Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
International Journal of Mass Spectrometry 253 (2006) 130–135
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Short communication

A calculation method to eliminate gain effect on isotopic measurement using the virtual amplifier multi-collector mass spectrometer

Zhuyin Chu *, Yueheng Yang, Guangsheng Qiao

State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

Received 5 November 2005; received in revised form 25 January 2006; accepted 26 January 2006
Available online 28 February 2006

Abstract

The virtual amplifier design employed in the ThermoElectron multi-collector mass spectrometers is a novel innovation for high precision isotopic measurement. With the virtual amplifiers, uncertainties of gain factors of amplifiers can be effectively averaged out, so that accuracy and external reproducibility on isotopic measurement can be improved. This paper presents a new calculation method on isotopic measurement using the virtual amplifier mass spectrometers such as ThermoElectron Triton and Neptune. With the calculation method, gain factors of the amplifiers can be completely eliminated out for both raw measured isotopic ratios and normalized isotopic ratios when exponential or power law is used to correct isotope fractionation effect, and therefore, gain calibration is unnecessary even for the high precision measurement purpose.

Keywords: Calculation method; Gain factor; Multi-collector; Mass spectrometer; Isotope measurement

1. Introduction

Thermal ionization and plasma source multi-collector mass spectrometer have been widely used for high precision isotopic measurement, which is becoming more and more important in geosciences, such as isotope geochemistry and geochronology. Instrumental improvements resulting in high precision isotope measurement were often the key for progress in geosciences. Electronic cross calibration of the amplifier gains can heretofore reach an uncertainty of 5 ppm, so external reproducibility of static isotope ratio measurements using multiple collectors is limited to about 7–10 ppm (1R.S.D.) [1,2]. The ThermoElectron Triton thermal ionization mass spectrometer and Neptune MC-ICP-MS have used dynamic zoom optics before the collectors, which enables to change the dispersion of ion beams so that perfect peak overlap can be achieved for all configurations used in the multi-dynamic sequence. Nevertheless, even aided by the dynamic zoom optics, it is still difficult to ensure ion beams to strike the same position of the Faraday cups during peak jumps, from which different cup efficiencies are resulted [2] and hence the precision of isotope ratio measurements is affected.

Recently, the ThermoElectron Neptune and Triton mass spectrometers have employed a novel technology named the "virtual amplifier" design [1,2]. Unlike the classical multiple collector current amplifier systems, the virtual amplifier design does not use a fixed connection between Faraday cup channels and current amplifiers. By using a relay matrix, it is possible to set up the system such that amplifiers are switched cyclically between different Faraday cups during the measurements, so that uncertainties of the gain factors of the amplifiers can be averaged out [1,2]. This design combines the advantages of static and multi-dynamic measurements with a multi-collector system, and long-term external reproducibility of 2–5 ppm can be achieved [3,4], which is almost identical to the internal precision of individual measurements. Although achievable accuracy in static multi-collection remains dependent on the Faraday cup bias, cup efficiencies are almost identical with state-of-the-art Faraday cups. This innovation is useful especially for extremely high precision isotopic analysis purposes such as distinguishing ^{142}Nd anomalies in early Archean rocks [3–5]. According

* Corresponding author. Tel.: +86 10 62007843; fax: +86 10 62010846.
E-mail address: zhychu@mail.igcas.ac.cn (Z. Chu).

1387-3806/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2006.01.034

Table 1
Amplifier switching scheme during the measurement

Number	Cup 1	Cup 2	Cup 3	Cup 4	Cup 5	Cup 6	Cup 7	Cup 8	Cup 9
Block 1	G_1	G_2	G_3	G_4	G_5	G_6	G_7	G_8	G_9
Block 2	G_2	G_3	G_4	G_5	G_6	G_7	G_8	G_9	G_1
Block 3	G_3	G_4	G_5	G_6	G_7	G_8	G_9	G_1	G_2
Block 4	G_4	G_5	G_6	G_7	G_8	G_9	G_1	G_2	G_3
Block 5	G_5	G_6	G_7	G_8	G_9	G_1	G_2	G_3	G_4
Block 6	G_6	G_7	G_8	G_9	G_1	G_2	G_3	G_4	G_5
Block 7	G_7	G_8	G_9	G_1	G_2	G_3	G_4	G_5	G_6
Block 8	G_8	G_9	G_1	G_2	G_3	G_4	G_5	G_6	G_7
Block 9	G_9	G_1	G_2	G_3	G_4	G_5	G_6	G_7	G_8

Amplifiers are switched between blocks; G_n denotes gain factor of amplifiers.

to the software algorithm of the ThermoElectron Trition or Neptune mass spectrometer, the gain calibration is still necessary for high precision isotopic measurements. This paper presents a new calculation method for virtual amplifier multi-collector mass spectrometer that can eliminate the gain factors (and so the corresponding uncertainties) of amplifiers completely for both raw measured isotopic ratios and normalized isotopic ratios when using exponential law or power law to correct isotope fractionation effect, and therefore, makes the gain calibration unnecessary.

2. Principle and calculation method

2.1. Calculation method

The ThermoElectron Triton and Neptune mass spectrometers can be operated in a virtual multi-dynamic mode [1,2]. The measurement is subdivided into groups of nine measuring blocks (time periods). After each measuring block, assignment of the nine electronic measuring systems to the nine Faraday cups is changed over via a relay matrix, with the result that after nine measuring blocks all ionic currents are measured with the same set of nine current amplifiers. The measuring cycle is illustrated in Table 1.

As an example to explain the calculation method with virtual amplifier system, Nd isotopes are analyzed using a virtual amplifier multi-collector mass spectrometer equipped nine Faraday cups. Isotopes ^{142}Nd, ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{148}Nd, and ^{150}Nd are measured with Faraday cups 2, 3, 4, 5, 6, 7, and 8, and ion beams into the Faraday cups are ^{142}I, ^{143}I, ^{144}I, ^{145}I, ^{146}I, ^{148}I, and ^{150}I, respectively. Fluctuation factors of ion beams during the integration time period from block 1 to block 9 are $f(t_1)$, $f(t_2)$, ..., and $f(t_9)$, respectively. Measured voltage values for each measuring channel then, can be expressed as those illustrated in Table 2 and consequently, measured Nd isotopic ratios of nine blocks refer to ^{144}Nd are shown in Table 3.

According to the software algorithm of the ThermoElectron Trition or Neptune mass spectrometer, the end results of isotopic ratios correspond to mean values of isotopic ratios of nine blocks. As an example, ^{143}Nd/^{144}Nd ratio should be:

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right) = \left(\frac{1}{9}\right)\left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}\right)\left[\left(\frac{G_3}{G_4}\right)+\left(\frac{G_4}{G_5}\right)+\left(\frac{G_5}{G_6}\right)+\left(\frac{G_6}{G_7}\right)+\left(\frac{G_7}{G_8}\right)+\left(\frac{G_8}{G_9}\right)+\left(\frac{G_9}{G_1}\right)+\left(\frac{G_1}{G_2}\right)+\left(\frac{G_2}{G_3}\right)\right] \quad (1)$$

According to Eq. (1), when the gain factor of each amplifier is well calibrated, the uncertainties of the gain factors can be averaged out and the external reproducibility of ^{143}Nd/^{144}Nd can be improved [1,2]. Nevertheless, although the uncertainties of gain factors can be almost averaged out completely, gain calibration is still necessary.

Table 2
Measured voltage value of each channel for Nd isotopic measurement with the matrix rotation mode

Number	Cup 2	Cup 3	Cup 4	Cup 5	Cup 6	Cup 7	Cup 8
Block 1	$^{142}IG_2f(t_1)$	$^{143}IG_3f(t_1)$	$^{144}IG_4f(t_1)$	$^{145}IG_5f(t_1)$	$^{146}IG_6f(t_1)$	$^{148}IG_7f(t_1)$	$^{150}IG_8f(t_1)$
Block 2	$^{142}IG_3f(t_2)$	$^{143}IG_4f(t_2)$	$^{144}IG_5f(t_2)$	$^{145}IG_6f(t_2)$	$^{146}IG_7f(t_2)$	$^{148}IG_8f(t_2)$	$^{150}IG_9f(t_2)$
Block 3	$^{142}IG_4f(t_3)$	$^{143}IG_5f(t_3)$	$^{144}IG_6f(t_3)$	$^{145}IG_7f(t_3)$	$^{146}IG_8f(t_3)$	$^{148}IG_9f(t_3)$	$^{150}IG_1f(t_3)$
Block 4	$^{142}IG_5f(t_4)$	$^{143}IG_6f(t_4)$	$^{144}IG_7f(t_4)$	$^{145}IG_8f(t_4)$	$^{146}IG_9f(t_4)$	$^{148}IG_1f(t_4)$	$^{150}IG_2f(t_4)$
Block 5	$^{142}IG_6f(t_5)$	$^{143}IG_7f(t_5)$	$^{144}IG_8f(t_5)$	$^{145}IG_9f(t_5)$	$^{146}IG_1f(t_5)$	$^{148}IG_2f(t_5)$	$^{150}IG_3f(t_5)$
Block 6	$^{142}IG_7f(t_6)$	$^{143}IG_8f(t_6)$	$^{144}IG_9f(t_6)$	$^{145}IG_1f(t_6)$	$^{146}IG_2f(t_6)$	$^{148}IG_3f(t_6)$	$^{150}IG_4f(t_6)$
Block 7	$^{142}IG_8f(t_7)$	$^{143}IG_9f(t_7)$	$^{144}IG_1f(t_7)$	$^{145}IG_2f(t_7)$	$^{146}IG_3f(t_7)$	$^{148}IG_4f(t_7)$	$^{150}IG_5f(t_7)$
Block 8	$^{142}IG_9f(t_8)$	$^{143}IG_1f(t_8)$	$^{144}IG_2f(t_8)$	$^{145}IG_3f(t_8)$	$^{146}IG_4f(t_8)$	$^{148}IG_5f(t_8)$	$^{150}IG_6f(t_8)$
Block 9	$^{142}IG_1f(t_9)$	$^{143}IG_2f(t_9)$	$^{144}IG_3f(t_9)$	$^{145}IG_4f(t_9)$	$^{146}IG_5f(t_9)$	$^{148}IG_6f(t_9)$	$^{150}IG_7f(t_9)$

G_n denotes gain factor of amplifiers; $f(t_i)$ denotes fluctuation factor of ion beam of different integration time period.