Available online at www.sciencedirect.com
SCIENCE DIRECT®
International Journal of Mass Spectrometry 244 (2005) 97–108
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Characterisation of secondary electron multiplier nonlinearity using MC-ICPMS

D.L. Hoffmann [a,*], D.A. Richards [a], T.R. Elliott [b], P.L. Smart [a], C.D. Coath [b], C.J. Hawkesworth [b]

[a] *School of Geographical Sciences, University of Bristol, University Road, BS8 1SS Bristol, UK*
[b] *Department of Earth Sciences, University of Bristol, Queen's Road, BS8 1RJ Bristol, UK*

Received 26 November 2004; accepted 19 May 2005
Available online 28 June 2005

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

* Corresponding author. Tel.: +44 117 9289111; fax: +44 117 9287878.
E-mail address: dirk.hoffmann@bristol.ac.uk (D.L. Hoffmann).

1387-3806/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2005.05.003

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.