

NOTE**Determination of relative Faraday cup efficiency factor using exponential law mass fractionation model for multiple collector thermal ionization mass spectrometry**

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A new method for determining the relative Faraday cup efficiency (RFCE) for nine Faraday cups has been developed using ^{86}Sr , ^{87}Sr , and ^{88}Sr isotope signals, and the exponential mass fractionation law. Ten different Faraday cup configurations, combined with a nonlinear solver calculation module in an Excel spreadsheet, allowed for accurate RFCE determination. This method serves as a useful diagnostic tool for characterizing the functionality of Faraday cups.

Keywords: Faraday cup, efficiency, TIMS, Sr isotope, exponential

INTRODUCTION

Static measurement using multiple Faraday cups has advantages over dynamic measurement in terms of rapid isotope ratio determination by mass spectrometry. However, the former is heavily affected by the relativity of the Faraday cup efficiency (FCE) and amplifier gain (Makishima and Nakamura, 1991). The amplifier gain is calibrated by applying a constant electric current. Recent thermal ionization mass spectrometry (TIMS) and multiple collector-inductively coupled plasma mass spectrometry (MC-ICPMS) utilize amplifier rotation relay matrix switching through different Faraday cup-amplifier combinations for eliminating amplifier gain uncertainty (Tuttas and Schwieters, 2003). In contrast, an FCE, which is obtained as a relative FCE (RFCE), is only obtained from a dynamic multiple Faraday measurement with a single isotope peak (Ramakumar and Fiedler, 1999) or from isotope ratio measurements with different Faraday cup combinations (Makishima and Nakamura, 1991). However, RFCE measurement is time-consuming; hence, it is not routinely used. Instead, standard reference materials such as NIST SRM 987 for Sr or JNdi-1 for Nd are used in accuracy and reproducibility evaluations (Takahashi *et al.*, 2009; Hirahara *et al.*, 2009).

The Faraday cup quality deteriorates with long-term exposure to ion beams during measurements. The bias introduced by the relative difference in the FCE results in inaccurate isotope ratios (Makishima and Nakamura, 1991). As such, the inaccuracy can be corrected by normalizing the ratios to those of the standards. However, Faraday cup deterioration also causes signal instability, which cannot be corrected until the cup is replaced. Measuring RFCE is useful for identifying damaged Faraday cups.

Makishima and Nakamura (1991) determined the RFCEs for five Faraday cups in five different Faraday configurations using Nd isotopes with the power law mass fractionation model. However, when the exponential law is used for calibrating mass-dependent fractionation, using the exponential law for the FCE correction is desirable (Supplementary Fig. S1).

In this paper, we present a new method for determining the RFCEs for nine Faraday cups using ten different Faraday cup configurations, by conducting measurements on ^{86}Sr , ^{87}Sr , and ^{88}Sr isotopes with the exponential law mass fractionation model.

EXPERIMENT

We conducted measurements using ^{86}Sr , ^{87}Sr , and ^{88}Sr isotopes of NIST SRM987, following the procedure reported by Takahashi *et al.* (2009). The measurements were performed on a Thermo-Finnigan Triton TI thermal ionization mass spectrometer (TIMS) equipped with nine

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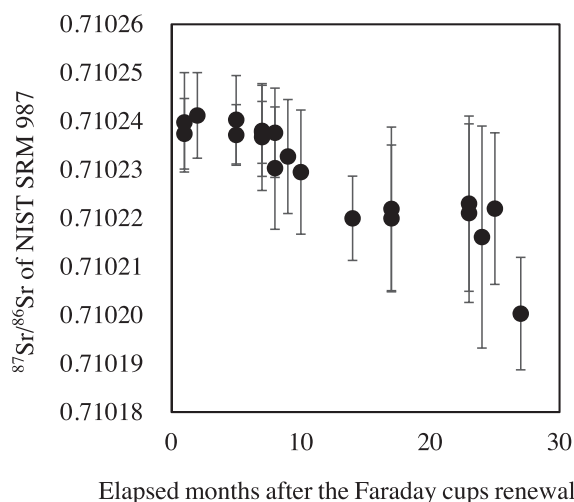


Fig. 1. Temporal changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of NIST SRM 987 measured over the past two years (April 2013 to August 2015) with the Faraday cup configuration C4 in Table S1.

Faraday cups, located at the Japan Agency for Marine Earth Science Technology (JAMSTEC). NIST SRM 987 (100 ng) was loaded on a Re single filament with a Ta activator.

The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ ratios of NIST SRM987 were measured for the ten different cup configurations listed in Supplementary Table S1. Gain calibrations of the Faraday amplifiers were performed prior to the measurements, and amplifier rotation was applied for each round of measurements. The ion beams' intensities were measured in the static mode. The measurement involved 9 blocks, with 12 cycles for each (108 cycles overall). The baseline was measured before starting each block. Five to nine replicate measurements were conducted for each configuration. The intensity of the ^{86}Sr ion beam was ~ 0.5 V during the measurement. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 8.375209. With no FCE difference among nine Faraday cups, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of each Faraday cup configuration should be 0.710240, even if the $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.710240 is measured by the specific Faraday cup configuration of C4 (Takahashi *et al.*, 2009). Correcting for rubidium interference is not necessary because Rb is undetectable in NIST SRM 987.

RFCE CALCULATION

Kimura *et al.* (2015) proposed a new gain calibration method for Faraday amplifiers equipped with 10^{13} Ω resistors, using an Excel spreadsheet with a nonlinear solver function in Excel. They applied the exponential law for mass fractionation correction and measured four different Nd isotope peaks for four Faraday cup-amplifier con-

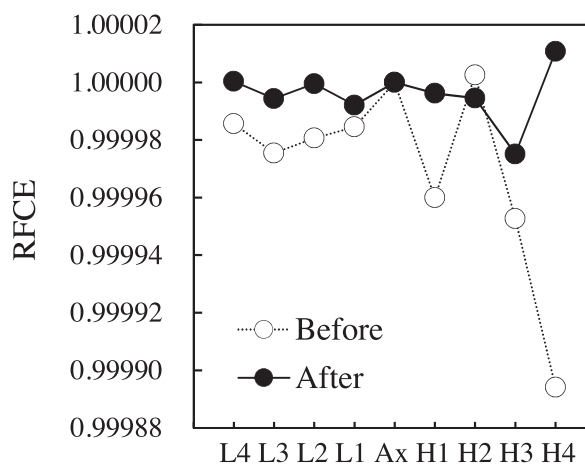


Fig. 2. Comparison of the RFCE values of each Faraday cup.

figurations. They assumed constant FCEs and determined the amplifier gain factors, owing to the unavailability of constant current gain calibration for the amplifiers. Here, we used the same approach, but treated FCEs as unknowns.

The “true” isotope ratio C_1 (amplifier gain-corrected) for the C1 cup configuration (Table S1) was solved using the exponential law, by applying the Sr isotope ratios for NIST SRM 987. The unknown FCE factors were substituted for the amplifier gain factors used in Kimura *et al.* (2015). In the case of the C1 configuration, the FCE factors of L2, L1, and Ax were f_{L2} , f_{L1} , and f_{Ax} , respectively, yielding Eq. (1):

$$C_1 = [({}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{measured}}) \times (f_{L1}/f_{L2}) \times ({}^{87}\text{M}/{}^{86}\text{M})]^{\ln(8.375209/8.375209)} \times (f_{Ax}/f_{L2})/\ln({}^{88}\text{M}/{}^{86}\text{M}), \quad (1)$$

where the atomic mass weights (^{86}M , ^{87}M , and ^{88}M) were obtained from the International Union of Pure and Applied Chemistry (IUPAC) and 8.375209 was the $^{88}\text{Sr}/^{86}\text{Sr}$ isotope ratio. The C_x values for the other Faraday configurations were given by similar equations for C_2 to C_{10} . All C_x values should be equal, yielding the following constraint:

$$C_1 = C_2 = C_3 = C_4 = C_5 = C_6 = C_7 = C_8 = C_9 = C_{10}. \quad (2)$$

We then obtained FCEs (f_{L4} , f_{L3} , f_{L2} , f_{L1} , f_{Ax} , f_{H1} , f_{H2} , f_{H3} , f_{H4}) by solving the equations in Excel. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all configurations (C_1 to C_{10}) were used. The FCEs were treated as variables. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of NIST SRM 987 was also treated as a variable (hereafter R_v), because in this method the true $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (without FCE) is unknown. The FCEs were calculated by minimizing the sum of all absolute differences between

C_x and R_v . Then, the RFCEs were obtained by dividing each FCE value by the axial Faraday FCE value (f_{Ax}). The Excel spreadsheet used in this study is available upon request from the third co-author, Jun-Ichi Kimura (JAMSTEC).

One advantage of our method is that it requires fewer Faraday configurations, as opposed to previous methods in which the number of Faraday configurations exceeded the number of examined Faraday cups. In the most extreme case, we can calculate all RFCEs by using three Faraday cup configurations (e.g., C_2 , C_5 , and C_7), although the accuracy may be poor in such a case.

RFCEs BEFORE AND AFTER FARADAY CUP REPLACEMENT

Figure 1 shows the temporal changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of NIST SRM 987 measured over the past two years (April 2013 to August 2015) using the Faraday cup configuration C4 in Table S1. In April 2013, all of the Faraday cups were new. An almost constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710239 ± 0.000009 (2 standard deviations (2SD), $n = 52$) was obtained during the first seven months. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio gradually decreased, and finally became 0.710200 after 27 months. The measurement's precision (captured by the 2SD of $n = 4$ –24 measurements made over several days in one session by different operators using the same method) also deteriorated, i.e., the value of 2SD increased fourfold (Fig. 1). During this period, we analyzed more than 1700 samples with standard runs for Sr, Nd, and Ce isotopes.

We determined RFCEs before and after the latest replacements of Faraday cups L3, L2, L1, Ax, H1, H2, and H3, in November 2015. Supplementary Table S2 shows the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the repeated measurements for each cup configuration, conducted before and after the replacement. The RFCEs before and after the replacement are listed in Supplementary Table S3. The H2 and Ax cups were heavily damaged, as shown by the large relative RFCEs (up to 109 ppm between H2 and H4) (Fig. 2).

After replacing the Faraday cups L3, L2, L1, Ax, H1, H2, and H3, the RFCEs range was reduced to about one-third of the original, suggesting the effect of Faraday cup replacement. The RFCEs of L4 to H2 were almost the same, but those of H3 and H4 were, respectively, lower and higher than others. Although more detailed investigations are necessary, these subtle differences may be owing to the geometric errors of the Faraday cups with respect to the ion beams.

The average FCE-corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratio after the replacement was 0.710238 ± 0.000005 (2SD, $n = 10$), within the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710239 ± 0.000009 (2SD, $n = 52$) obtained for the C4 configuration immediately following the previous cup replacement (April 2013).

CONCLUSION

We developed a new method for determining RFCEs using exponential law mass fractionation correction and nonlinear solver calculations in an Excel spreadsheet. We also presented an example for determining the RFCEs using Sr isotope signals before and after replacing the Faraday cups. The proposed method is useful for reducing FCE-related analytical errors and for diagnosing Faraday cups.

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SUPPLEMENTARY MATERIALS

URL (<http://www.terrapub.co.jp/journals/GJ/archives/data/50/MS439.pdf>)

Figure S1
Tables S1 to S3