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Precise Re isotope ratio measurements by negative thermal ionization mass spectrometry (NTI-MS) using total evaporation technique

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Abstract

High precision rhenium isotope ratios, $^{187}\mathrm{Re}/^{185}\mathrm{Re}$, have been determined by negative thermal ionization mass spectrometry (NTI-MS) using a total evaporation technique. The salient features of this method are evaporation of the entire sample and simultaneous integration of the signal from each isotope, which effectively eliminates isotope fractionation effects during the evaporation process. The $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratio is obtained with a high reproducibility (1.6755 ± 0.0014 (2σ), R.S.D. $= 0.083\%$, $n = 28$) for 50 pg–1 ng of a Re natural standard using the total evaporation with NTI-MS. This value is within analytical uncertainty of the previously reported accurate $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratio (1.6740 ± 0.0011) adopted by IUPAC as the Re isotopic composition, and is significantly more precise than the ratio obtained from conventional NTI-MS isotopic measurements in our laboratory (1.6772 ± 0.0037 (2σ), R.S.D. $= 0.22\%$, $n = 34$). Based on these results, the total evaporation technique allows us to precisely determine Re isotope ratios, even for small sample amounts. In addition, this method is effective for highly precise Re abundance determinations using isotope dilution.

Keywords: Re isotope ratio; Total evaporation; Negative thermal ionization mass spectrometry; High precision; High sensitivity

1. Introduction

Observed isotopic ratios generally change throughout thermal ionization mass spectrometric (TIMS) analyses because of mass fractionation (discrimination) effects. Therefore, measured isotope ratios suffer from a bias specific to the measurement conditions. The mass fractionation effect is caused by the tendency of the lighter isotopes of an element to preferentially evaporate at a lower temperature (Rayleigh law). To correct for this bias, the measured isotope ratios of reference materials can be compared with certified values, for example as in conventional U and Pu isotope ratio measurements. This external correction technique is affected by different filament temperatures and different filament loading conditions (e.g., [1,2]). Another approach for elements with more than two isotopes, such as Sr and Nd, is internal correction utilizing the isotope ratio of two of the stable isotopes (e.g., [3]), or using the isotope ratio of added amounts of well-characterized isotopes of an element (e.g., double-spike, [4–7]), such as is used for Pb [8–11], combined with conventional mass spectrometry. However, precise calibration of the isotope materials is time-consuming and the expense is high for certain elements. Further, an internal standard cannot be used for an element with only two natural isotopes without using artificial radioactive isotopes, which requires particular facilities.

An alternative and effective way to circumvent the mass fractionation problem is the “total evaporation” method [12], where a sample evaporates completely from the filament and the total ion beam of each isotope is simultaneously integrated using a multi-collector mass spectrometer system. The advantages of the total evaporation procedure are three fold: (1) higher precision, reproducibility, and accuracy can be obtained than by using the conventional technique; (2) a smaller amount of a sample is required because nearly all

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the sample on the filament is evaporated; and (3) a shorter measurement time is necessary (commonly 5–15 min per sample).

The total evaporation method has been used for precise analysis of isotopes of U and Pu [13–16]. Uranium and Pu isotope ratios with extremely high reproducibility (R.S.D. $<$ 0.05%) were obtained in these studies. In addition, the results obtained using the total evaporation method are closer to the certified values for U and Pu isotopic standards such as NBS SRM-946, SRM-947, SRM-948, IRM-199, compared with data obtained from conventional measurements.

Rhenium is comprised of two isotopes, ^{185}Re and ^{187}Re, which are sensitively detected in the form of negative ions of oxides (ReO_4^-) in TIMS analysis [17,18]. As this element has only two isotopes, limiting the precision of the isotope measurement, the total evaporation method is expected to be effective for more precise and accurate isotopic ratio determinations. For isotope dilution measurements in particular, isotope fractionation limits the precision of Re abundance determination. In this contribution, the procedure for Re isotopic ratio measurement using total evaporation combined with negative TIMS is described and the obtained results are compared with those obtained from conventional measurements.

2. Experimental/materials and methods

2.1. Apparatus

A commercially available thermal ionization mass spectrometer (Finnigan MAT 262, Bremen, Germany) equipped with nine Faraday cups, an ion counting detector and an air leak valve in Kyoto University at Beppu was used in the present study. The gains of the amplifiers for the Faraday cups were calibrated every day. Resolving power of the mass spectrometer was ca. 500, and the accelerating voltage was set to 10 kV. The amplifiers for the Faraday cup collectors were equipped with 10^{11} ohm resistors and a beam intensity of 1 V corresponds to 10^{-11} A. Single Pt filaments were employed for isotope measurement. Typical ion source chamber and analyzer tube vacuums were ca. 2×10^{-7} mbar and 8×10^{-9} mbar, respectively.

2.2. Reagents

The Re standard solution was prepared by dissolving Re ribbon (Niloco Co., Japan) with concentrated nitric acid. The Re spike was purchased from Oak Ridge National Laboratory (USA) and dissolved with aqua regia in a closed glass tube. All acids used in this study were ultrapure-grade acids (Tama Chemicals., Japan). A highly pure Pt filament (99.99%, 1 mm × 0.025 mm, Tanaka Precious Metal Co., Japan) was used for isotope measurements, and was baked in air to a bright orange-color temperature for more than three minutes prior to loading the Re samples [19]. Some researchers have reported high Re loading blanks for Pt filaments and favored Ni, V_2O_5-coated Ni, or Ta filaments [19–22]. We found that the loading blank for Pt filaments used here is as low as 0.3 pg [23], which is negligible in the measurements conducted in this study. In addition to Re impurities in Pt filaments, when Re filaments are used for isotopic measurements of elements such as Sr, Nd and U, spattered Re from Re filaments is a source of the significant Re background. Therefore, we carefully examined the source of the Re background in the ion source chamber and decided to use filament holders, sample wheel (turret), and Pt-filament preparation devices that had not been used for Re filament. The low Re loading blank of 0.3 pg mentioned above is the results from through examination of the Re background sources. An amount of 10 μg Ba was loaded as an activator to reduce the working function of Pt and to promote negative ion emission. A custom-made 10,000 ppm $Ba(NO_3)_2$ solution (CLALITAS PPT, SPEX, US) was used. The Re blank of the reagents was less than 0.01 pg, which is negligible in the present work.

2.3. Analysis procedure

Rhenium isotopic ratios were measured in static multiple Faraday collector mode. The standard instrument operating software provided by Finnigan MAT Co. was modified for analysis using total evaporation. The measurement protocol used in the present study is similar to that for U and Pu measurement (e.g., [14]).

Step 1: The Pt sample (evaporation) filament was heated to 750 °C (ca. 2050 mA, depending on filament shape and size). When the $^{187}ReO_4^-$ ion beam was observed, electric lenses were optimized in an ion counting mode with an ion beam intensity of 1–3 mV (60,000–180,000 cps in the ion counting). The ion beam intensity of 1 mV corresponds to 10^{-14} A. The detector was then switched to a Faraday mode and lens settings were re-optimized with an ion beam intensity of around 5–10 mV. Duration of ion lens optimization was approximately 5 min, which did not consume much Re ions compared with the total ions in the measurement and did not affect the final results.

Step 2: The isotope with the higher beam intensity was chosen for monitoring, and the peaks centered. The baseline was measured with the isolation valve closed and the ion source high voltage off. Delay time prior to the integration of baseline (32 s.) was 15 s.

Step 3: The filament current was increased until the ion beam intensity reached preset threshold value (typically 10 mV). Integration of the beam intensity for each isotope was started. The isotopes, ^{187}Re and ^{185}Re, were measured using Faraday Cups no. 6 (center) and 8, respectively. The integration time of a scan was 4 s.

Step 4: The filament current was increased by 10 mA per scan until the beam intensity reached a preset maximum value (e.g., 7 V, for 1 ng Re), while the beam intensity of each isotope was integrated. If the intensity increased beyond the preset value, the filament current was kept constant or reduced in order to keep the Re ion beam intensity nearly constant.

Step 5: When the sample was entirely consumed and the monitored ion beam fell below a preset threshold value, the integration of the beam intensity terminated and the baseline was again measured with the isolation valve closed and ion source high voltage off. The final isotope ratios were calculated from the integrated ion intensity of each isotope after subtraction of the baseline intensity.

As ion lens were optimized at a low ion beam intensity, we observed that the slight increase (typically 1–10%) in an ion beam intensity when ion lens settings were re-optimized at a high ion beam intensity such as 7 V. However, the integrated $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ isotopic ratios were within uncertainty of the value obtained from the total evaporation measurements (Table 1 and Fig. 3), which showed that lens optimization performed at a low ion beam intensity does not affect the final results.

Table 1
Results of Re standard measurements using total evaporation technique

Sample size and run #	251/249 measured	$^{187}\mathrm{Re}/^{185}\mathrm{Re}$ corrected	Deviation from IUPAC value (%)
1 ng-1	1.68329	1.67511	0.08
1 ng-2	1.68388	1.67570	0.11
1 ng-3	1.68245	1.67427	0.03
1 ng-4	1.68386	1.67565	0.11
1 ng-5	1.68415	1.67597	0.13
1 ng-6	1.68431	1.67613	0.14
1 ng-7	1.68285	1.67467	0.05
1 ng-8	1.68453	1.67635	0.15
1 ng-9	1.68403	1.67585	0.12
1 ng-10	1.68393	1.67575	0.13
1 ng-11	1.68443	1.67625	0.15
1 ng-12	1.68390	1.67572	0.11
1 ng-13	1.68314	1.67496	0.07
1 ng-14	1.68462	1.67644	0.16
1 ng-15	1.68457	1.67639	0.16
1 ng-16	1.68478	1.67659	0.17
500 pg-1	1.68223	1.67405	0.02
500 pg-2	1.68333	1.67515	0.08
500 pg-3	1.68407	1.67589	0.12
500 pg-4	1.68364	1.67546	0.10
100 pg-1	1.68411	1.67592	0.13
100 pg-2	1.68335	1.67517	0.08
100 pg-3	1.68326	1.67508	0.08
100 pg-4	1.68363	1.67545	0.09
100 pg-5	1.68377	1.67559	0.11
50 pg-1	1.68252	1.67434	0.03
50 pg-2	1.68283	1.67465	0.05
50 pg-3	1.68417	1.67598	0.13
	Average ± 2σ ($n = 28$)	1.6755 ± 0.0014 (R.S.D. = 0.083%)	

Measured isotope ratios of (mass 251/mass 249) were corrected for oxygen isotopes using the ratios $^{17}\mathrm{O}/^{16}\mathrm{O} = 0.00037$ and $^{18}\mathrm{O}/^{16}\mathrm{O} = 0.002047$ [24] to obtain $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratios.

The $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratio adopted by IUPAC [26] is 1.6740±0.0011 [25]. The $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratio obtained in this study is identical to this $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratio, within analytical uncertainties.

Measured Re isotope ratios were corrected for oxygen isotopes using the ratios $^{17}\mathrm{O}/^{16}\mathrm{O} = 0.00037$ and $^{18}\mathrm{O}/^{16}\mathrm{O} = 0.002047$ [24]. For conventional measurements, the running temperature of the filaments was 850–890 °C. 100 ratios were typically obtained for each sample and the data were treated statistically after the oxygen isotope correction.

3. Results and discussion

A typical intensity profile of $^{187}\mathrm{ReO_4}^-$ and the filament current ramp over the total evaporation procedure are shown in Fig. 1 as a function of scan (4 s per scan). The beam intensity rose rapidly and was kept at a preset value (in this case, 7 V), and subsequently dropped rapidly on entire consumption of the loaded Re sample. This profile is similar to those reported for U and Pu [13,14]. The rapid drop in intensity on sample exhaustion is important for reducing the effect of the termination intensity levels on the integrated ratios. Integration time was generally 15–25 min for a 1 ng Re sample, but the time depended on the amount of sample loaded on the filament and the maximum value for the ion intensity, i.e., 7 V in Fig. 1.

Fig. 2 presents the behavior of the instantaneous $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratio and filament current ramp during the total evaporation procedure. Fluctuations in the $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratio are observed, especially in the early stage of the measurement, and the ratios increase monotonously with time, reflecting the change of the isotopic composition of the sample evaporating on the filament. Such fluctuations were also reported for total evaporation measurements of Pu and U [13,14]. As the Re oxide molecule ion with the lighter isotope ($^{185}\mathrm{Re}^{16}\mathrm{O_4}^-$) evaporates preferentially (Rayleigh law) whereas that with the heavier isotope ($^{187}\mathrm{Re}^{16}\mathrm{O_4}^-$) remains preferentially on the filament, the $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratio increases with time.

The raw isotopic ratios (251/249) and oxygen-corrected $^{187}\mathrm{Re}/^{185}\mathrm{Re}$ ratios measured for the Re samples of 50 pg–1 ng using the total evaporation method are given in Table 1. The raw isotope ratios (251/249) with a standard

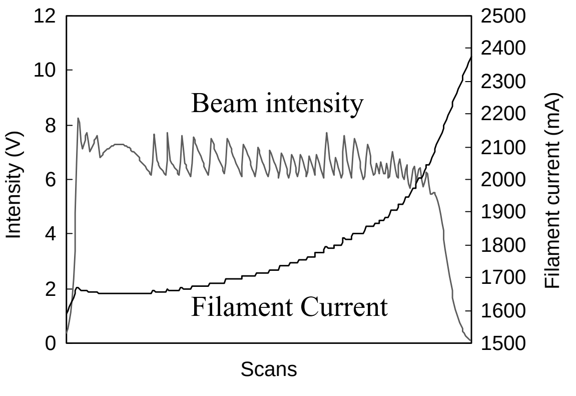

Fig. 1. A typical intensity profile for $^{187}\mathrm{Re}$ and the filament current ramp during the total evaporation procedure as a function of scan (4 s per scan).

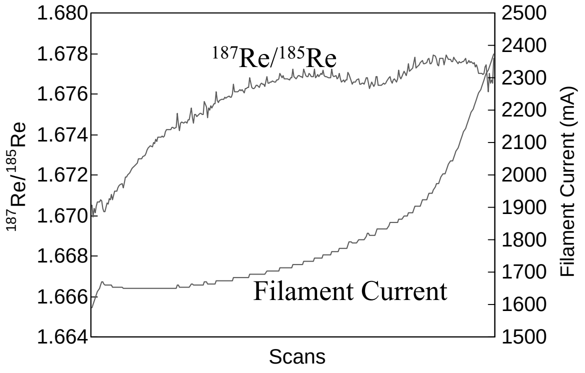

Fig. 2. A typical fluctuation profile of the $^{187}Re/^{185}Re$ ratio compared to the filament current ramp during the total evaporation procedure as a function of scan (4 s per scan).

error ($1\sigma_m$) for each measurement and the oxygen-corrected $^{187}Re/^{185}Re$ ratios obtained using the conventional NTI-MS method are presented in Table 2. The total evaporation and conventional measurement results are compared in Fig. 3. The $^{187}Re/^{185}Re$ ratio was obtained with an extremely high reproducibility (1.6755 ± 0.0014 (2σ), R.S.D. = 0.083%, $n = 28$) for a wide range of sample amounts, 50 pg–1 ng Re standard, using total evaporation with NTI-MS. This value agrees within analytical uncertainty with the previously reported precise $^{187}Re/^{185}Re$ ratio of 1.6740 ± 0.0011 [25] that is adopted by IUPAC as the Re isotopic composition [26]. This previously reported value was determined using the conventional PTI-MS method with a large amount of Re natural standard (ca. 40 μg) with correction of mass spectrometer bias using the mixture of known amounts of Re spike enriched in each isotope. The standard deviation of our $^{187}Re/^{185}Re$ ratio is comparable to that of the previously reported precise measurement [25], which is about three times more precise than the ratio obtained using the conventional NTI-MS method in our laboratory (1.6772 ± 0.0037 (2σ), R.S.D. = 0.22%, $n = 34$). Even if a large fractionation of the $^{187}Re/^{185}Re$ ratio (i.e., from 1.670 to 1.678) is observed throughout the integration, as shown in Fig. 2, no significant change in the final ratios for each measurement of 50 pg–1 ng of natural Re standard can be seen, which implies that the fluctuations in the $^{187}Re/^{185}Re$ ratio do not significantly affect the final ratios obtained using the total evaporation method. This indicates that the evaporation manner as a whole is similar for a range of sample sizes. The Re isotopic ratios obtained in the total evaporation technique also yield highly reproducible data for a wide range of sample amounts (50 pg–1 ng). Fiedler et al. [14] reported that the results obtained using the conventional TIMS measurement show significant varia-

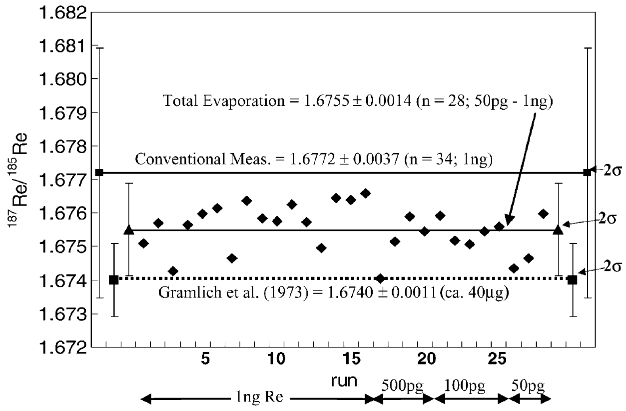

Fig. 3. Variations in the $^{187}Re/^{185}Re$ ratios obtained for 50 pg–1 ng of the natural Re standard using the total evaporation method. Error bars indicate two standard deviations. The average $^{187}Re/^{185}Re$ ratios, with two standard deviation error bars, obtained using conventional method, and the IUPAC value [26] that is originally derived from Gramlich et al. [25], are also shown for comparison. The total evaporation method data are both more precise and closer to the IUPAC value than the conventional method data.

Table 2
Results of Re standard measurements using conventional isotopic measurement

Run #	251/249 measured	Standard error ($1\sigma_m$)	$^{187}Re/^{185}Re$ corrected
1	1.68519	0.00002	1.6770
2	1.68627	0.00004	1.6781
3	1.68730	0.00002	1.6791
4	1.68785	0.00002	1.6797
5	1.68809	0.00002	1.6799
6	1.68801	0.00002	1.6798
7	1.68790	0.00003	1.6797
8	1.68787	0.00004	1.6797
9	1.68761	0.00004	1.6794
10	1.68763	0.00004	1.6794
11	1.68550	0.00002	1.6773
12	1.68524	0.00003	1.6771
13	1.68513	0.00004	1.6770
14	1.68529	0.00005	1.6771
15	1.68194	0.00008	1.6738
16	1.68360	0.00008	1.6754
17	1.68591	0.00006	1.6777
18	1.68680	0.00002	1.6786
19	1.68687	0.00002	1.6787
20	1.68569	0.00004	1.6775
21	1.68575	0.00002	1.6776
22	1.68581	0.00003	1.6776
23	1.68577	0.00004	1.6776
24	1.68577	0.00004	1.6776
25	1.68121	0.00009	1.6730
26	1.68327	0.00003	1.6751
27	1.68288	0.00003	1.6747
28	1.68270	0.00004	1.6745
29	1.68325	0.00005	1.6751
30	1.68391	0.00008	1.6757
31	1.68371	0.00010	1.6755
32	1.68389	0.00011	1.6757
33	1.68421	0.00012	1.6760
34	1.68483	0.00013	1.6766
	Average ± 2σ ($n = 34$)		1.6772 ± 0.0037 (R.S.D. = 0.22%)

Measured isotope ratios of (mass 251/mass 249) were corrected for oxygen isotopes using the ratios $^{17}O/^{16}O = 0.00037$ and $^{18}O/^{16}O = 0.002047$ [24] to obtain $^{187}Re/^{185}Re$ ratios. Rhenium sample size was 1 ng for each run.

Table 3
Results of ^{185}Re-enriched spike measurements using total evaporation technique

Run #	251/249 measured	^{187}Re/^{185}Re corrected
1	0.06800	0.05982
2	0.06757	0.05939
3	0.06767	0.05949
4	0.06771	0.05953
5	0.06780	0.05962
6	0.06774	0.05956
7	0.06786	0.05967
8	0.06767	0.05949
9	0.06764	0.05946
10	0.06757	0.05939
	Average ± 2σ ($n = 10$)	0.05954 ± 0.00027 (R.S.D. = 0.45%)

Measured isotope ratios of (mass 251/mass 249) were corrected for oxygen isotopes using the ratios $^{17}O/^{16}O = 0.00037$ and $^{18}O/^{16}O = 0.002047$ [24] to obtain ^{187}Re/^{185}Re ratios. Rhenium sample size was 1 ng for each run.

tions in the ^{235}U/^{238}U ratios for 0.5–2 μg U, whereas the data obtained using total evaporation were not significantly affected by the sample amount. Other researchers using the total evaporation procedure [13–16] reported U and Pu isotope ratios with extremely high reproducibilities (R.S.D. $< 0.05\%$), and with apparently greater accuracy, based on a comparison with the certified values of several U and Pu isotopic standards.

The Re isotopic ratios of the ^{185}Re-enriched spike used in our laboratory were measured (0.05954 ± 0.0027 (2σ), R.S.D. = 0.45%, $n = 10$) using the total evaporation method (Table 3). The calculated two standard deviation is larger than that obtained for the Re standard because of the large difference in the abundance of the two Re isotopes in the spike. The isotope dilution method is the most effective way to determine the precise concentration of an element in a sample. Based on the results presented here, a combination of the isotope dilution method with the total evaporation procedure will allow significantly more precise and accurate Re concentrations to be obtained.

4. Conclusions

The Rhenium isotope ratio, ^{187}Re/^{185}Re, was determined with extremely high reproducibility (1.6755 ± 0.0014 (2σ), R.S.D. = 0.083%, $n = 28$) for 50 pg–1 ng of a natural Re standard using the total evaporation technique. This value is identical to the precise ^{187}Re/^{185}Re ratio previously reported (1.6740 ± 0.0011) [25], within analytical uncertainty, and is more precise than the ratio obtained using conventional NTI-MS isotopic measurements in our laboratory (1.6772 ± 0.0037 (2σ), R.S.D. = 0.22%, $n = 34$). The outstanding features of this method are the evaporation of the entire sample, which effectively eliminates the effects of isotope fractionation during the evaporation process. Based on these results, the total evaporation technique allows us to precisely determine the Re isotope ratio even for small sample amounts.

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