup yield. To derive similar experimental results as for the ICPMS experiments with a yield derived by external standard measurements at a constant intensity, the TIMS SEM–Faraday cup yield was measured after tuning with a ^{238}U beam always at the same intensity of 2.3×10^5 cps for all measurements. The yield correction was done online. Therefore all results are relative to the yield at that intensity. After the yield was determined the filament was carefully heated to a temperature of 1700 °C.

Due to the low ^{235}U intensities it is not possible to derive a static $^{235}U/^{238}U$ ratio, with both isotopes measured on Faraday cups. Therefore no mass fractionation correction was possible due to a lack of a reference value and all TIMS data presented in this study are not corrected for mass fractionation. However, absolute mass fractionation is small for TIMS at high masses and its variability between samples small. As for ICPMS measurements, corrections for dead time, baseline and darknoise are done online.

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