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Short communication

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

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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

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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.

Table 3
Measured Nd isotopic ratios refer to ^{144}Nd of nine blocks

Number	^{142}Nd/^{144}Nd	^{143}Nd/^{144}Nd	^{145}Nd/^{144}Nd	^{146}Nd/^{144}Nd	^{148}Nd/^{144}Nd	^{150}Nd/^{144}Nd
Block 1	$^{142}I/^{144}IG_2/G_4$	$^{143}I/^{144}IG_3/G_4$	$^{145}I/^{144}IG_5/G_4$	$^{146}I/^{144}IG_6/G_4$	$^{148}I/^{144}IG_7/G_4$	$^{150}I/^{144}IG_8/G_4$
Block 2	$^{142}I/^{144}IG_3/G_5$	$^{143}I/^{144}IG_4/G_5$	$^{145}I/^{144}IG_6/G_5$	$^{146}I/^{144}IG_7/G_5$	$^{148}I/^{144}IG_8/G_5$	$^{150}I/^{144}IG_9/G_5$
Block 3	$^{142}I/^{144}IG_4/G_6$	$^{143}I/^{144}IG_5/G_6$	$^{145}I/^{144}IG_7/G_6$	$^{146}I/^{144}IG_8/G_6$	$^{148}I/^{144}IG_9/G_6$	$^{150}I/^{144}IG_1/G_6$
Block 4	$^{142}I/^{144}IG_5/G_7$	$^{143}I/^{144}IG_6/G_7$	$^{145}I/^{144}IG_8/G_7$	$^{146}I/^{144}IG_9/G_7$	$^{148}I/^{144}IG_1/G_7$	$^{150}I/^{144}IG_2/G_7$
Block 5	$^{142}I/^{144}IG_6/G_8$	$^{143}I/^{144}IG_7/G_8$	$^{145}I/^{144}IG_9/G_8$	$^{146}I/^{144}IG_1/G_8$	$^{148}I/^{144}IG_2/G_8$	$^{150}I/^{144}IG_3/G_8$
Block 6	$^{142}I/^{144}IG_7/G_9$	$^{143}I/^{144}IG_8/G_9$	$^{145}I/^{144}IG_1/G_9$	$^{146}I/^{144}IG_2/G_9$	$^{148}I/^{144}IG_3/G_6$	$^{150}I/^{144}IG_4/G_9$
Block 7	$^{142}I/^{144}IG_8/G_1$	$^{143}I/^{144}IG_9/G_1$	$^{145}I/^{144}IG_2/G_1$	$^{146}I/^{144}IG_3/G_1$	$^{148}I/^{144}IG_4/G_1$	$^{150}I/^{144}IG_5/G_1$
Block 8	$^{142}I/^{144}IG_9/G_2$	$^{143}I/^{144}IG_1/G_2$	$^{145}I/^{144}IG_3/G_2$	$^{146}I/^{144}IG_4/G_2$	$^{148}I/^{144}IG_5/G_2$	$^{150}I/^{144}IG_6/G_2$
Block 9	$^{142}I/^{144}IG_1/G_3$	$^{143}I/^{144}IG_2/G_3$	$^{145}I/^{144}IG_4/G_3$	$^{146}I/^{144}IG_5/G_3$	$^{148}I/^{144}IG_6/G_3$	$^{150}I/^{144}IG_7/G_3$

Here, a different calculation method is presented, that is, the average values of nine blocks are multiplied and then power the product with one-ninth and, an end result of an isotopic ratio is obtained. As an example, the end results of isotopic ratio of ^{143}Nd/^{144}Nd can be obtained as shown in Eq. (2):

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right) = \left\{\left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}\right)^9 \left[\left(\frac{G_3}{G_4}\right)\left(\frac{G_4}{G_5}\right)\left(\frac{G_5}{G_6}\right)\left(\frac{G_6}{G_7}\right)\left(\frac{G_7}{G_8}\right)\left(\frac{G_8}{G_9}\right)\left(\frac{G_9}{G_1}\right)\left(\frac{G_1}{G_2}\right)\left(\frac{G_2}{G_3}\right)\right]\right\}^{(1/9)} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}\right) \tag{2}$$

According to Eq. (2), employed this calculation for measured isotopic ratios, the gain factors can be completely eliminated out for the end result.

As known, ^{143}Nd/^{144}Nd result in Eq. (2) is the measured ratio that contains factors of mass fractionation or mass bias. Mass fractionation or mass bias effect should be corrected in real time. If the interested element has at least two stable isotopes, internal normalization method can be used to correct the mass fractionation or mass bias effect. Several methods are used for internal correction of the isotope fractionation effect, including linear, power, exponential or Rayleih's law [6–8]. The exponential law and the power law are commonly used.

If the exponential law is used, for Nd isotope analysis, ^{143}Nd/^{144}Nd value is normalized to ^{146}Nd/^{144}Nd using ^{146}Nd/^{144}Nd = 0.7219 as normalization value. Hence, the normalized ^{143}Nd/^{144}Nd value can be expressed as Eq. (3):

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_\mathrm{c} = \left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_\mathrm{m} \left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_\mathrm{t}/(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_\mathrm{m}]/\ln(m_{146}/m_{144})\}} \tag{3}$$

where subscript c means the corrected value, subscript t means the true value, and m denotes the measured value. m_{143}, m_{144}, and m_{146} are masses of ^{143}Nd, ^{144}Nd, and ^{146}Nd isotopes.

The fractionation-corrected isotopic ratio (^{143}Nd/^{144}Nd)$_\mathrm{c}$ of nine blocks then can be expressed as follows:

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{c}1} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_3/G_4\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_\mathrm{t}/(^{146}\mathrm{I}/^{144}\mathrm{I}G_6/G_4)]/\ln(m_{146}/m_{144})\}} \tag{4}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{c}2} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_4/G_5\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_\mathrm{t}/(^{146}\mathrm{I}/^{144}\mathrm{I}G_7/G_5)]/\ln(m_{146}/m_{144})\}} \tag{5}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{c}3} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_5/G_6\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_\mathrm{t}/(^{146}\mathrm{I}/^{144}\mathrm{I}G_8/G_6)]/\ln(m_{146}/m_{144})\}} \tag{6}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{c}4} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_6/G_7\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_\mathrm{t}/(^{146}\mathrm{I}/^{144}\mathrm{I}G_9/G_7)]/\ln(m_{146}/m_{144})\}} \tag{7}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{c}5} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_7/G_8\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_\mathrm{t}/(^{146}\mathrm{I}/^{144}\mathrm{I}G_1/G_8)]/\ln(m_{146}/m_{144})\}} \tag{8}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{c}6} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_8/G_9\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_\mathrm{t}/(^{146}\mathrm{I}/^{144}\mathrm{I}G_2/G_9)]/\ln(m_{146}/m_{144})\}} \tag{9}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{\mathrm{c}7} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_9/G_1\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_\mathrm{t}/(^{146}\mathrm{I}/^{144}\mathrm{I}G_3/G_1)]/\ln(m_{146}/m_{144})\}} \tag{10}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c8} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_1/G_2\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t/(^{146}\mathrm{I}/^{144}\mathrm{I}G_4/G_2)]/\ln(m_{146}/m_{144})\}} \tag{11}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c9} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_2/G_3\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t/(^{146}\mathrm{I}/^{144}\mathrm{I}G_5/G_3)]/\ln(m_{146}/m_{144})\}} \tag{12}$$

In Eqs. (4)–(12), subscripts 1–9 represent blocks 1–9.

If the fractionation-corrected isotope ratios of nine blocks are multiplied and then power the product with one-ninth, an end result of $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ ratio is obtained as following:

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}\right)\left(\frac{m_{143}}{m_{144}}\right)^{\{\ln[(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t/(^{146}\mathrm{I}/^{144}\mathrm{I})]/\ln(m_{146}/m_{144})\}} \tag{13}$$

According to Eq. (13), when using exponential law, the end result of $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ ratio does not contain any gain factors. This means that gain factors can be completely eliminated out for real-time fractionation-corrected isotopic ratios. Similarly, if the power law is considered:

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c} = \left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{m}\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_m}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{14}$$

The fractionation-corrected isotopic ratio $(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_c$ of nine blocks using power law is shown as follows:

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c1} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_3/G_4\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I}G_6/G_4)}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{15}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c2} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_4/G_5\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I}G_7/G_5)}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{16}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c3} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_5/G_6\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I}G_8/G_6)}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{17}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c4} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_6/G_7\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I}G_9/G_7)}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{18}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c5} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_7/G_8\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I}G_1/G_8)}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{19}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c6} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_8/G_9\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I}G_2/G_9)}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{20}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c7} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_9/G_1\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I}G_3/G_1)}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{21}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c8} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_1/G_2\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I}G_4/G_2)}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{22}$$

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c9} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}G_2/G_3\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I}G_5/G_3)}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{23}$$

In Eqs. (15)–(23), subscripts 1–9 correspond blocks 1–9.

Similarly, when the fractionation-corrected isotope ratios of nine blocks are multiplied and then power the product with one-ninth, the end result of $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ ratio also does not contain any gain factor as shown in Eq. (24). Gain factors of the amplifiers can be also completely eliminated out:

$$\left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_{c} = \left(\frac{^{143}\mathrm{I}}{^{144}\mathrm{I}}\right)\left(\frac{(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_t}{(^{146}\mathrm{I}/^{144}\mathrm{I})}\right)^{[(m_{143}-m_{144})/(m_{146}-m_{144})]} \tag{24}$$

Table 4
La Jolla Nd isotopic ratios measured on a ThermoElectron Neptune MC-ICP-MS using the virtual dynamic mode

	$(^{143}Nd/^{144}Nd)_c$	$(^{142}Nd/^{144}Nd)_c$	$(^{145}Nd/^{144}Nd)_c$	$(^{146}Nd/^{144}Nd)_m$	$(^{148}Nd/^{144}Nd)_c$
Results of this study	0.5118492	1.141856	0.3484195	0.7433811	0.2415491
S.E. (abs.)	6.4E−06	1.6E−05	3.0E−06	7.6E−06	4.8E−06
Patent method	0.5118495	1.141856	0.3484195	0.7433779	0.2415489
S.E. (abs.)	6.6E−06	1.8E−05	3.3E−06	1.5E−05	4.8E−06

Subscript c means normalized ratios and m means measured ratios.

Table 5
JMC 475 Hf isotopic ratios measured on a ThermoElectron Neptune MC-ICP-MS using the virtual dynamic mode

	$(^{176}Hf/^{177}Hf)_c$	$(^{178}Hf/^{177}Hf)_c$	$(^{179}Hf/^{177}Hf)_m$	$(^{180}Hf/^{177}Hf)_c$
Result of this study	0.2821624	1.467245	0.7447662	1.886707
S.E. (abs.)	2.4E−06	5.8E−06	4.1E−06	1.2E−05
Patent method	0.2821629	1.467245	0.7447665	1.886705
S.E. (abs.)	2.5E−06	5.7E−06	4.3E−06	1.2E−05

Subscript c means normalized ratios and m means measured ratios.

It should be noted, the measurement process for the calculation method of this paper is the same as that for the patent method. The difference is only in the calculation method. To get the end results, we multiply the average values of isotopic ratios of nine blocks and then power the product with one-ninth, whereas the software algorithm of the Trition or Neptune averages the mean values of isotopic ratios of nine blocks.

2.2. Calculation of error

The error calculation of each measurement can be explained with the following example.

Each measurement is composed of nine blocks contains several scans, for example 10 scans. The relative standard deviations of the raw measured isotopic ratios or fractionation-corrected isotopic ratios of nine blocks are $R.S.D._1$, $R.S.D._2$, $R.S.D._3$, $R.S.D._4$, $R.S.D._5$, $R.S.D._6$, $R.S.D._7$, $R.S.D._8$, and $R.S.D._9$, respectively. According to the error propagation equation, relative standard deviation (R.S.D.) of the end result of an isotopic ratio can be expressed as following:

$$R.S.D. = (1/9)\sqrt{[(R.S.D._1)^2 + (R.S.D._2)^2 + (R.S.D._3)^2 + (R.S.D._4)^2 + (R.S.D._5)^2 + (R.S.D._6)^2 + (R.S.D._7)^2 + (R.S.D._8)^2 + (R.S.D._9)^2]} \quad (25)$$

The precision of an end result of individual measurement obtained by the calculation method in this paper is close to that by the patent method. As effect of the gain factors (and so their uncertainties) of amplifiers are eliminated, accuracy and external reproducibility of isotopic analysis are expected to be improved. External reproducibility of independent measurements can be close to the internal precision of individual measurement, when other error sources are well controlled.

3. Example for a test

Analytical results of Nd and Hf isotopic measurement on standard solutions La Jolla and JMC475 using the ThermoElectron Neptune MC-ICP-MS with the virtual multi-dynamic mode were re-calculated by using the calculation method presented in this paper. Data acquisition was taken as nine blocks and 10 scans per block. $^{143}Nd/^{144}Nd$, $^{142}Nd/^{144}Nd$, $^{145}Nd/^{144}Nd$, and $^{148}Nd/^{144}Nd$ ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$ and $^{176}Hf/^{177}Hf$, $^{178}Hf/^{177}Hf$, and $^{180}Hf/^{177}Hf$ ratios were normalized to $^{179}Hf/^{177}Hf = 0.7325$ using the exponential law. The calculation results and a comparison with those obtained by the patent method are given in Tables 4 and 5. The results obtained from both the calculation methods are almost identical, suggesting that the calculation method can be a reasonable choice for high precision isotopic measurement.

4. Conclusions

A different calculation method to calculate isotopic ratios obtained by the virtual amplifier multi-collector mass spectrometers, such as the ThermoElectron Triton or Neptune mass spectrometers is proposed here. When using this method, gain factors of the amplifiers can be completely eliminated out for both raw measured isotopic ratios or normalized isotopic ratios when the exponential law or power law are employed to correct isotope fractionation effect. Gain calibration is unnecessary when this calculation method is considered. This method can be useful especially for such isotopic analysis purpose to discriminate ^{142}Nd anomalies in early Archean rocks.

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