

Optimization techniques for improving the precision of isotopic analysis by thermal ionization mass spectrometry, taking strontium, neodymium, lead, and osmium as examples

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ABSTRACT

Several optimization techniques have been suggested to improve the signal and precision of analyses by thermal ionization mass spectrometry. Our work shows that tungsten filament is likely the most efficient for ionizing strontium when selecting from tungsten, rhenium, and tantalum filament. Deviations of isotopic ratios could be due to the degradation of the Faraday cups. This disadvantage could be avoided through eliminating the imperfect cup from the cup configuration. The high background produced from usage of rhenium filament could be decreased by cleaning the ion source and baking the source housing.

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Introduction

The thermal ionization mass spectrometer (TIMS) is an important instrument for accurately analyzing isotope ratios. Analytical results demonstrate that the isotopic ratios have excellent stability and good long-term reproducibility by the newest TIMS. For example, the best precision of $^{142}\text{Nd}/^{144}\text{Nd}$ can be $\sim 2\text{--}5$ ppm (10^{-6}),^[1,2] that of $^{87}\text{Sr}/^{86}\text{Sr}$ can be < 5 ppm,^[3] that of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ can be < 650 ppm^[4] and < 200 ppm,^[5] respectively, and that of $^{187}\text{Os}/^{188}\text{Os}$ can be < 10 ppm^[6] by Faraday cup analysis. To achieve higher precision and accuracy for TIMS analyses, researchers are constantly striving to improve the instrument's performance through TIMS hardware upgrades, such as upgrading the electronic system, HV (high voltage), electrical lens system, magnetic sector, amplifier system, vacuum system, cooling system, and collector system. On the other hand, maintenance of the instrument and the separation of the measured elements in the sample are also significant factors. Just as importantly, the determination conditions can significantly affect the precision and accuracy of the TIMS analyses. The isotopes of strontium (Sr), neodymium (Nd), lead (Pb), and osmium (Os) are the primary indicators of trace element evolutionary processes and date important events during the formation of the Earth and other planetary bodies.^[7–14] In this study, we analyzed the isotopes of Sr, Nd, Pb, and Os in reference standard materials using the TRITON TIMS in State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Science. Some experimental conditions, such as different filament materials [rhenium (Re), tungsten (W), and tantalum (Ta)], different cup configurations for the same isotopes, and different activators (using different proportions of H_3PO_4 and silica-gel) with the

same amount of sample, were tested to compare the precision of the analytical results. The results indicate that different analytical conditions may indeed influence the data precision. Therefore, this paper suggests several optimization techniques for use during the preparation and measurement of the samples that will improve precision and accuracy by TIMS analysis.

Experimental preparation

This paper focuses on discussing the analytical conditions that influence precision and/or accuracy during TIMS analysis; however, the chemical separation processes will not be discussed. These analytical conditions include sample loading procedures and instrument settings and configurations, such as the selection of suitable filament materials and additives that can increase the ionization efficiency (called activators) and setting the cup configuration. Several international standard reference materials are used to test the precision and accuracy of different operating conditions. These materials are NIST987 (Sr), NIST981 (Pb), Merck Os, and La Jolla (Nd). NIST987 (Sr) and NIST981 (Pb) were produced by the National Institute of Standards and Technology, USA; Merck Os was purchased from Merck Corporation, Germany; and La Jolla (Nd) was provided by Prof. Castillo, UCSD, USA. Filaments adopted in this study are high purity ribbon of Re, Pt (platinum), Ta (99.995%, 0.025 mm \times 1 mm), and W (99.995%, 0.04 mm \times 0.7 mm), which were bought from H. Cross Company, USA. Several reagents used for preparing the activators were purchased from Alfa Aesar China Co., Ltd., Shanghai, China. These reagents include tantalum chloride (TaCl_5 , purity of compound is 99.8%), barium hydroxide octahedral [$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, purity of compound is $> 98\%$], silicon chloride (SiCl_4 , purity of

compound is 99.998%), silicic acid hydrate ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$, powder, 100 mesh, reagent grade), and orthophosphoric acid (H_3PO_4 , 14.7 M). The emitter Ta_2O_5 was made of 2% TaCl_5 + 1% H_3PO_4 + 1% HF + 12% HNO_3 by weight in water (reference to Birck, 1986^[15]). The emitter $\text{Ba}(\text{OH})_2$ was diluted 3% $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ by weight in water. The silica-gel emitter will be introduced in detail in “The Activator” section. Every filament has been degassed prior to use. All filaments of Re, W, and Ta were degassed at 4.5 A for 30 min in an outgassing device. Meanwhile, high purity Pt-filaments were degassed at 3 A for 3 min in air. The sample loading procedures in this paper refer to the use of manuals provided by ThermoFisher (detailed in section “Filament: Elimination of Source Contamination of Rhenium During Osmium Analysis”). All analyses were performed on the TRITON TIMS instrument at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, CAS. The TIMS is equipped with 9 Faraday cups: L4, L3, L2, L1, C/SEM, H1, H2, H3, and H4. Among the faraday cups, the center cup with a secondary electron multiplier (SEM) is fixed, while the others are movable.

Results and discussion

Matched ribbon material of filaments

During TIMS analyses, it is very important to select a suitable filament for the element you wish to measure. The materials for filaments should generally have physical and chemical properties as follows: stable at high temperature, excellent resistance to corrosion, high melting point, good electrical conductivity, ductility, and malleability. Accordingly, W, Re, Ta, and Pt are often used as filaments for TIMS analyses. These elements' properties are shown in Table 1. In most cases, Re ribbon is suitable for making filaments because of its high melting temperature and moderate electrical and thermal conductivity, which usually produces a stable signal and high ion yield during TIMS analyses. Moreover, the price of filaments is also a factor to be considered during selection, for example, ribbon of Pt and Re are much more expensive than W and Ta; therefore, the latter are more widely used. Taken together, we have recognized that some important factors should also be considered when choosing filament material. The details of how different filaments affect the ion yield under the same conditions will be discussed.

In this study, both Sr standard NIST987 and Nd standard La Jolla are diluted in 1 M HNO_3 for loading. A sandwich technique is used for Sr isotopes analyzed using a single filament (Re, Ta, W). First, 1 μL of Ta_2O_5 solution (activator) is loaded and dried at 0.8 A. Then, 1 μL containing 150 ng of Sr sample is loaded onto the activator spot and dried at 0.8 A. 1 μL of activator is added on the sample spot and dried. The current is

increased to 1.8 A slowly and held there for 1 min. Then the current is increased slowly until the filament becomes dull red, held there for 5–10 s, and finally, the current is decreased and the loading is finished. The current at which Re and Ta glow a dull red is about 2.2 A, while that of W is about 4 A. Double-Re-filament loading is simple, 150 ng of Sr sample is loaded onto the filament and dried at 0.8 A. The filament is heated slowly to a dull red for 10–20 s, after which the loading is complete. Nd samples are loaded on a double filament of Ta, W, and Re; and no additives are needed for sample preparation. 1 μL containing 150 ng of Nd sample is loaded on a filament, dried at 0.8 A, and then, the current is increased to 2.0 A slowly and held there for 1 min. The running temperature for Sr is in the range of 1200–1400°C. The current reference procedure for analyzing Nd with a double filament is to establish 3800–4200 mA on the ionization filament, and 1200–2500 mA on the evaporation filament (1400–1500°C). The filament current is increased at a rate of 150 mA/min. Mass fractionation is corrected by an exponential law using the internal standard ratio of $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$ for Sr and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ for Nd, since they are constant in nature.

Lighter isotopes will be excited earlier than heavier isotopes; therefore, the value of $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{146}\text{Nd}/^{144}\text{Nd}$ becomes larger with increasing current. Determination should start when the $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{146}\text{Nd}/^{144}\text{Nd}$ values approach 8.375209 and 0.7219, respectively. Two hundred data points were collected with 10 blocks and 20 cycles measured for each analysis. The integration time of each cycle is 4 s. The virtual amplifier measurement technique was used in the analysis. The baseline was measured before each block. In this study, each loaded sample was measured under optimum conditions (as high intensity and good stability as possible). All measurements are made on a static Faraday cup. Our work shows that an element may produce different signal strengths (intensity) on different filament materials. It has also been recognized that different elements loaded on the same filament material with the same amount of sample may also produce different signal strengths. In order to compare the intensity difference of three filament types (Re, Ta, and W), each filament type was loaded 10 times with 150 ng of Sr or Nd sample, including both single and double filament measurements. Figure 1a shows that signal intensity differences for Sr resulting from different filaments are very clear. For example, both single and double Re-filaments can obtain the maximum signal for ^{88}Sr at about 10 V, while single Ta filaments may reach an intensity of about 8 V, slightly lower than that of Re. However, it is noted that the single W filaments can produce a maximum intensity from 16 to 26 V and even higher than 26 V in one case. These results indicate that for Sr isotopes with the same amount of Sr loaded on the different filaments, the ion yield of the W filament is higher than that of the Re

Table 1. Material properties of tungsten, rhenium, tantalum, and platinum filaments.

Ribbon material	Atomic number	Melting point (°C)	Electrical conductivity ($10^9/\text{cm}\Omega$)	Thermal conductivity (W/cmK)	First ionization potential (V)
Tungsten (W)	74	3410	189	1.74	7.98
Rhenium (Re)	75	3180	54.2	0.479	7.88
Tantalum (Ta)	73	2996	76.1	0.575	7.89
Platinum (Pt)	78	1772	96.6	0.716	9.0

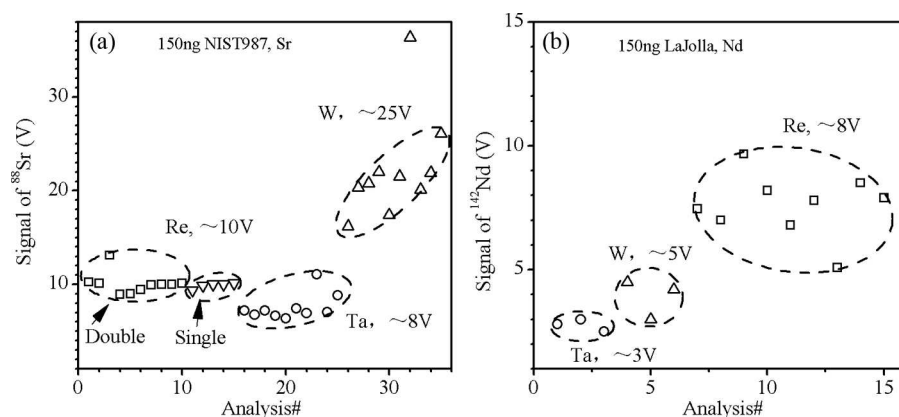


Figure 1. The corresponding signal was analyzed for isotopes of strontium and neodymium on different filament materials: Sr: strontium; Nd: neodymium; W: tungsten; Re: rhenium; Ta: tantalum.

and Ta filaments. In addition, we loaded 150 ng of Nd on double filaments of Re, W, and Ta. The Nd isotopic ratios for the different filaments were analyzed and the results are shown in Fig. 1b. Although 150 ng of Sr on both the single and double Re-filaments produced intensities similar to those of the 150 ng of Nd on the double filaments (~10 V), it can be concluded that the W filament is likely more efficient for ionizing Sr, than Re and Ta filaments (Fig. 1a), and Re-filament can produce a higher intensity of Nd isotopes than W and Ta filaments (Fig. 1b).

The activator

A suitable activator can greatly improve ion yield and maintain ion stability, especially for ultra-low concentration samples. Here, we discuss the activator for Pb isotopes as an example to illustrate the activator's importance.

In this study, the same conditions were used when loading the samples and activators, loading processes and mass fractionation corrections were the same as in Liu et al. (2013).^[4] For all samples, 20 ng of Pb in NIST981 standard solution was loaded and was measured by static Faraday cups at 1100–1300°C. Both a SiCl_4 reagent and Si-gel powder were used for conditioning. Seven methods were divided into four groups, which were used as activators for analyzing Pb isotopes (Table 2). The first group (I) was prepared using 10% SiCl_4 , 5% or 1% H_3PO_4 , and H_2O . In this case, the ^{208}Pb signal intensity of 20 ng of Pb is only 20–40 mV. Thus, the stimulating effect of group (I) is undesirable. The second group (II) was prepared using 5% SiCl_4 , 2% H_3PO_4 , and 93% H_2O . The signal intensity of ^{208}Pb may reach about 0.3 V when loading this mixture and NIST981 for Pb isotopic analysis. It is significantly better than the first group

formulations, but it is not good enough. Then, for the third group (III), a silicic acid-gel powder was replaced by a SiCl_4 reagent to blend the third group with 5% silicic acid-gel; 1.5%, 1.0%, or 0.3% H_3PO_4 ; and H_2O . Using this mixture as an activator, signal intensities of ^{208}Pb are higher than those of the former two groups; meanwhile, signal increases with decreasing H_3PO_4 content. Based on these results, the fourth group (IV) was prepared with more silicic acid-gel (10%) and less H_3PO_4 (0.6%). Signal intensities of ^{208}Pb can reach 1.65 V when using this mixture as an activator for Pb isotopic analysis, which was a satisfactory outcome. Thus, with the improvement of signal intensity by choosing a suitable activator, the precision of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios can be greatly elevated, two times standard deviation from >7‰ to <3‰ (Fig. 2).

Interference from contaminated faraday cups and filaments

Faraday cup efficiency deterioration

When a TIMS has been running for a long time, the impact on a Faraday cup of the different isotopes could become distinct. The different intensity of the isotopes could affect the analytical sensitivity of a Faraday cup or cups, but the influence on each cup is not the same, which results in analytical discrepancies among the different faraday cups. The accumulation of these discrepancies may cause some isotopic ratios to gradually deviate from their real values. In the present study, the standard material reference NIST987 was chosen to observe the variation in Sr isotopic values due to these deviations. A recommended range of $^{87}\text{Sr}/^{86}\text{Sr}$ values for NIST987 is reported by Thirlwall (1991)^[3] as 0.710242–0.710248. We used 150 ng of NIST987-Sr in 1 M HNO_3 to optimize the instrument and measure its

Table 2. The activators made with different component proportions resulted in different effects; Pb: lead; 2SD = 2 times standard deviation; H_3PO_4 : phosphoric acid; SiCl_4 : silicon chloride; Si-gel: silica gel; composition of activator is expressed in weight %.

Group	Pb-content (NIST981, ng)	Activator	Signal (^{208}Pb , V)	n	2SD ($^{206}\text{Pb}/^{204}\text{Pb}$, ‰)
I	20	10% SiCl_4 + 5% H_3PO_4 + 85% H_2O	0.02–0.04	4	–
	20	10% SiCl_4 + 1% H_3PO_4 + 89% H_2O	0.02–0.04	5	–
II	20	5% SiCl_4 + 2% H_3PO_4 + 93% H_2O	0.20–0.32	9	7.4
	20	5% Si-gel + 1.5% H_3PO_4 + 93.5% H_2O	0.40–0.50	3	6.1
III	20	5% Si-gel + 1% H_3PO_4 + 94% H_2O	0.40–0.55	3	6.2
	20	5% Si-gel + 0.3% H_3PO_4 + 94.7% H_2O	0.50–0.60	3	5.8
IV	20	10% Si-gel + 0.6% H_3PO_4 + 89.4% H_2O	1.20–1.65	9	3.4

Note: “–” signal too low to measure.

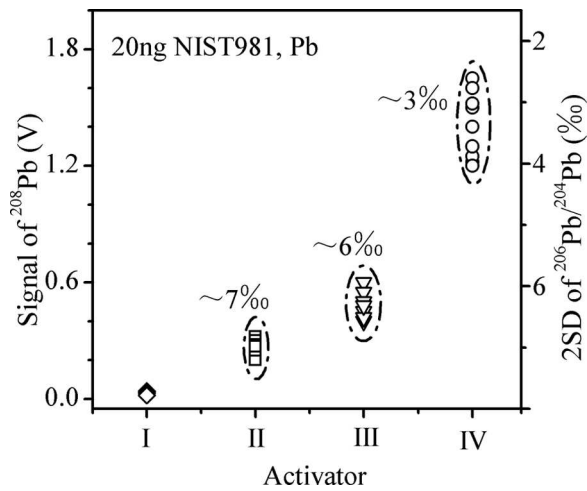


Figure 2. The relationship between activator, signal, and precision; the dotted oval is the range of precision of $^{206}\text{Pb}/^{204}\text{Pb}$ in per mil (‰); Pb: lead; 2SD = 2 times standard deviation.

performance every day before sample determination. It has been observed that the $^{87}\text{Sr}/^{86}\text{Sr}$ values gradually increased (Fig. 3) for analyses that used collector configuration 1, from 0.710249 ± 5 (2SE, $n = 25$) in 2009 to 0.710267 ± 2 (2SE, $n = 41$) in 2013. Meanwhile, the $^{87}\text{Sr}/^{86}\text{Sr}$ values obtained using collector configuration 2 gradually decreased from 0.710240 ± 2 (2SE, $n = 5$) in 2009 to 0.710225 ± 8 (2SE, $n = 5$) in 2013 when the TIMS had been running for an extended period of time (Table 3). Clearly, the value of H1/C ($^{87}\text{Sr}/^{86}\text{Sr}$ ratios using configuration 1) is higher than that of C/L1 ($^{87}\text{Sr}/^{86}\text{Sr}$ ratios using configuration 2) in 2013. Both of the analyzed $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are not the accepted value for NIST987 (0.710242–0.710248).^[3] The most likely reason for the discrepancies described above is that the intensities recorded by the C cup are lower than the actual intensities. In order to solve this problem, we suggest a new cup configuration, configuration 3, which avoids the C cup by arranging H1/L1 so that it corresponds to $^{87}\text{Sr}/^{86}\text{Sr}$. The results show that the ratio of $^{87}\text{Sr}/^{86}\text{Sr}$

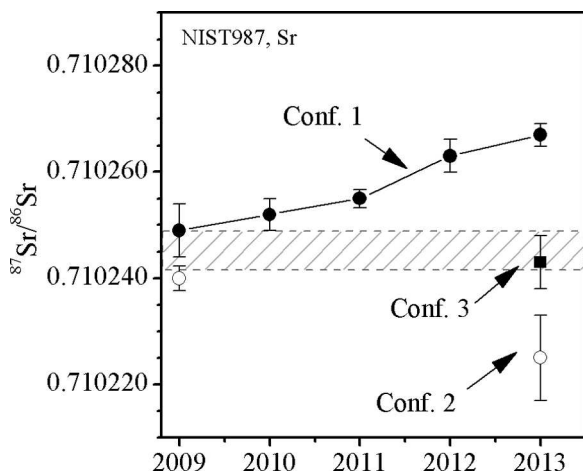


Figure 3. Variation of $^{87}\text{Sr}/^{86}\text{Sr}$ caused by degradation of the C cup; the solid circles are values of $^{87}\text{Sr}/^{86}\text{Sr}$ measured by cup configuration 1, from 2009 to 2013; the hollow circles are values of $^{87}\text{Sr}/^{86}\text{Sr}$ measured by cup configuration 2, from 2009 and 2013; and the solid square is the value of $^{87}\text{Sr}/^{86}\text{Sr}$ measured by cup configuration 3; the gray shaded area is the recommended range of accepted values for NIST987; Conf.: cup configuration; Sr: strontium.

Table 3. The cup configurations for isotopic measurement of strontium; conf.: cup configuration; sr: strontium; L4-H4: the order of the faraday cup.

Faraday Cup	L4	L3	L2	L1	C/SEM	H1	H2	H3	H4
Conf. 1			^{84}Sr	^{85}Rb	^{86}Sr	^{87}Sr	^{88}Sr		
Conf. 2		^{84}Sr	^{85}Rb	^{86}Sr	^{87}Sr	^{88}Sr			
Conf. 3		^{84}Sr	^{85}Rb	^{86}Sr	86.5	^{87}Sr			^{88}Sr

is 0.710243 ± 5 (2SE, $n = 6$), which exactly agrees with the recommended value for NIST987. Therefore, these experimental results support our supposition.

The center cup, C, is affected particularly severely when the TIMS is in operation for a long period of time because it is always used for monitoring the signal and optimizing the parameters of all isotopes during measurements on this instrument. So, the sensitivity of the C cup will be affected more than that of the other cups. To avoid the above problem, this paper suggests the following schemes: (1) the Faraday cup should be changed when it is seriously degraded, which will not be often because replacement of a Faraday cup is complex and expensive; (2) it is viable to use different Faraday cups in turn to monitor signal and optimize the parameters of isotopes; (3) another option is to avoid the degraded cup and reset a new cup configuration, as proposed for Sr analysis by this paper above. In addition, if there are too many isotopes to avoid the degraded cup, a possible option would be dynamic double or triple collector approaches, shifting isotopes between cup configurations within each measurement cycle (as Thirlwall^[9] did).

Filament: Elimination of source contamination of rhenium during osmium analysis

It is known that isobaric interference between samples and filament material should be avoided during TIMS analyses. For example, during Os isotopic analyses, rhenium filament could contribute ^{187}Re to overlap ^{187}Os and W filament could contribute ^{184}W and ^{186}W to overlap ^{184}Os and ^{186}Os .

Indeed, our lab has recognized that ion counts of Re isotopes become higher at times when we once again start to analyze Os isotopes after using Re-filament for a period. In order to confirm that contamination of Re resulted from usage of Re-filament and evaluate the degree of contamination, this study has analyzed the Os isotopic composition of a blank sample. Without Os sample, only $1\ \mu\text{L}$ of $\text{Ba}(\text{OH})_2$ is loaded as an enhancer onto a single Pt-filament, dried at 0.5 A, the current is increased slowly to 1.8 A until the loaded material turns white, and then held for 3 min at this current to achieve complete drying. The loaded material should appear as a small spot, not spread out too much on the filament. The filament was a high purity degassed Pt-filament. The TIMS had been running to analyze Nd and Pb isotopes using Re-filament, for about 1 month. We reinstalled a clean ion source and a clean sample wheel before loading the Pt-filament with the blank sample, but we did not handle any other sections in the source housing. A mass scan (from atomic mass units 232–236) was operated when the current reached 1950 mA, $\sim 800^\circ\text{C}$. This current and temperature are suitable to most Os sample measurements. Our results show that the signal for mass 233 ($^{185}\text{ReO}_3$) and 235 ($^{187}\text{ReO}_3$) were up to about 220 cps and 360 cps, respectively (Fig. 4a). After removing the sample wheel, the source was baked for 2 hr by routine procedure of the instrument. Then,

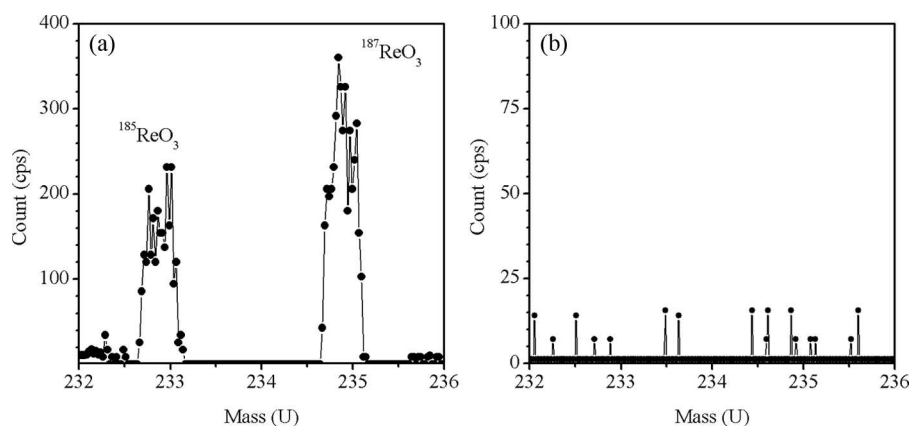


Figure 4. Contamination of ^{185}Re and ^{187}Re from evaporation of Re-filament: (a) a mass scan from atomic mass units 232–236, without having handled any sections in the source housing; (b) a mass scan after baking the sample housing; cps: counts per second.

the analysis described above was repeated, and from this, we found that the signal of both $^{185}\text{ReO}_3$ and $^{187}\text{ReO}_3$ was reduced to within the normal dark noise range, lower than 15 cps (Fig. 4b). It is most likely that Re or ReO_3 had been evaporated and pumped out during the source baking process. After a heating procedure involving Re-filaments, Re or ReO_3 could attach to the surface of parts within the source housing or on its wall, such as glass tubes and halogen lamps. When we increase the current of the filament for another sample measurement, ions can collide with these residual Re particles which results in a higher background Re signal.

Thus, if it is necessary to use a TIMS for analyzing both Os isotopes and other isotopes, the use of Re ribbon should be avoided. The reason for this is that it is likely that evaporating Re from the filament will contaminate the ion source and sections of the source housing. Even if the ion source has been cleaned, the counts of $^{185}\text{ReO}_3$ and $^{187}\text{ReO}_3$ measured for a blank will still be very high.

Conclusions

Operation of instruments and preparation of samples are also significant factors that can affect the precision of TIMS analyses, in addition to instrument hardware. In this study, we provide four optimization techniques to obtain high-precision isotopic ratio data using TIMS.

First, it is concluded that the best TIMS signals are obtained for Sr using W signal filaments and for Nd using Re double filaments. In previous study, different lab uses their respective way to analyze Sr and Nd. Some labs have obtained perfect data for Sr and Nd isotopic analysis by TIMS for application to sub-nanogram samples. For example, Koornneef (2013)^[16] used single Re-filament for Sr and double Re-filament for Nd to do their analyses by 10^{12} ohm current amplifiers. Misawa et al. (2000),^[17] Charlier et al. (2006),^[18] Font et al. (2012),^[19] and Caro et al. (2006)^[2] used single W-filament, single Re-filament, and double Re-filament for Sr or Nd measurements using 10^{11} ohm resistors, respectively. Nevertheless, no experiment shows the discrepancy from different filament materials at same running conditions. We have established that W filament is likely the most efficient for ionizing Sr when selecting from W, Re, and Ta; meanwhile, double Re-filament can produce a higher intensity for Nd isotopes than W and Ta

filament can. It is important to choose a suitable filament material for isotopic measurements.

Second, our study indicates that choosing a suitable activator can greatly elevate the precision of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios during Pb isotopic measurements. Gerstenberger et al. (1997)^[20] have contributed a highly effective emitter substance for mass spectrometric Pb isotope ratio determinations. Our experiment shows that the optimum proportion of silica gel and phosphoric acid is important to get high signal intensity and precision. The preparation of the activator plays a key role in the analysis of some isotopic ratios. As well as, we have suggested a new scheme to make an activator by using a mixture of 10% Si-gel + 7.5% H_3PO_3 + 82.5% H_2O (weight %).

Third, it is necessary to reset the cup configuration to avoid cup degradation when operating for a long period of time (a year or more). We propose a new cup configuration to avoid this disadvantage during Sr isotopic analyses.

Finally, the contamination of ^{187}Re and ^{185}Re after using Re-filament could be eliminated by cleaning the ion source and baking the source housing. Both of the last conclusions have not been published by other researchers.

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