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Linearity tests for secondary electron multipliers used in isotope ratio mass spectrometry

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Abstract

Methods are described for testing the linearity in the count-rate response of discrete dynode secondary electron multipliers (SEM), widely used to detect the smallest ion currents in various fields of mass spectrometry. The results consistently reveal small degrees of nonlinearity and demonstrate the need to test and characterize the response of SEMs to achieve accurate measurements. Recommendations and mathematical algorithms are given to improve the measurement results of secondary electron multipliers used in isotope ratio mass spectrometry. Analyses of a certified uranium reference material (CRM U500, $^{234}U/^{235}U/^{236}U/^{238}U \approx 0.01/1/0.0015/1$) using a SEM in ion-counting mode yielded deviations from linearity ranging up to 1.5% in the measured $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios. Because the dead time of the ion-counting electronics was determined independently, the observed deviations could be distinguished from the dead-time effect, indicating that nonlinearity was inherent to the SEM. It is shown that the deviations have a similar dependence on count rate for four SEMs produced by ETP and two SEMs produced by MasCom: for count rates below $\sim 2 \times 10^4$ counts per second no deviations were found, and consequently, no correction is required. Beyond that rate, the output response of the SEM starts to increase linearly with the logarithm of the applied count rate, with slopes ranging between 0.2% and 0.9% per decade of count rate for the SEMs investigated in this work. Based on the observed deviations, an appropriate correction algorithm, called restricted logarithmic rate effect (RLR), was developed and tested by further measurements of Certified Reference Materials U030A, U050, U200, U500, and U900. A comparison with the uncorrected data and the overall logarithmic corrected data shows the excellent performance of the RLR correction for achieving accurate isotope ratio results. For the proper reporting of ion-counting measurements, the uncertainty in quantifying the nonlinearity component should be included in the total uncertainty budget. The RLR correction is associated with an increase in the uncertainty budget by a factor of 1.1–1.5, even for count rates beyond 10^5 counts per second. Furthermore, the deviations from linearity show a small dependence on the high voltage applied to the SEM. Surface charge effects at the final dynode stages of the SEM are inferred to be responsible for the observed nonlinearity. These effects occur within different manufactured varieties of discrete dynode electron multipliers. These observations indicate that linearity checks are required when a SEM is used for high-accuracy isotope ratio measurements of small quantities of analyte. (Int J Mass Spectrom 206 (2001) 105–127) © 2001 Elsevier Science B.V.

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1. Introduction

Discrete dynode secondary electron multipliers (SEM) are used extensively as single-charged-particle detectors in various types of spectrometers. Technical details of SEM design and operational characteristics can be found in references [1] and [2]. Their ability to amplify small ion currents by a factor of 10^4–10^8 to easily measurable electrical currents or to create countable electric pulses out of single-particle events has made them valuable in various areas of measurement science where a highly sensitive detection method is required. There are generally two ways the SEM can be operated: In analogue mode, the input ion current is first amplified by the SEM and then measured as a voltage across a high-ohmic resistor. The output voltage signal is used as a measure of the input ion current, but this depends strongly (exponentially) on the high voltage applied to the SEM dynode array. In this operation mode, the electronic background noise is a limiting factor in the detection of very small ion currents.

In pulse-counting mode, each incident ion or particle creates an electron cascade (usually $\sim 10^7$–10^8 electrons) in the SEM, generating an electrical pulse that is counted with appropriate digital counter/timer electronics. A high voltage (HV) is applied to the SEM dynode array to produce an output count rate that is only slightly dependent on the high voltage. This relationship is generally described as the plateau region on a plot of count rate on the ordinate and high voltage on the abscissa. When the plateau is reached, almost all incident particles or ions are detected. Therefore, in pulse-counting mode, the final output of the SEM is less dependent on the SEM high voltage than on the analogue mode. Another advantage of the pulse-counting mode is a generally lower detection limit for particle or ion currents.

SEMs operated in the pulse-counting mode are used in various types of isotope ratio mass spectrometry, for example, thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS). They are currently among the most sensitive detectors for measuring extremely small ion currents ($<10^{-15}$A) or particle count rates, a requirement for the detection of low abundant isotopes and/or for isotopic analysis of very small quantities of analyte.

SEMs developed and manufactured by ETP (ETP-SGE, Ermington, Australia; a detailed description can be found in [3]) joined the market in the early 1990s. For example, the types AF150H(M9) and AF180H(M9) from ETP are used in TIMS instruments manufactured by Finnigan MAT (Bremen, Germany) in various fields such as geochemistry and nuclear chemistry. These instruments, capable of the highest precision and accuracy for isotope ratio measurements, depend on a linear response of each detector system.

Compared to other SEMs, the ETPs have several advantages that include low dark noise of <1 cpm (count per minute) in ion-counting mode and a high dynamic range of 10^5–10^6. In combination with a Faraday cup detector, the dynamic range can reach 10^8–10^{10} (e.g., using the Finnigan MAT262-RPQ-PLUS [4,5]). Furthermore, they are small in size ($10 \times 2 \times 2$ cm^3), and the AL-based dynode surfaces are supposed to be stable in air. All dynodes (2×0.3 cm^2) are mounted between and perpendicular to two ceramic plates (10×2 cm^2) that insulate the dynodes from each other. The resistors are mounted onto the outside of the ceramic plates. The inner surfaces of the insulating ceramic plates are, however, not shielded against the electron avalanche developed through the dynode chain.

Recently, MasCom GmbH (Bremen, Germany) restarted the production of the Reinhardt series of SEMs. As shown on the web site http://www.mascom-ms.de, MasCom supplies a discrete dynode SEM with Cu-Be-coated dynodes (type MasCom MC-12/17), which can be adapted to various types of mass spectrometers. They are slightly larger in size than the ETPs, $\sim 12 \times 4 \times 4$ cm^3. The dynodes (4×0.5 cm^2) are mounted sequentially on ceramic rods insulated from each other by ceramic spacers. The ceramics are shielded against the electron avalanche by an appropriate dynode design.

In addition to the SEM design characteristics, there are various physical processes involved in any SEM operation that can affect the count-rate response. These include the velocity and incidence angle of ion impact on the first dynode, the release of electrons at the first and successive dynodes, the acceleration of electrons between the dynodes, surface charge effects at the final dynodes or the collector end of the SEM, and so forth. Count-rate effects attributed to these physical processes have been observed for discrete dynode multipliers, channeltrons, and microchannel plates (MPCs) [6–8]. Therefore, the relationship between input ion current and output SEM response should be empirically determined or verified for any type of SEM.

Because of the laboratory's role in certifying nuclear materials and to achieve the required measurement accuracy and traceability, testing of a variety of SEMs for use in mass spectrometry was initiated at New Brunswick Laboratory.

2. SEM linearity

The most accurate pulse-counting SEM measurements ideally require a linear relationship between the sample ion current applied to the SEM and the output count rate. For this linear relationship, the intercept represents the dark noise, which is the output count rate registered by the counting electronics in the case where there are no incident ions. The dark noise can be measured and corrected for mathematically and is usually very small compared to the measured count rates. The slope of the linear relationship represents the relative yield of the SEM, which is the ratio between the measured count rate (corrected for dark noise) and the true rate of ions entering the SEM. If a SEM is linear, the relative yield, an inherent property of the SEM, is independent of the count rate applied to the SEM.

The relative yield of most SEMs is ~90%–100% when the applied HV is set to just above the "knee" of the HV–count rate plateau curve. The relative yield is usually defined in comparison to a Faraday cup, whose ion detection efficiency is close to 100% but is known only to about ±1%. This is because of the uncertainty of the resistance for the 10^{11} Ω resistor used in Faraday current amplifiers. The high ohmic precision resistor, however, is extremely stable and does not influence isotope ratio measurements. When the linearity of a SEM is to be checked, certified isotope reference materials (CRMs) are used to define measurement bias and to achieve traceability. The approach used at New Brunswick Laboratory for assessing the linearity of a SEM assumes that the relative yield is the same for all count rates and, therefore, that the isotope ratio measurements of CRMs agree with their certified values. Practically, if a variety of different CRMs covering the entire count-rate range have been analyzed and show agreement with the certified values, it can be assumed that linearity is given and the SEM is linear. In the case where only some of the measurements of CRMs agree with the certified values, linearity may be limited to a narrow range of count rates for that SEM. However, if deviations from linearity occur, results based on CRM measurements could be used to define an empirically determined correction algorithm.

In this study, two experimental procedures are introduced that provide a check of SEM linearity. First, there is the SEM-only procedure: a series of peak-jumping measurements performed using only the SEM over the desired range of count rates. If the SEM response is linear, the measured isotope ratios should agree with certified ratios. Second, there is the SEM/FAR procedure: combined SEM-Faraday cup measurements where the SEM is used to detect a low-abundance isotope of a CRM and Faraday cups for the major isotopes. Given accurate measurements on the Faraday cups, the dynamic range of the SEM could then be investigated by changing the overall ion beam intensity in a step-by-step process. The uncertainty of the intercalibration between the SEM and the Faraday cup (yield of the SEM relative to a Faraday cup), performed before the linearity check by switching one ion beam of appropriate size between the SEM and a Faraday cup, has to be taken into account for any combined SEM/FAR measurement. This may lead to a significantly increased uncertainty. The range of count rates covered by this method is limited

by the relative CRM abundances, for example, in the case of the CRM U500, the $^{236}U/^{235}U$ ratio (value $\sim 1.5 \times 10^{-3}$) only covers about three orders of magnitude. Examples of both procedures are given in the experimental section and include a discussion of the results and advantages of each method.

3. Use of certified reference materials for linearity checks

To perform a linearity check, suitable CRMs are needed 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 that can be used for mass fractionation correction. Any nonlinearity in the SEM could then by nullified by rationing isotopes of comparable count rate. There are several CRMs that fulfil both requirements, two representatives of which are described briefly here: First is the IRMM-072/1-13 series, developed at the Institute for Reference Materials and Measurements (IRMM) in the 1980s [9]. This series consists of 13 CRMs and is characterized by a $^{238}U/^{235}U$ ratio close to unity, certified with an uncertainty of 0.02% (2 σ). The series has $^{233}U/^{235}U$ ratios ranging in 13 steps between 1 and 0.000002, certified with an uncertainty of 0.03% (2 σ). Therefore, the IRMM-072/1-13 series fulfils both requirements mentioned above. The IRMM-072/1-13 series has the advantage that a series of measurements can be performed with uniform ion current intensities of ^{235}U and ^{238}U. Unfortunately, the supplies of this reference material are nearly exhausted, but diluted samples are currently in preparation.

Reference [9] provides an example of a linearity test using IRMM-072/1-10, performed on a SEM in analogue mode. In this example, the ^{235}U and ^{238}U ion beams were kept constant at an ion current size of $\sim 6 \times 10^{-13}$A, corresponding to a count rate of $\sim 3.75 \times 10^{6}$ counts per second. Because of the variation in abundances of ^{233}U in different members of the IRMM-072 series, the ^{233}U ion current varied in intensity between 6×10^{-13}A and 1.2×10^{-16}A, corresponding to a count rate range from 3.75×10^{6} down to 7.5×10^{2} counts per second. The $^{233}U/^{235}U$ results of all runs are compared to the certified values in Fig. 1, which shows the relative deviations of the measured isotope ratios from the certified values versus the ion current of the minor isotope ^{233}U. The results indicate that the SEM used in this test is clearly nonlinear, exhibiting significant deviations of up to several percent from the certified ratios. Fig. 1 also shows a quadratic fit (dashed line), which reasonably approximates the measured nonlinear results. It is difficult, however, to find a single physical process that can explain this pattern. It seems more likely that there are at least two processes responsible for the observed pattern. For high ion currents, charging effects at the final dynodes of the SEM might be responsible for an (initial) increase of the SEM yield. At low ion currents, the influence from the peak tail of ^{235}U may slightly increase the $^{233}U/^{235}U$ isotope ratio. Although this effect is not related to the SEM, it might cause a bias in the SEM response. The quadratic fit shown in Fig. 1 can be used to develop a correction algorithm where the correction factor is defined as the inverse of the calculated quadratic fit, as represented by the bold line in Fig. 1. The correction algorithm is normalized to an ion current value where no bias from the certified ratio was observed, in this case where the quadratic fit to the data crosses the unity line in Fig. 1.

The test results clearly show that SEMs can indeed be nonlinear and that linearity checks should be performed before a SEM is qualified and used for measuring accurate isotope ratios. Because the SEM in this test using the IRMM series was operated in analogue mode, no dead time correction was required in this experiment. The nonlinearity in the analogue operation of the SEM indicates that the nonlinearity is not necessarily a dead-time effect.

The NBL CRM U500 is another widely used standard that can be used for assessing linearity. The isotopic composition of CRM U500 is characterized by a $^{238}U/^{235}U$ ratio close to unity and by a range of minor isotopic ratios ($^{234}U/^{235}U = 0.0104$ and $^{236}U/^{235}U = 0.0015$). The minor ratios are similar to those of $^{233}U/^{235}U$ in IRMM-072/7-9; however, the U500 can only be used to measure three intensity-ratio data points (including the unity point) for Fig. 1 instead of

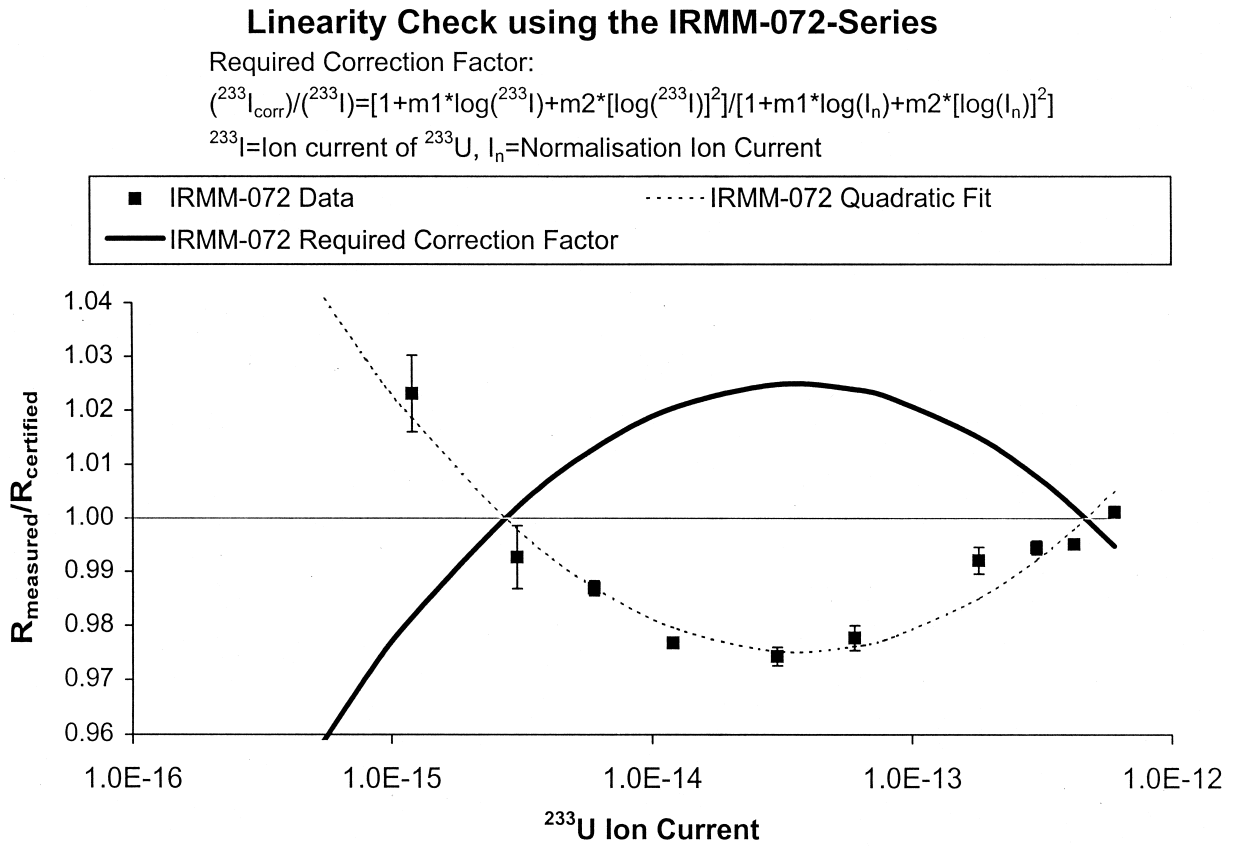

Fig. 1. Results of a linearity check using the IRMM-072 series, applied to a SEM operated in analogue mode. Data are regressed using a quadratic fit, which is used to obtain a correction algorithm.

10 points using the IRMM-072-series. These three points allow for a quadratic fit, but they cover only a dynamic range of less than three orders of magnitude, which is not sufficient for many applications.

To obtain more information on linearity using the U500 and to cover a broader range of count rates, a series of ratio measurements at different ^{235}U (and ^{238}U) intensities has to be performed. The measured ^{234}U/^{235}U and ^{236}U/^{235}U ratios, however, may be subject to count rate–dependent nonlinearity effects in both the numerator (^{234}U, ^{236}U) and denominator (^{235}U) isotopes. These effects may be difficult to distinguish from each other. If any deviation from linearity is found, the task for the analyst is to find a uniform correction algorithm that is only a function of the count rate (or ion current) applied to the SEM and does not depend on the ratio between abundances of two isotope masses. An example for a correction algorithm derived from ratio measurements within a broad range of count rates is given in the experimental section.

Unfortunately, the uncertainties of the certified ^{234}U/^{235}U and ^{236}U/^{235}U ratios in U500 are much larger (0.18% and 0.42%, respectively, 2 σ) than those of the ^{233}U/^{235}U ratio in IRMM-072 (0.03%). To obtain more precise and accurate values for these minor isotope ratios, static measurements on a Faraday multicollector were performed, the results of which are shown in the experimental section. These data allowed the use of CRM U500 for deciphering nonlinearity effects with sufficient precision.

Using the SEM/FAR experimental procedure, first a logarithmic algorithm was applied to correct for deviations from linearity. This algorithm is character-

ized predominantly by the rate effect parameter m, which gives the deviation per decade of the measured count rate from the true count rate:

$$c_{\text{corrected}} = c_{\text{measured}}\{1 + m[\log(c_{\text{measured}}) - \log(c_{\text{N}})]\};$$

$c_{\text{corrected}}$ denotes the corrected count rate, and c_{measured} denotes the measured count rate, which is already dead-time corrected (for details about dead-time determination and correction see the experimental section). The count rate c_{N} is a user-defined normalization value. The value of the rate-effect parameter, m, is usually about a few per-mil and is always negative. However, the actual value of the rate-effect parameter has to be determined individually for each SEM.

Uranium is quite suitable for testing the linearity of a SEM because a variety of certified U reference materials are available. Linearity corrections should also be determined for elements other than uranium. As shown by Fehn [10,11], the ion–electron conversion on the first dynode, and consequently the yield of a SEM, depends strongly on the atomic number of the impacting ion. Therefore, the nonlinearity effects observed for one element are not necessarily the same for all elements.

4. Description of experimental methods

At New Brunswick Laboratory, three of the thermal ionization mass spectrometers equipped with SEMs operated in ion-counting mode were used for linearity testing. The MS1 is a fixed multicollector Finnigan MAT261 equipped with SEMs of type ETP AF150H(M9) (called SEM1 and SEM2) and, later, with a MasCom MC-12/17 (called SEM6). The SEM in the fixed multicollector Finnigan MAT261 cannot be used simultaneously with any of the Faraday cups, as the magnetic field has to be switched by ~3.6% to deflect the ion beam into the SEM. For peak-jumping measurements involving both the SEM and the Faraday cups, an intercalibration between the two detectors is performed. This intercalibration was found to depend strongly on the focusing of the ion beam using the conventional electrostatic lens source.

The second mass spectrometer, MS2, is a variable multicollector Finnigan MAT261/262. The SEM (type ETP AF150H(M9), called SEM3) in this instrument can be used as an alternative to a central Faraday cup located axially in the variable multicollector array. Therefore, it is integrated into the multicollector system, and the ion beam can be switched between the SEM and the center Faraday cup just by switching an appropriate deflection voltage without changing the magnetic field. With this instrument, simultaneous measurements can be performed using the SEM together with Faraday cups.

The third mass spectrometer, MS3, used for linearity testing of SEMs is the Finnigan MAT TRITON. A detailed description of this new thermal ionization mass spectrometer is given in [12]. The TRITON is also a variable multicollector instrument, where the SEM is integrated into the multicollector system in a similar way as in the MAT261/262. The TRITON was first equipped with an ETP AF180H(M9) (called SEM4), which is similar to the type AF150H(M9) but modified to be compatible with the ion optics of the TRITON. Later, a MasCom MC-Z-19-Triton (called SEM5) was installed on the TRITON for linearity testing.

This article describes linearity checks performed at New Brunswick Laboratory within a 6-mo period using six SEMs on three mass spectrometers (SEM1, SEM2, and SEM6 on MS1; SEM3 on MS2; and SEM4 and SEM5 on MS3). Because the IRMM-072 series of CRMs was not available, CRM U500 was used extensively to define a correction algorithm. Other CRMs, such as U030A, U050, U200, and U900, were used to check the validity of the correction algorithm developed on the basis of the U500 results. The work was scheduled as follows: First, a static Faraday remeasurement of CRM U500 was performed using the TRITON to reduce the uncertainties of the minor isotope ratios $^{234}U/^{235}U$ and $^{236}U/^{235}U$ for the purpose of this linearity experiment.

Second, peak-jumping measurements of CRM U500 on all SEMs (SEM1 to SEM6) were performed at various count rates using the SEM-only method:

Intensities for ^{235}U, ^{238}U ranged from 2×10^4 cps (counts per second) to 5×10^5 cps; consequently, ^{234}U ranged from 2×10^2 cps to 5×10^3 cps and ^{236}U from 3×10^1 cps to 8×10^2 cps. This was done to check the linearity of these SEMs. The SEM peak-jumping mode was chosen to circumvent the additional uncertainty inherent in performing an intercalibration between SEM and Faraday cups, which is necessary when both detectors are used.

Finally, linearity checks using the SEM/FAR method were performed on MS1 and MS2. During this measurement, the overall ion beam intensity was decreased in a stepwise manner by reducing the filament temperature to obtain the desired range of count rates for the minor isotopes, preferentially ^{236}U. Temperature changes in a thermal ionization source can change the focus of an ion beam and, therefore, produce a change in the yield of the SEM relative to the Faraday cup array. Therefore, the relative yield was checked several times during the run, the details of which checking are explained below. For MS1, the relative yield between SEM and Faraday cups was found to be strongly dependent on the focusing of the ion beam. The relative yield for MS1 varied by as much as 0.8% during the course of this linearity check, which is an unacceptable amount of drift for defining linearity. For MS2, the SEM/FAR method was performed with a much smaller variation in SEM yield (~0.2%). This is in part because of the much faster measurement capability (simultaneous multicollection of all isotopes) compared with MS1.

For all measurements performed in this work, degassed Re filaments were used. All uranium samples were loaded as $UO_2(NO_3)_2$ solutions containing 1 μg/μL uranium. The SEMs were always operated at a voltage higher than the knee of the counting plateau so that a SEM yield of at least 95% relative to a Faraday cup was achieved. The dark noise of each SEM was checked regularly and, in all cases, was <1 cpm. Data-reduction algorithms supplied with the mass spectrometers were used to calculate the dead-time correction at all count rates as well as a quadratic-drift correction in case of peak-jumping measurements.

The dead time of the secondary electron multiplier is comparable in duration to the signal pulse width of 10–15 ns. The dead time of the pulse amplifier (44.7 ns, model WRE PAD 05-MAT 191290 from Winkelnkemper, Morschen, Germany) is generated electronically and is significantly longer than the SEM output pulses. Therefore, the dead time of the entire SEM detection system is dominated by the dead time of the pulse amplifier. The long dead time of the pulse amplifier also helps to avoid the counting of secondary pulses occuring a few tens of nanoseconds after the ion enters the SEM. The pulse amplifier dead time was measured by the manufacturer using a pulse generator and an oscilloscope and checked at New Brunswick Laboratory using comparable equipment. The measurements were performed by applying artificial double pulses to the pulse amplifier of the SEM. To measure the dead time, the delay time is increased (or decreased) so that the output pulse of the delayed primary pulse just appears (or disappears) on the oscilloscope. At that point, the delay time is equal to the dead time. The result of the dead time was found to be ~44.7 ns (repeated measurements with an uncertainty of about ± 0.5 ns). This type of dead-time determination has the advantage that it is not affected by any kind of bias occurring in isotope ratio measurements as mass fractionation, ion current drift, or unknown nonlinearity effects originating within the SEM itself.

The dead-time correction formula is given by

$$c_{\text{corrected}} = \frac{c_{\text{measured}}}{1 - c_{\text{measured}}\tau},$$

where τ is the dead time of the pulse amplifier (44.7 ns) and $c_{\text{corrected}}$ and c_{measured} are the corrected and measured count rates. This formula, however, is truly valid only when the incident pulses are totally regular in time, which is not completely correct in this case. Nonetheless, Hayes and Schoeller [13] showed that a random sequence of counted events can be effectively approximated with this formula. In case of CRM U500 measurements, the dead-time correction is significant predominantly for the major isotopes (^{235}U and ^{238}U). Because the count rates of these isotopes are usually below 3×10^5 cps, the product $c_{\text{measured}}\tau$

Table 1
Isotope ratio measurements of the certified reference material U500, performed in static multicollector mode using Faraday cups for all isotopes on MS3, the TRITON

Isotope Abundances given in the certificate				
Isotope	^{234}U	^{235}U	^{236}U	^{238}U
Atom percentage	0.5181	49.6960	0.0755	49.7110
Uncertainty (95% CL)	0.0008	0.0500	0.0003	0.0500
Relative uncertainty (95% CL)	0.15%	0.10%	0.40%	0.10%
Isotope ratio ^{m}U/^{235}U	0.01042539	1	0.00151924	1.00030184
Isotope ratio uncertainty (95% CL)	0.00001921	...	0.00000623	0.00100030
Relative uncertainty (95% CL)	0.184%	...	0.41%	0.10%*
Far Runs				
Mean Ratio m/^{235}U	0.01042836	...	0.00152380	Used
Uncertainty (95% CL)	0.00000082	...	0.00000044	For
Relative uncertainty (95% CL)	0.008%	...	0.028%	Normalization
Far Runs, including uncertainty from normalization				
Mean Ratio m/^{235}U	0.01042836	...	0.00152380	Used
Uncertainty (95% CL)	0.00000358	...	0.00000066	For
Relative uncertainty (95% CL)	0.034%	...	0.043%	Normalization
Deviation between measured new results and certified values	0.028%	...	0.300%	
Uncertainty Budget Static Multicollector Far Runs	Relative uncertainty (95% CL)	Relative contribution to total uncert.	Relative uncertainty (95% CL)	Relative contribution to total uncert.
FAR RUN uncertainty:	0.008%	5.3%	0.028%	42.3%
Normalization uncertainty:	0.033%	94.7%	0.033%	57.7%
Sum	...	100%	...	100%

* Given explicitly on certificate.

is always below 0.015, and thus, this approximation is valid with an accuracy of 0.01% [13] in the count rate, which is far below the usual uncertainties because of counting statistics and counter/Faraday inter-calibration ($\geq$0.1%). The dead-time correction becomes a significant component of measurement uncertainty ($>$0.1%) only at count rates greater than $\sim 3 \times 10^5$ cps.

5. Results of linearity tests

5.1. Faraday detector analysis of CRM U500

To reduce the uncertainties when quantifying non-linearity effects, the minor isotope ratios ^{234}U/^{235}U and ^{236}U/^{235}U in CRM U500 were reevaluated from a set of 26 samples analyzed on the TRITON (MS3) in static Faraday multicollector mode. The results, shown in Table 1, were obtained by averaging data from four different cup configurations. For this experiment, 6 μg of CRM U500 were loaded onto each sample filament to obtain a stable ion current of $\sim$1.5 $\times 10^{-13}$A for ^{236}U, corresponding to $\sim 10^{-12}$A for ^{234}U and 10^{-10}A for ^{235}U and ^{238}U. The measured ^{234}U/^{235}U and ^{236}U/^{235}U isotope ratios were normalized to the value of the ^{238}U/^{235}U ratio given in the U500 certificate, which has an uncertainty of 0.10% (95% CL). Because of this normalization, the uncertainty of the ^{238}U/^{235}U ratio contributes significantly to the uncertainty budget of the remeasured minor ratios, limiting their uncertainties to a minimum of one-third of the uncertainty of the ^{238}U/^{235}U ratio (spanning 3 mass units), which is $\sim$0.033% (95% CL). For both the ^{234}U/^{235}U and the ^{236}U/^{235}U isotope ratios, the normalization uncertainty is the main contributor (95% and 57%, respectively) to the total uncertainty.

To ensure that all Faraday cups were intercali-

brated properly during these runs, a cup-efficiency test was performed. This was done in a peak-jumping experiment by switching a ^{235}U ion beam of $10^{-11}A$ into each of the Faraday cups. The efficiencies (after electronic gain calibration) of all Faraday cups were equal within uncertainties of <0.003%. An additional test was performed to assess the linearity of the Faraday cups. In this test, U500 was measured with ^{234}U ion currents ranging from $10^{-13}A$ to $10^{-12}A$. The agreement between the normalized $^{234}U/^{235}U$ ratios at varying ion currents shows that, at least within the range of ion currents used for the minor isotopes ($1.5 \times 10^{-13}A$ to $10^{-12}A$), there is no Faraday nonlinearity effect. However, a deviation of 0.30% in the measured $^{236}U/^{235}U$ was observed in the static U500 measurements. The linearity test indicates that this small deviation in the $^{236}U/^{235}U$ ratio is not caused by the Faraday detectors but, rather, is caused by an inconsistency in the certified minor isotope abundances of U500.

In conclusion, the remeasured minor isotope ratios for U500 were obtained using instrumentation that was optimally controlled (by virtue of cup efficiency and linearity tests) and whose results are linked to the well-certified $^{238}U/^{235}U$ ratio of CRM U500 via the mass fractionation correction.

The uncertainties for the minor isotope ratios $^{234}U/^{235}U$ and $^{236}U/^{235}U$ obtained in this way are about a factor of 6 and 9, respectively, smaller than the original uncertainties given in the certificate (Table 1). Furthermore, while no significant deviation was found for $^{234}U/^{235}U$ (0.028% ± 0.034%, 95% CL), a more obvious deviation of 0.300% ± 0.043% (95% CL) was obtained for the $^{236}U/^{235}U$ ratio. The use of biased $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios for linearity tests would lead to false conclusions about the degree of linearity and result in improper derivation of correction algorithms. The new measured minor ratios are nonetheless within the uncertainty limits of the U500-certified values (0.18% RSD for $^{234}U/^{235}U$ and 0.41% RSD for $^{236}U/^{235}U$, 95% CL).

The $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios measured in this study were used as reference values for all subsequent minor isotope ratio measurements of CRM U500 in tests for SEM linearity. A more detailed study about static as well as multidynamic isotope ratio measurements of CRM U500 on the Triton, is in preparation.

5.2. SEM linearity testing by peak-jumping measurements of CRM U500

The results of peak-jumping measurements of U500 using SEM1 on MS1 were obtained at various count rates and are shown in Table 2. To obtain small uncertainties in the low per-mill range for count rates $<10^3$ cps, the integration and run times were adjusted accordingly. The runs times ranged between 2 and 10 h, depending on the count-rate intensity and integration times. The count rate was maintained within a ±20% range during all individual runs. As the data show, with increasing count rates the measured minor isotope ratios increasingly deviate from the reference ratios, represented by the results of the static multicollector Faraday runs described in the previous section. The deviations R_{meas}/R_{ref} for $^{234}U/^{235}U$ and $^{236}U/^{235}U$ are plotted versus the count rate of the index isotope ^{235}U in Fig. 2a, 2b. The abscissa shows only the ^{235}U count rates measured in these experiments and ranges between 2×10^4 and 3×10^5 cps. Count rates for ^{236}U and ^{234}U as low as a few hundred counts per second were reached, which are outside the abscissa scale in Fig. 2a, 2b.

Although SEM1 is obviously nonlinear, we have been able to establish a correction algorithm that allows this SEM to be used for quantitative measurements. The observed deviations are very similar for both $^{234}U/^{235}U$ and $^{236}U/^{235}U$, suggesting that the nonlinearity effect occurs predominantly in the range of count rates associated with the common denominator isotope, ^{235}U. Because the $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios decrease with increasing ^{235}U count rate, the SEM is characterized as having a greater yield at high count rates, starting at $\sim 2 \times 10^4$ cps. Below this limit, no deviations from the reference values are statistically significant.

Combining the regressions of R_{meas}/R_{ref} for $^{234}U/^{235}U$ and $^{236}U/^{235}U$ (Fig. 2c) gives a set of parameters that can be used to describe the observed bias in the count rate of ^{235}U. The mean regression line inter-

Table 2
Results of the linearity check of SEM1 on MS1, performed by peak-jumping measurements of CRM U500

Count rate ^{235}U	Count rate ^{234}U	Count rate ^{236}U	$^{234}U/^{235}U$	2SE	$^{236}U/^{235}U$	2SE
16200	169	25	0.0104312	0.0000215	0.0015238	0.0000055
29200	304	44	0.0104203	0.0000319	0.0015267	0.0000056
37150	387	56	0.0103984	0.0000295	0.0015242	0.0000067
52350	546	80	0.0104062	0.0000226	0.0015145	0.0000045
83700	873	127	0.0103742	0.0000197	0.0015139	0.0000035
124000	1293	188	0.0103389	0.0000210	0.0015132	0.0000053
140000	1460	213	0.0103691	0.0000169	0.0015129	0.0000051
178000	1856	270	0.0103525	0.0000145	0.0015151	0.0000035
217100	2263	330	0.0103207	0.0000152	0.0015103	0.0000040
310000	3232	471	0.0103235	0.0000116	0.0015076	0.0000027
311000	3242	472	0.0103327	0.0000070	0.0015075	0.0000030
319000	3326	485	0.0103244	0.0000100	0.0015079	0.0000030
386500	4029	587	0.0103207	0.0000115	0.0015041	0.0000027
420000	4379	638	0.0103235	0.0000110	0.0015065	0.0000037
532000	5546	808	0.0102992	0.0000111	0.0015061	0.0000018

Note. Measurements are compared to the values measured in static multicollector mode using Faraday cups only (Table 1).

cepts $R_{meas}/R_{ref} = 1$ at ~22,800 cps and has a slope of −0.00877 per decade of count rate.

On the basis of the parameters of the mean regression, a count rate–dependent correction algorithm can be formulated that accommodates the observed increase in SEM yield at count rates greater than ~22,800 cps with a slope of +0.00877 per decade of count rate.

For $c_{measured} > c_{limit}$,

$$c_{corrected} = c_{measured}\{1 + m[\log(c_{measured}) - log(c_{limit})]\}.$$

For $c_{measured} \leq c_{limit}$,

$$c_{corrected} = c_{measured}.$$

The parameters of this correction algorithm are given with a 95% confidence limit as $m = -0.00877 \pm 0.00020$ and $c_{limit} = 22{,}800$ cps (−5300 + 24,500) cps. This type of correction will be named the restricted logarithmic rate effect, represented by the acronym RLR. The RLR correction incorporates, as one component, the overall logarithmic rate effect (OLR) suggested earlier. But the RLR algorithm also correctly takes into account those count rates below a certain limit of 22,800 cps that do not require any correction, at below this limit for all isotopes no deviation was found when performing peak-jumping measurements on U500.

At low count rates where $c_{corrected} = c_{measured}$, the mass fractionation–corrected, measured $^{236}U/^{234}U$ ratios were in agreement with the reference value of 0.146121 (±0.000081), as shown in Fig. 2d. This agreement, established with an uncertainty of ~0.1% (95% confidence limit), suggests that the correction algorithm is valid at low count rates.

Fig. 3 shows the form of the RLR correction algorithm together with a modified function that diminishes the discontinuity between the low and high count-rate ranges. This modified algorithm yields a more realistic continuous function that fulfils the two basic requirements of the original RLR. First, the function asymptotically approaches the unity line ($c_{corrected} = c_{measured}$) for low count rates and second, it asymptotically follows the logarithmic rate effect with the calculated slope m for count rates beyond the limiting count rate. The continuous function is modeled using the inverse trigonometric tangent function and is given mathematically by

$$c_{corrected} = c_{measured}[\mathrm{L}(c_{measured})\mathrm{FL}(c_{measured}) + \mathrm{H}(c_{measured})\mathrm{FH}(c_{measured})],$$

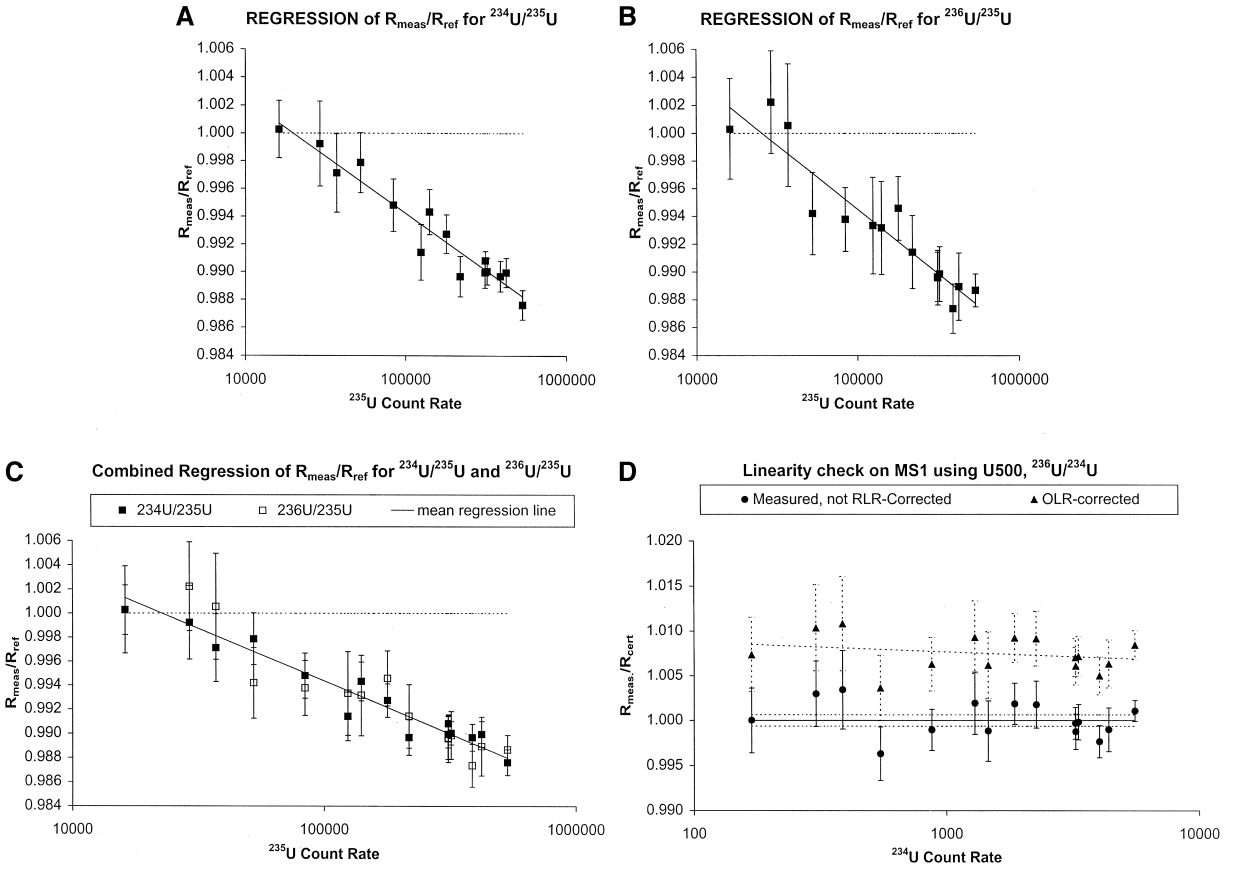

Fig. 2. (*a*, *b*) Results of peak-jumping measurements of CRM U500 on TIMS MS1, equipped with SEM1, performed at various count rates. The deviations R_{meas}/R_{ref} for $^{234}U/^{235}U$ and $^{236}U/^{235}U$, corrected for mass fractionation using the $^{238}U/^{235}U$ ratio, are plotted versus the count rate of the index isotope ^{235}U. The lower count rates achieved for the isotopes ^{234}U and ^{236}U are not shown in this plot. All error bars represent 2 SE. (*c*) Combined regression line, taking into account R_{meas}/R_{ref} data of both $^{234}U/^{235}U$ and $^{236}U/^{235}U$, corrected for mass fractionation using the $^{238}U/^{235}U$ ratio. (*d*) Plot of R_{meas}/R_{ref} for $^{236}U/^{234}U$ (dots), calculated from the measured $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios, corrected for mass fractionation using the $^{238}U/^{235}U$ ratio. The solid line represents $R_{meas}/R_{ref} = 1$; the dashed lines next to it indicate the uncertainty of the reference value, measured in static multicollector mode using Faraday cups. The triangles show R_{meas}/R_{ref} for $^{236}U/^{234}U$ if an overall logarithmic correction algorithm is applied using the rate-effect parameter $m = -0.00877$. A regression of these data demonstrates the shift compared to the measured and not RLR-corrected data.

where the functions L, FL, H, and FH are defined as follows:

$$L(c_{measured}) = 1,$$

$$H(c_{measured}) = \{1 + m[\log(c_{measured}) - \log(c_{limit})]\},$$

$$FL(c_{measured}) = \arctan\{a(\log(c_{limit}/(1+b)) - \log(c_{measured})]\}/\pi + 0.5,$$

$$FH(c_{measured}) = -\arctan[a(\log(c_{limit}/(1-b)) - \log(c_{measured}))]/\pi + 0.5.$$

Values for the parameters a and b, which provide a smooth curve around c_{limit}, are $a = 2.0$ and $b = 0.00001$. The smoothed continuous function is preferred to the original RLR function, although the choice of mathematical form is not based on physical knowledge of the nonlinearity processes. From an experimental point of view, uncertainties of at least 0.2% are obtained for any isotope ratio measurement involving count rates close to c_{limit}. Therefore, the difference between the smoothed curve and the orig-

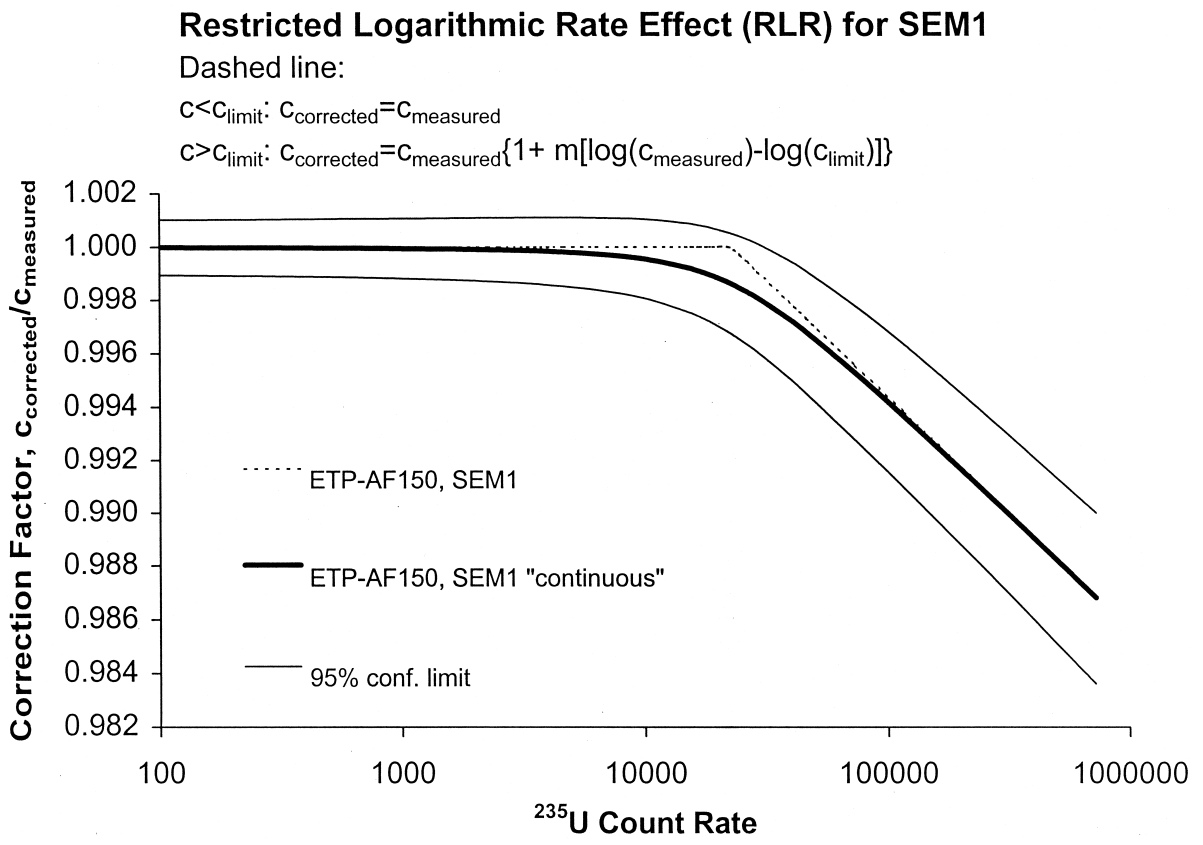

Fig. 3. Plot of the RLR algorithm ($c_{\text{corrected}}/c_{\text{measured}}$ versus count rate) together with a modified algorithm, which produces a smooth, continuous function between the low and high ranges of count rates.

inal RLR pattern is not significant and the correction can be performed either way.

If an OLR using the same rate-effect parameter $m = -0.00877$ (± 0.00020) is applied to the measured U500 data, all ratios are increased proportionately to their logarithms. This increase is by an amount twice that of the rate effect parameter m for $^{234}U/^{235}U$ (ratio is $\approx 10^{-2}$) and by approximately an amount 2.8 times that of the rate effect parameter m for $^{236}U/^{235}U$ (ratio is $\approx 1.5 \cdot 10^{-3}$). This shift is the same for all count rates but different for the different ratios, as shown in Fig. 4a, 4b. As shown in Fig. 2d for the $^{236}U/^{234}U$ ratio (ratio is $\approx 1.5 \cdot 10^{-1}$) at count rates below $\sim 5 \times 10^3$ cps, the OLR would cause a significant shift about 0.8 times that of the rate-effect parameter m. The OLR yields results that do not agree with reference values and, therefore, is not appropriate for linearity correction for this SEM.

5.3. Comparison to other SEMs

Two additional SEMs, the same as SEM1 on MS1 (ETP type AF150H(M9)), were tested using peak-jumping measurements with CRM U500. Both of these SEMs (SEM2 on MS1 and SEM3 on MS2) produced similar deviations from linearity for the $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios. Similar deviations were also observed for SEM4 (ETP AF180H(M9)) and SEM5 (MasCom MC-Z-19-Triton), which were tested on MS3, the TRITON, and also for SEM6 (MasCom MC-12/17) used on MS1. The results of all 6 SEMs investigated in this work are compared to

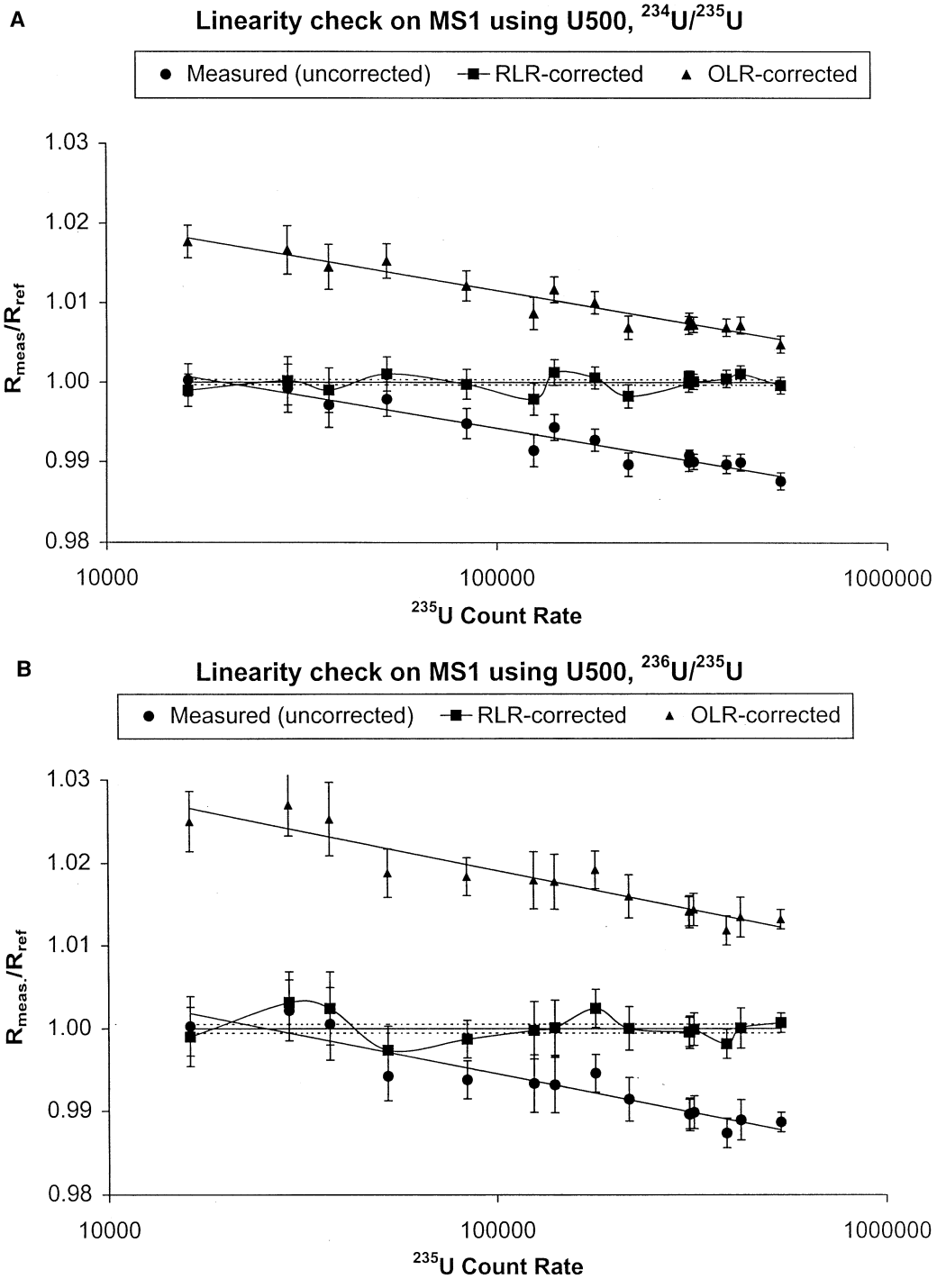

Fig. 4. Comparison of deviations R_{meas}/R_{ref} for $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios (corrected for mass fractionation using the $^{238}U/^{235}U$ ratio): original data, corrected data using RLR, and overall logarithmic corrected data using $m = -0.00877$. Regressions are shown for the original and overall logarithmic corrected data only. The horizontal solid line represents $R_{meas}/R_{ref} = 1$; the dashed lines next to it indicate the uncertainty of the reference value, measured in static multicollector mode using Faraday cups.

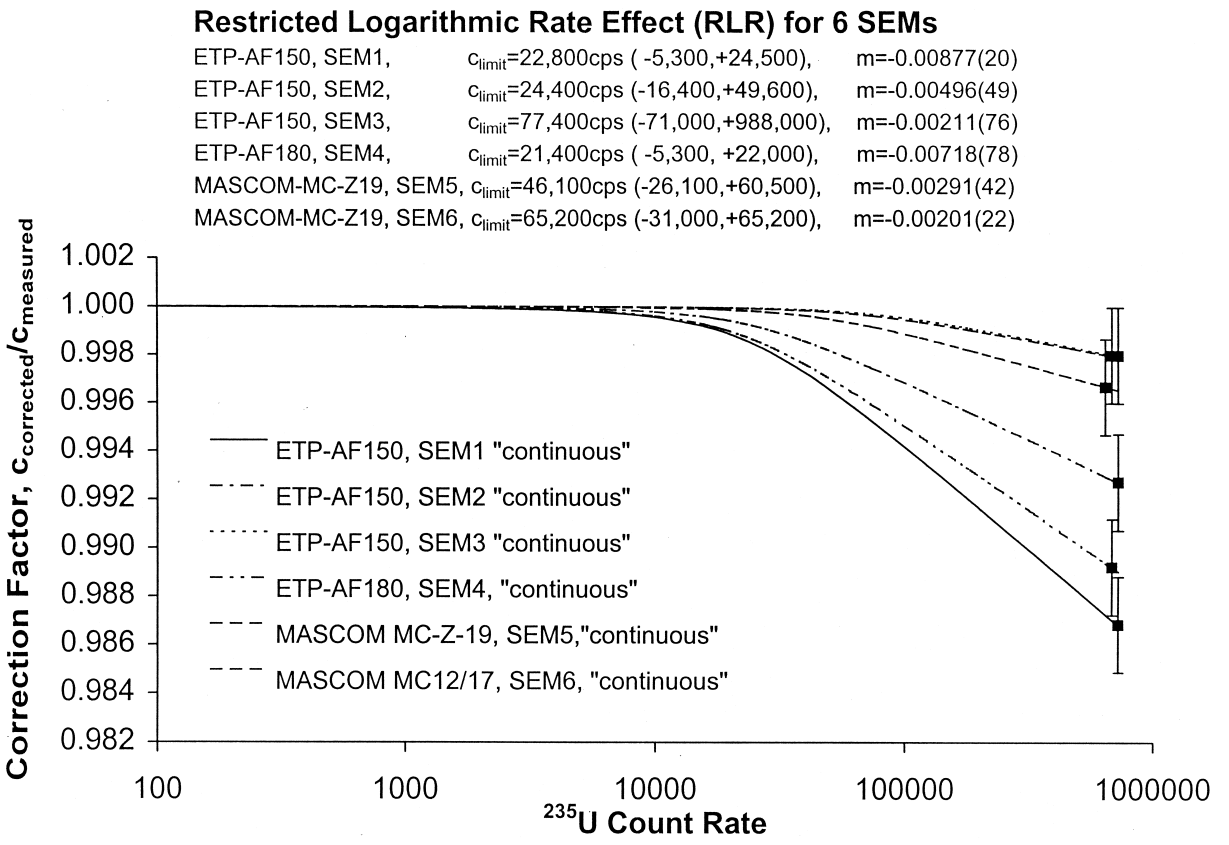

Fig. 5. Graphical comparison of RLR correction algorithms for 6 SEMs. The parameter values c_{limit} and m are given with a 95% confidence limit. The error bars represent the uncertainties of the RLR correction for individual SEMs.

each other in Fig. 5. The values of c_{limit} for the six SEMs range between 21,000 and 65,000 cps and within uncertainties (Fig. 5), they do not show significant differences from each other. Values for the rate effect parameter, m, vary significantly for different SEMs and range between -0.00201 and -0.00877.

5.4. Origin of nonlinearity

The RLR correction algorithm is empirical only, and its mathematical form has not been derived from an analysis of the physics of the processes leading to nonlinearity in the SEM. But the discussion that follows is aimed at qualitatively understanding the empirical model.

The previously described observations clearly show an increase in the count-rate response with increasing count rate. In principle, an increase in the SEM count rate response can only be caused by either decreasing the pulse amplifier threshold or increasing the pulse heights, which causes a higher number of pulses exceeding the threshold. But the pulse-amplifier threshold was not changed during the experiments. However, one well-known way to increase the pulse heights is to increase the high voltage applied to the SEM, but that also was not changed during the experiments. Also, the impedance of the SEM power supply was tested to ensure that it is low enough to guarantee stable high voltage for the range of count rates encountered in this study.

One can therefore conclude that the pulse heights must have been increased by some other effect, which is dependent on the rate of the pulses themselves. This could be because of a count rate–dependent memory

effect that influences the SEM amplification. To achieve a high secondary electron yield on each dynode of the multiplier, which corresponds to a high amplification of the SEM, the surface of the dynodes is covered by a thin metal-oxide layer (containing Cu, Be, or Al). The electrical conductivity of the dynode surfaces is therefore diminished relative to a pure metal surface. Initiated by the ion to electron conversion process on the first dynode of the SEM, an electron pulse becomes progressively magnified on each dynode step by a factor of two to five. Finally, the electron pulse yields as much as $\sim 10^7$–10^8 electrons per pulse at the last dynode (19-stage multiplier) to generate a short voltage pulse (typical: FWHM ~10 ns, 40 mV pulse height), well above the discriminator level of the pulse-counting electronics. As has been pointed out earlier, the surfaces of the dynodes are covered by a thin oxide layer of limited electrical conductance. In particular, at the last set of dynodes where the charge density of the electron pulse is greatest, there may be some surface charge trapped even if the high-density electron pulse has passed. If the ceramic insulators between the dynodes are not properly shielded against the electron avalanche, they may also trap some electrical charge. This trapped electric surface charge would fade away by an exponential function with time, similar to the discharge of an electrical capacitor. For high count rates, some charge may remain trapped on the oxide surface layer, altering the voltage distribution inside the SEM, whereas for low count rates, the surface charge will have faded away and the voltage distribution will have settled to stable conditions. This means that the voltage distribution within the dynode/resistor array might depend on the time interval between two pulses, that is, count rate. As the actual voltage distribution across the dynode array has a strong influence on the amplification of the SEM, this might be one reason for a count rate–dependent memory effect. Each new pulse might receive interference from a decaying predecessor pulse. The size of the mutual signal interference depends on the time interval between subsequent pulses. Because the signal decay is exponential, the pulse heights and, consequently, the count rate should increase logarithmically with the count rate. This might qualitatively explain the observed logarithmic rate effect for high count rates.

For very low count rates where there is a long time interval between subsequent pulses, the mutual interference is minimal because of the lack of residual charge or memory on the dynode surfaces. The transition between the low and high count rate ranges is supposed to be rather continuous rather than abrupt, as illustrated in Fig. 3.

It is remarkable that the deviation from linearity becomes significant at about the same count rate range of 10,000–30,000 cps for all SEMs. This might be because of similarities in basic design characteristics such as applied high voltage (~2000 V), total resistance (10–16 MΩ), and number of dynode stages (15–20) resulting in similar pulse-height distributions for all of these discrete dynode SEMs.

If the overall pulse height is increased by additionally raising the high voltage of the SEM, the interference between subsequent pulses should increase as well. Therefore, it can be predicted that an increase of the SEM high voltage should increase the observed nonlinearity effects. This prediction was checked using SEM2 on MS1. As long as the SEM is operated in the plateau region, the count rate (yield) is only affected slightly by change in the high voltage (≈0.2%/V). The SEM plateau of SEM2 on MS1 is shown in Fig. 6. The effect of SEM high voltage on linearity is shown in Fig. 7, a plot of $R_{\mathrm{meas}}/R_{\mathrm{ref}}$ (not RLR corrected) for U500 peak-jumping measurements at various high voltages, performed on SEM2 on MS1. The smallest deviations from unity are observed at the high voltages corresponding to the initial segment of the horizontal operating plateau, or just past the knee of that curve. This setting is therefore recommended, as it also maximizes the longevity of the SEM. For high voltages below the operating plateau voltage, the deviations for both isotope ratios $^{234}U/^{235}U$ and $^{236}U/^{235}U$ are on the order of 5%, which would show dramatic nonlinearity effects. For voltages along the plateau, significant deviations for ^{234}U and ^{236}U from the reference values were also found, the deviations increasing by

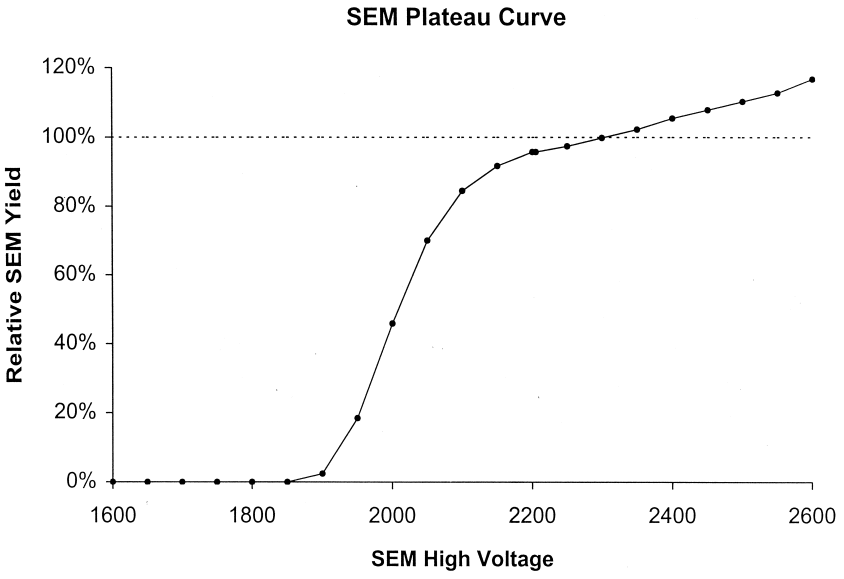

Fig. 6. Count rate versus SEM high voltage for SEM2 on MS1, showing a conventional operating plateau.

~0.2% for each 100 V increase in the SEM high voltage.

If the count rate is further increased, the gain and, therefore, also the yield of the multiplier finally drops by several orders of magnitude because of the lack of signal recovery between successive pulses. This kind of saturation phenomenon has been described in the literature many times (e.g., [6,7] and references therein), but the comparatively small initial increase in the SEM yield with count rate has rarely been observed.

The effects found to be responsible for the observed nonlinearity do not occur at the first dynode, where the ion–electron conversion takes place and where there is a recognized dependency on the atomic number of the impacting ions [10,11]. Therefore, the described nonlinearity effects should not be dependent on the element analyzed. The RLR correction can therefore be considered as a universal description for deviations from linearity observed for high count rates. However, the linearity was not checked for elements other than uranium in this work, and small quantitative differences in the deviations from linearity for different elements can not be excluded. Furthermore, it can be inferred that the observed deviation will occur not only when a SEM is used for the detection of ions. A similar nonlinearity can be predicted for various SEMs when used, for example, as photon detectors. Therefore, this nonlinearity effect may also apply to Daly detectors used in isotope mass spectrometry using a combination of an ion–electron-conversion dynode and a photo-multiplier for ion detection.

5.5. Test measurements of various CRMs for validation of the RLR correction

The RLR correction has been validated in test measurements of various CRMs including U030A, U050, U200, U500, and U900 using SEM1 on MS1. Fig. 8a, 8b shows the relative deviations of the measured $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios from their reference values. For $^{236}U/^{235}U$, the results of U030A are not shown because the count rates were only a few counts per second and peak centering was not possible. The $^{238}U/^{235}U$ normalization ratio used in these CRM measurements is different from unity (except the case U500) and, therefore, also is influenced by the linearity correction. Comparing the RLR-corrected results with the uncorrected (only normalized for mass fractionation) and the overall logarithmic

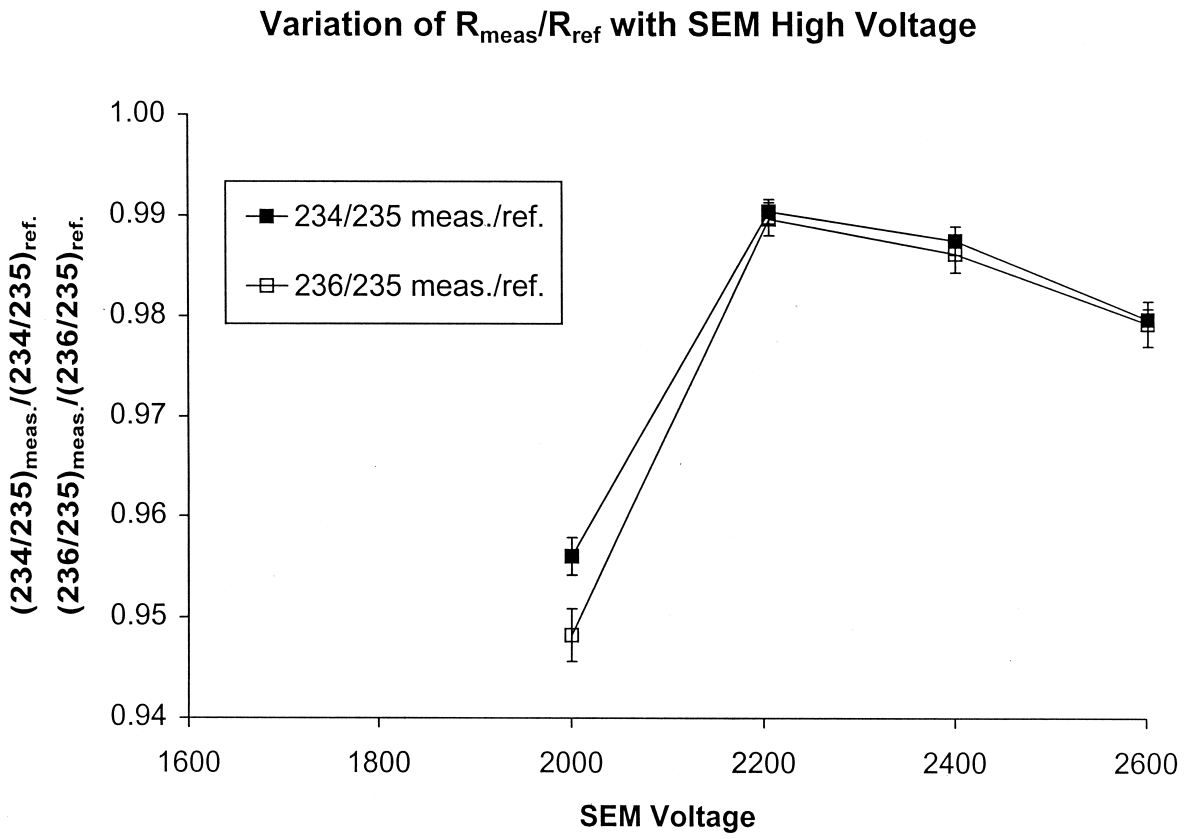

Fig. 7. R_{meas}/R_{ref} data for U500 peak-jumping measurements using SEM2 on MS1 at various high voltages, corrected for mass fractionation using the $^{238}U/^{235}U$ ratio but not RLR-corrected.

corrected (and normalized) results, we find that the RLR approach gives the only agreement with the certified reference values. Calculated uncertainty budgets for the RLR technique (Table 3) show that counting statistics are the main source of the total uncertainty of the isotope ratios measurements in SEM peak-jumping runs (2SE) for low count rates and can only be reduced using much longer counting times. For higher count rates of a few 10^5 cps, the uncertainty caused by the RLR correction becomes similar to the counting statistics and, therefore, increases the total uncertainty by a factor of ~1.5 compared to the uncorrected results. The uncertainty contributions from use of the reference materials (also based on static Faraday multicollector measurements) are of minor influence.

5.6. Linearity correction versus dead-time determination

Nonlinearity may also be observed for a SEM when the dead time is improperly determined and subsequently used in the calculation of the corrected count rate. Although it is possible to correctly determine the unknown dead time of a counting system by measurements of certified reference materials ([14,15]), the use of a SEM that exhibits significant internal nonlinearity as observed in this work will obviously yield incorrect results.

As an example of a misinterpretation of a nonlinearity effect, the dead time of the MS1 counting system, equipped with SEM1, was calculated using the deviations R_{meas}/R_{ref} observed for the $^{234}U/^{235}U$

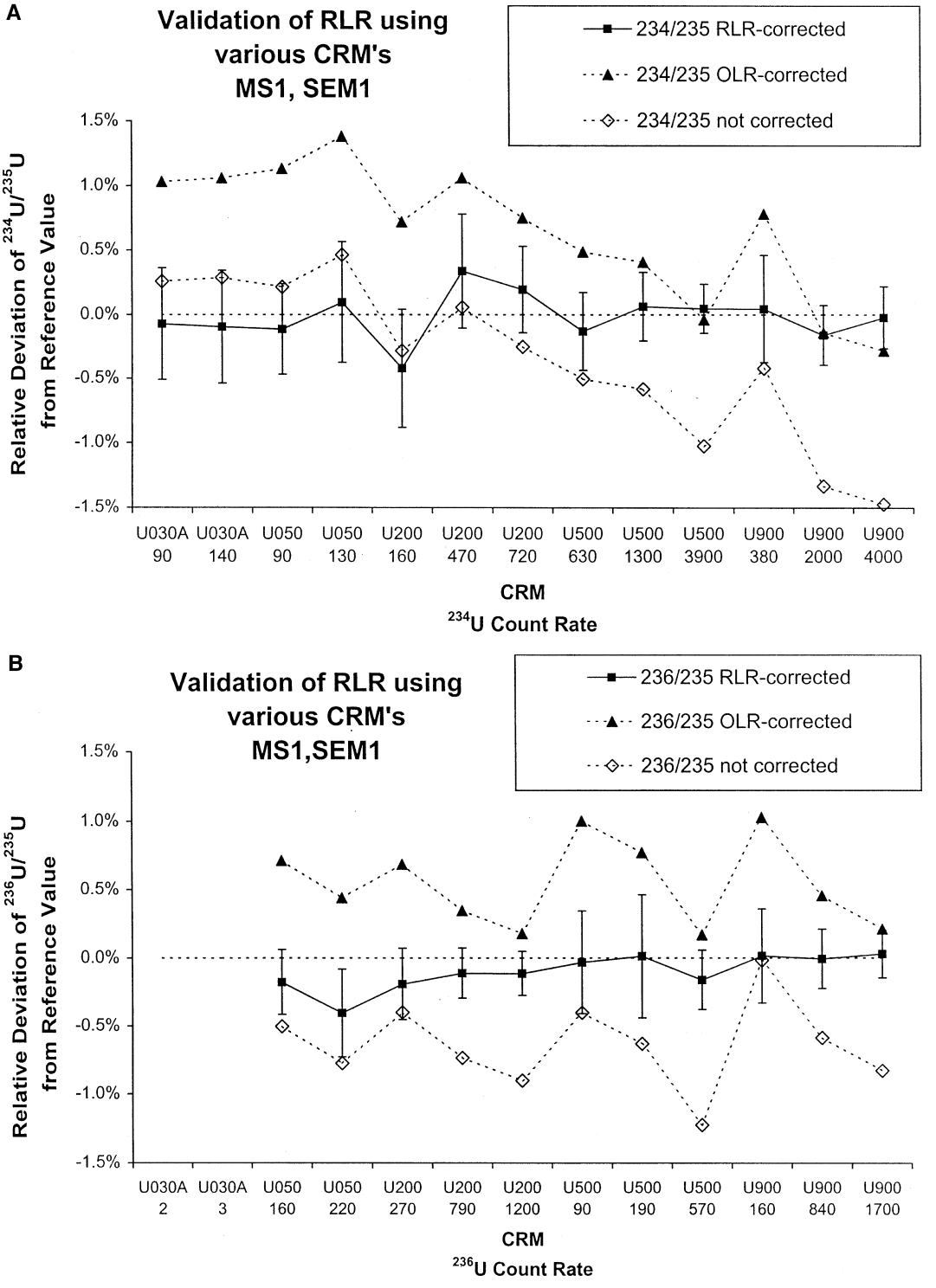

Fig. 8. Test measurements in peak-jumping mode performed using SEM1 on MS1, using various CRMs as U030A, U050, U200, U500, and U900. All $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios are corrected for mass fractionation using the $^{238}U/^{235}U$ ratio.

Table 3
Uncertainty budget for the SEM peak-jumping measurements of various CRMs, performed using SEM1 on MS1

$^{234}U/^{235}U$ Uncertainty Budget				$^{236}U/^{235}U$ Uncertainty Budget		
CRM, Count rate ^{234}U	2stderr run	Reference Materials	RLR	2stderr run	Reference Materials	RLR
U030A 90	93%	7%	0.0%			
U030A 140	93%	7%	0.0%			
U050 90	92%	8%	0.0%	82%	18%	0.0%
U050 130	87%	4%	8.9%	80%	9%	10.8%
U200 160	89%	2%	9.2%	80%	4%	16.6%
U200 470	86%	2%	11.1%	59%	7%	33.9%
U200 720	76%	4%	19.8%	47%	9%	43.8%
U500 630	75%	2%	22.6%	89%	3%	8.2%
U500 1300	66%	3%	31.0%	92%	2%	5.8%
U500 3900	30%	6%	63.8%	65%	10%	25.4%
U900 380	88%	1%	11.9%	89%	1%	9.8%
U900 2000	57%	2%	41.9%	73%	2%	25.2%
U900 4000	57%	1%	41.7%	57%	3%	40.2%

ratio. The dead time is determined from the slope of a linear regression performed on the $^{234}U/^{235}U$ data. As shown in Fig. 9, the measured deviations would lead to a negative dead time of about −28 ns, which is not reasonable because the data are already corrected using the electronically determined dead time of 44.7 (±0.5) ns. Using the uncorrected original $^{234}U/^{235}U$ ratios leads to a regression line associated with a dead time of 16.7 (±3.6) ns, which is far below the true value determined independently for the amplifier circuitry. In addition, the data corrected using this improperly determined dead time of 16.7 (±3.6) ns do not show a strong linear relationship and do not agree well with the reference value.

Furthermore, because the dead time is dependent only on the response of the pulse amplifier electronics, the observed deviations in R_{meas}/R_{ref} should be the same for SEM1 and SEM2, which have been used on MS1 in combination with the same pulse amplifier. But this is not the case, as shown by the rate-effect parameter values m for SEM1 and SEM2, which are significantly different from each other (Fig. 5). If the observed deviations in R_{meas}/R_{ref} for SEM1 and SEM2 on MS1 were used to determine the dead time of the pulse amplifier electronics, the results would be different for both SEMs. Therefore, for SEMs exhibiting inherent nonlinearity effects, the dead-time determination by measurement of CRMs yields incorrect (usually too low) results.

5.7. Linearity check using combined SEM/FAR measurements on MS2

Because MS2 is capable of measuring ^{235}U and ^{238}U simultaneously on Faraday cups and ^{236}U on the SEM, this instrument is suitable for performing the SEM/FAR linearity check method. The results of this procedure are tabulated in Table 4 and shown graphically in Fig. 10.

The yield of the SEM relative to the Faraday cup array was determined by switching an ion beam between the center Faraday cup and the SEM. To achieve a reasonable signal to noise ratio on the Faraday cup of approximately 1/1000, the ion current for the SEM/FAR intercalibration should be above $\sim 5 \times 10^{-14}$A. This ion current corresponds to 3×10^5 cps, which equals the upper limit of the count rate routinely applied to the SEM, chosen to ensure the longevity of the SEM and to avoid significant uncertainties caused by the dead-time correction. Therefore, the overlap of the ion current ranges applicable to Faraday cups and SEMs, which can be used for the intercalibration, is a quite narrow range of about ±20% around 5×10^{-14}A. The intercalibration was

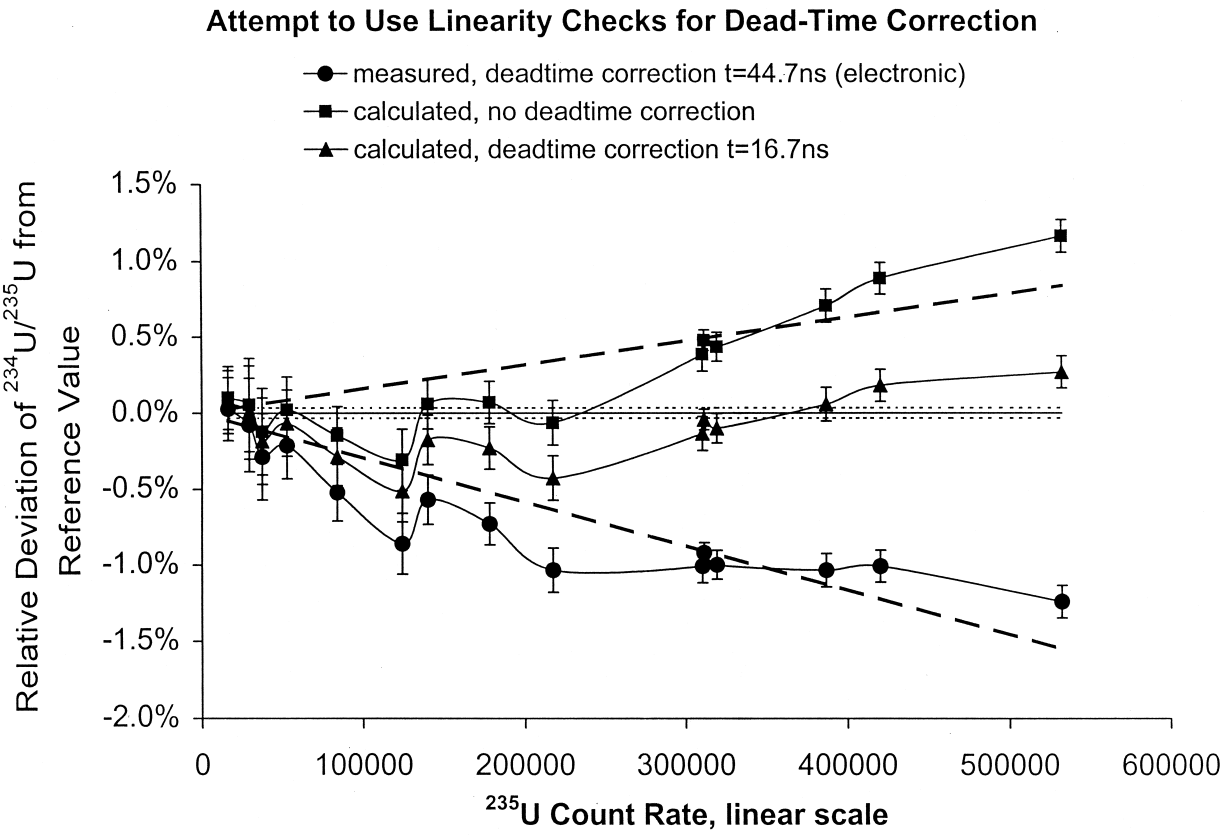

Fig. 9. Dead-time determination using observed deviations in $^{234}U/^{235}U$ from linearity.

repeated during the procedure in steps outlined below only where there was an appropriate sized ion current.

This linearity check also shows a relationship of increasing SEM yield with increasing count rate. When starting the linearity test procedure with high intensities, the $^{236}U/^{235}U$ ratio first decreases to levels significantly below the previously determined RLR pattern for this SEM (see steps 4–6 in Fig. 10). At low intensities, the ratio increases slightly (step 7) and approaches the RLR results. The SEM/FAR results obtained for steps 1–6 with decreasing intensity do not agree with the results for steps 8–11 with increasing intensity, making the results of the overall measurement ambiguous. Apparently, it is not possible to measure the relative SEM yield in each intensity step during this procedure because an appropriate ion beam is not always available (e.g., steps 3, 5, 6, 8, 9, and 10, marked "N" in Table 4). The standard deviation of the SEM yield was ~0.2%, but that does not explain the observed differences, e.g., for example, between steps 6 and 8 or 4 and 9. Thus, there might be an additional uncertainty component that is not taken into account. The variation in temperature at different intensity levels for ^{236}U achieved during the experiment might have caused changes in the focus of the ion beam and therefore produced changes in the yield of the SEM, which could not be controlled in each step. This is a limiting factor for the reliability of linearity tests using the FAR/SEM method also for MS2, although it is capable of fast simultaneous collection of all isotopes.

The other disadvantage of the SEM/FAR method is the limited range of count rates covered by this method. Table 4 shows the upper and lower count rates of ^{236}U applied in this experiment. The lower limit is given by the count rate of the minor isotope

Table 4
Results of SEM/FAR linearity checks using SEM3 on MS2, performed using simultaneous detection of ^{235}U and ^{238}U in Faraday cups and ^{236}U in the SEM

Step	Relative SEM Yield (%), 2SE	^{235}U [V] (similar to $10^{-11}A$)	^{234}U [V] (similar to $10^{-11}A$)	^{236}U [cps]	Rel. Dev. (%) $^{236}U/^{235}U$ from Reference 2SE
*	94.73 (13)	3.9011	0.0407	350769	*
1	95.04 (08)	3.9011	0.0407	350769	−0.05 (09)
2	95.06 (11)	3.6788	0.0384	331564	−0.03 (13)
3	N	1.8035	0.0188	162381	−0.20 (13)
4	95.10 (04)	0.5702	0.0060	51194	−0.42 (06)
5	N	0.0982	0.0010	8781	−0.61 (08)
6	N	0.0472	0.0005	4221	−0.66 (12)
7	94.63 (04)	0.0053	0.0001	474	−0.26 (19)
8	N	0.0515	0.0005	4590	−0.29 (15)
9	N	0.5013	0.0052	44827	−0.07 (08)
10	N	1.8689	0.0195	167801	0.09 (05)
11	94.81 (10)	4.1543	0.0433	373949	0.08 (11)

Note. The yield of the SEM relative to the Faraday cup array was obtained by switching an ion beam of appropriate size ($5 \times 10^{-14}A$, corresponding to 3×10^5 cps) between one Faraday cup and the SEM.

* SEM yield measurement before start of linearity test, no measurement of $^{236}U/^{235}U$.

N: no SEM yield measurement performed at that step, because no appropriate ion beam available, see text.

(^{236}U, ∼500 cps) achieved when the most abundant isotope (^{235}U) has reached the minimum ion current for Faraday cup detection ($5 \times 10^{-14}A$). This ion current just corresponds to the upper-limit count rate of $\sim 3 \times 10^5$ cps. Thus, the ratio between the lower and upper count-rate limits for this method equals the isotope ratio between the minor isotope measured in the SEM (^{236}U) and the most abundant isotope (^{235}U), which is $\sim 1.5 \times 10^{-3}$ in this example.

Linearity checks using the SEM/FAR method have the only advantage of completing measurements over a smaller time period.

6. Conclusions

Linearity checks on six SEMs using Certified Reference Materials show significant deviations of measured isotope ratios from their respective reference values. For all SEMs investigated, the deviations showed a similar dependence on the count rate (or ion current in analogue mode) applied to the SEM. No deviation is found for count rates below a limit of $\sim 2 \times 10^4$ cps, which is equivalent to an ion current of $\sim 3 \times 10^{-15}A$. For count rates (or ion currents) beyond this limit, a logarithmic increase in the SEM yield was observed with slopes between 0.2% and 0.9% per decade of the count rate. These deviations amount to 1%–1.5% for count rates of 5×10^5 cps. A correction algorithm, called the restricted logarithmic rate effect (RLR), has been developed to correct for the observed deviations. Test measurements using various CRMs demonstrated that the best accuracy was achieved using the RLR correction algorithm compared with a overall logarithmic correction type. These test measurements using the RLR correction reproduced the CRM ratios accurately but also indicated that additional uncertainty contributions are associated with the RLR linearity correction. Because of counting statistics, isotope ratio measurements requiring the smallest uncertainties are preferentially performed using high count rates of a few 10^5 cps for the major isotopes. But taking into account the uncertainties of the RLR parameters used for correction, the total uncertainty is increased by a factor of ∼1.1–1.5 for these measurements, leading to total uncertainties of ∼0.2%–0.4% (2 σ).

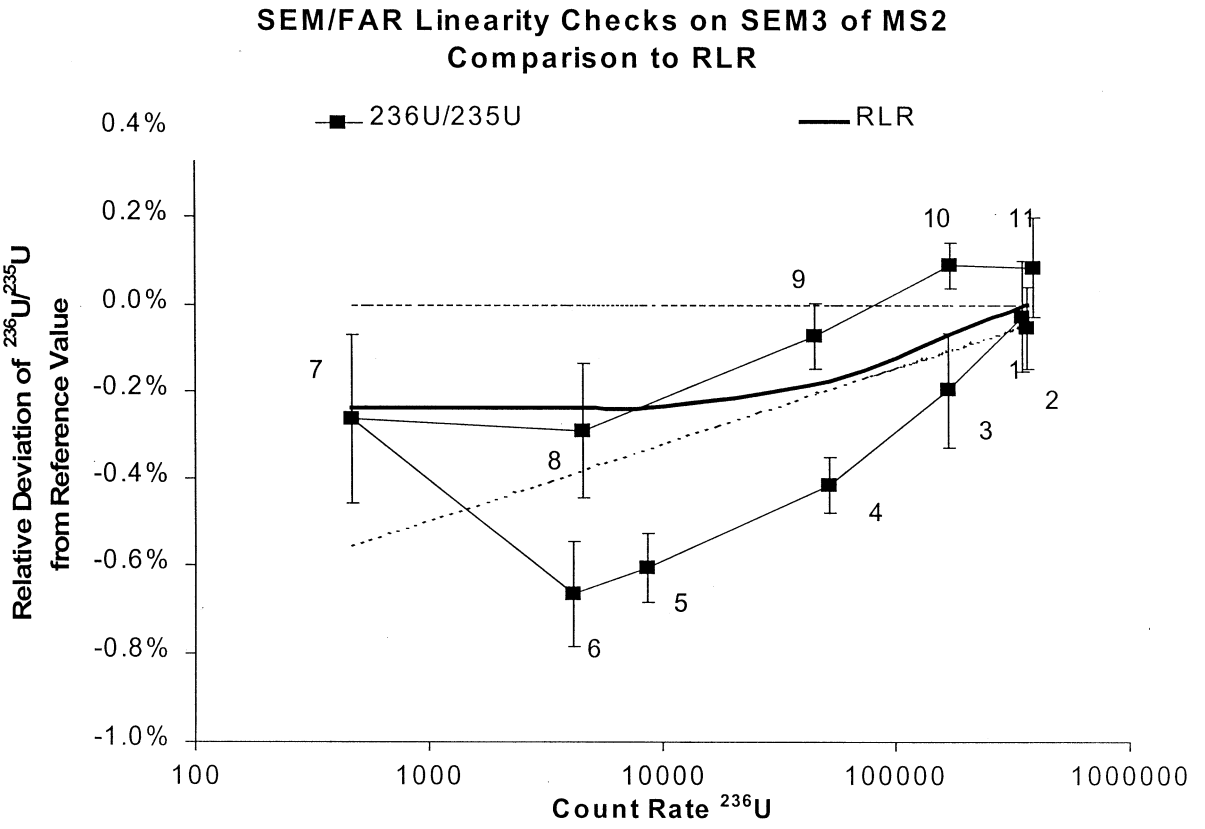

Fig. 10. SEM/FAR linearity checks using SEM3 on MS2, performed using simultaneous detection of ^{235}U and ^{238}U in Faraday cups and ^{236}U in the SEM, and comparison with RLR algorithm. The dashed lines show the reference (horizontal) and a linear regression line of the measured data. The numbers next to the data points give the order in which they were acquired.

Using the RLR algorithm derived from measurements of U500, the ability to achieve excellent agreement with certified values for other CRMs in the minor ratios justifies both the efficacy of the algorithm and the reference values obtained from the remeasurement of U500 in Faraday multicollector mode.

Although the observed type of nonlinearity is expected in principal for any SEM because of the physical processes going on within the SEM, the deviations measured for the ETP SEMs (AF150H(M9), AF180H(M9)) seem to be quite significant in most cases. The nonlinearity starts at a moderate count rate of $\sim 2 \times 10^4$ cps (ion current $\sim 3 \times 10^{-15}$A) and requires significant correction as count rates increase beyond 10^5 cps, which is the range commonly used for high-precision ion counting measurements. The MasCom SEMs show smaller nonlinearity effects, possibly because of a better shielding of the ceramic insulators between dynodes. However, they are associated with a slightly higher dark noise (several counts per minute) compared to those from ETP. Because of its lower dark noise, the SEMs from ETP ($<$1 cpm) are appropriate detectors for measuring primarily in the low–count rate range, where linearity is not as much of a concern. This low dark noise is an important requirement for the analysis of isotopes having extremely low relative abundances like ^{230}Th [5] or ^{236}U [6].

For any type of SEM, it is necessary to check for deviations from linearity before the SEM is used for

high-accuracy isotope ratio measurements. The parameters used for the correction algorithm have to be determined carefully and checked regularly. Within the scope of this work, a long-term study of the variation of the parameters was not done. But to compensate for the permanent loss of gain of any SEM as a function of time, the applied high voltage needs to be routinely checked and adjusted to achieve a setting adjacent to the knee of the plateau curve (Fig. 6). Because deviations from linearity have been shown to depend on the setting of the high voltage (Fig. 7), it is recommended that linearity checks be repeated whenever the SEM high voltage is readjusted.

Furthermore, it has been found that linearity checks can only be used to correctly determine the dead time of a counting system if internal linearity has been proven for the specific SEM.

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