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Application of the total evaporation technique to chromium isotope ratio measurement by thermal ionization mass spectrometry

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Abstract

The total evaporation technique of thermal ionization mass spectrometry was applied to the isotopic analysis of chromium. High measurement reproducibility of the chromium isotope ratios was verified (2 S.E. $< 0.05\%$ (^{53}Cr/^{52}Cr)), while a clear mass fractionation effect was observed by using conventional measurement technique. The chromium isotope ratios analyzed by the total evaporation method were not affected by the sample amount on the rhenium filament (50–500 ng Cr). The isotopic analysis under the coexistence of zinc was also performed, and its effect to the chromium isotope ratios was confirmed.

Keywords: Chromium; Isotope ratio; Isotopic analysis; Thermal ionization mass spectrometry; Multi-collector; Total evaporation; Molten salt; Liquid metal; Isotope effect

1. Introduction

Thermal ionization mass spectrometry (TIMS) is well known in the analysis of precise and accurate isotope ratios. The ion source of TIMS is equipped with a filament which evaporates and ionizes the sample on it. Since the lighter isotope tends to evaporate at a lower temperature, the isotopes are fractionated on the filament during the analysis. The mass fractionation effect results in a bias which is specific to the analytical condition.

The total evaporation method is effective at cutting off the mass fractionation effect. The sample is evaporated from the filament completely, and the total ion beam of each isotope is integrated. Since a mass spectrometer equipped with the multi-collector system can integrate ion beams simultaneously, it enables us to obtain accurate data by the total evaporation method. In the nuclear science discipline, the total evaporation method is accepted in the isotopic analysis of uranium [1,2]. Though the total evaporation technique is the fractionation free method, its application appeared to be limited for uranium and plutonium. Recently, the total evaporation technique has been adopted for obtaining the precise isotope ratios of rhenium [3] and radium [4]. Since the mass fractionation effect is more significant in the light elements, its application to the lighter elements should be most effective.

Chromium has four stable isotopes, ^{50}Cr, ^{52}Cr, ^{53}Cr, and ^{54}Cr. There are no stable isotopes of any other element with masses 52 and 53. Since ^{50}Ti, ^{50}V, and ^{54}Fe are isobars of ^{50}Cr and ^{54}Cr, chromium samples must not be contaminated with titanium, vanadium, and iron. Oxide ions of other elements (alkali and alkaline earth) do not yield mass 50–54. The large isotopic dispersion from 50 to 54 and the smaller isotopic interferences enable us to demonstrate the effectiveness of the total evaporation method for chromium as a light element.

The chromium isotope ratios of an isotopic reference standard (SRM979) were analyzed by TIMS with the total evaporation technique. The precision and accuracy of measured isotope ratios were discussed by comparing to the data obtained by the conventional method. The fluctuation of the isotope ratios under the coexistence of other elements was also studied.

2. Experimental

2.1. Isotopic analysis by the total evaporation method

The isotopic reference standard SRM979 was obtained from the US National Institute of Standard and Technology. The

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hydrated chromium nitrate, $[Cr(NO_3)_3{\cdot}9H_2O]$, was dissolved in nitric acid to create a chromium solution containing 100 ppm Cr in 1 mol dm^{-3} (M) HNO_3. To avoid the isotopic interference of ^{50}Ti, ^{50}V, and ^{54}Fe on ^{50}Cr and ^{54}Cr, nitric acid purchased from Tama Chemicals Co., Ltd was used, in which the concentration of each metallic impurity was certified to be under 0.01 ppb.

Each 2 μL aliquot was placed on a sample filament, in which the filament used was rhenium ribbon prepared via zone melting. The total amount of Cr loaded on the filament was 200 ng. The filaments with 50 ng Cr and 500 ng Cr were also prepared in the same manner. The isotopic analysis was performed using a mass spectrometer with a multi-collector system (Finnigan, MAT262).

A rhenium double filament was loaded into the mass spectrometer. Because the natural abundance of ^{52}Cr (83.79%) is greatest, its ion beam was monitored and $^{m}Cr/^{52}Cr$ was measured (the superscript *m* means mass number 50, 52, or 53). Ion beam intensity at mass number 51 was monitored to check the background. The measurement protocol was as follows. The ionization filament was heated to 4 A in 10 min. The sample (evaporation) filament was heated to attain 3×10^{-13} A ion current of ^{52}Cr, and then peak centering and focusing were quickly completed. The measurement was performed with the increase of the sample filament current by 20 mA/scan, in which the integration time of 1 scan was 4 s. The upper limit of the ^{52}Cr ion current was set at 7.5×10^{-11} A. The data acquisition was terminated when the ^{52}Cr ion current fell below 2×10^{-13} A. Thirteen to 20 samples for each sample amount were analyzed.

2.2. Isotopic analysis by the conventional method

Ten filaments for each sample amount of Cr (50 ng, 200 ng, and 500 ng) were prepared in the same manner as the total evaporation method, and a rhenium double filament was loaded into the mass spectrometer. The ionization filament was heated to 4 A in 10 min. The sample filament was gradually heated to 1.2–1.5 A in 10 min to attain the steady state of an ion beam with an adequate ion current of ^{52}Cr. The peak centering and focusing were done within this heat up procedure. The ion currents of ^{52}Cr were about 4.0×10^{-12} A (50 ng Cr) and 3.0×10^{-11} A (200 ng Cr or 500 ng Cr). Forty ratios (in two blocks of 20 ratios each) were measured in 8 min.

After the measurement, the sample filament was slightly heated up to recover the same ion beam current before the measurement. Then the isotope ratios were measured again. This procedure was repeated again. Totally, isotopic analysis was performed three times for each sample.

2.3. Effect of coexisting zinc in the isotopic analysis of chromium with the total evaporation technique

The performance of the total evaporation method under the coexistence of other elements is important. The isotopic analysis of chromium with the total evaporation technique was performed under the coexistence of zinc.

Anhydrous $CrCl_3$ was a product of Anderson Physics Laboratory Engineered Materials (APL) (99.99% in purity). Zinc nitrate is a product of Wako Chemicals Co., Inc. By using anhydrous $CrCl_3$, chromium solution containing 200 ppm Cr in 1 M HNO_3 was prepared (which is similarly denoted in the following section in detail). A 200 ppm Cr solution containing 40 ppm Zinc in 1 M HNO_3 was also prepared. These were supplied to the isotopic analysis, and the filaments with 200 ng Cr and 200 ng Cr + 40 ng Zn were prepared. Nine samples for each sample were analyzed by the total evaporation method.

2.4. Pyrometallurgical bi-phase extraction

In order to verify the accuracy of isotopic analysis with the total evaporation technique, a pyrometallurgical bi-phase extraction, which has been studied as a reprocessing technique for the spent nuclear fuels [5], was performed, and the isotope fractionation of chromium in this system was similarly studied.

Anhydrous $CrCl_3$ and LiCl–KCl eutectic mixture (mole ratio of lithium to potassium = 59/41) were products of Anderson Physics Laboratory Engineered Materials (99.99% in purity). Zinc metal (over 99.9% purity) was a product of Kanto Chemicals Co., Inc. Anhydrous $CrCl_3$ was dissolved in the LiCl–KCl eutectic to create a solution, 0.2 M $CrCl_3$, at 873 K in a quartz tube. This was contacted with the liquid zinc at 873 K for 20 h (6 h is time enough to achieve an equilibrium [5]). The volumes of two phases at 873 K were 4 mL (molten salt phase) and 1 mL (liquid Zn). Trivalent chromium in the molten salt phase was reduced and extracted by metallic zinc. After achieving the extraction equilibrium, the molten salt phase was drawn into a quartz tube for analysis. The extraction experiment was carried out in a glove box system filled with dry Ar continuously purified to remove oxygen and humidity. The content of impurities O_2 and H_2O in the inside atmosphere was continuously maintained less than 1 ppm.

The concentration of chromium in the drawn salt sample was analyzed by an ICP spectrophotometer (Shimadzu, ICP-1000TR). The ratio of [Cr] in the equilibrated molten salt phase to that of the initial condition was $[Cr]_{equilibrated}/[Cr]_{init} = 0.063$. Most of Cr(III) in the molten salt phase was reduced to Cr^0 and extracted into the liquid zinc phase. This means that the electrically equivalent amount of Zn^0 was oxidized to Zn(II) and dissolved into the molten salt phase.

The drawn salt sample was dissolved in a NH_3 solution, whose Eh was controlled by adding hydrazine monohydrochloride, and Cr(III) was recovered as $Cr(OH)_3$. Lithium and potassium were completely removed by this precipitation procedure, but the separation factor of chromium and zinc was not high: mole ratio of zinc to chromium in the recovered $Cr(OH)_3$ was 1/5. The recovered $Cr(OH)_3$ containing zinc was dissolved in nitric acid to create a chromium solution of 1 M HNO_3, and by using this, the filament with 200 ng Cr was prepared for isotopic analysis. Ten samples were analyzed by the total evaporation method.

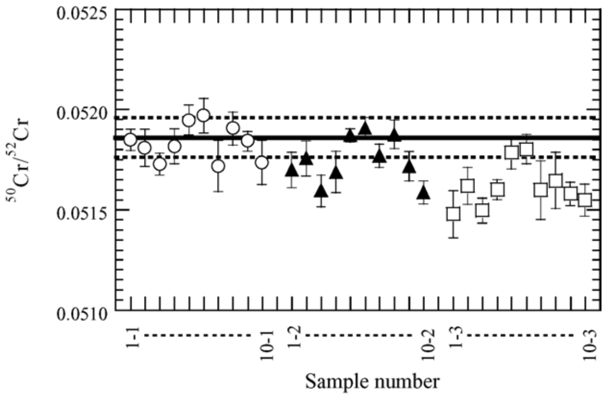

Fig. 1. Chromium isotope ratio, ^{50}Cr/^{52}Cr, measured by the conventional method. The sample amount is 200 ng. The errors are 2 S.D.

3. Results and discussion

3.1. Mass fractionation effect of the conventional method

Fig. 1 shows the raw data of the ^{50}Cr/^{52}Cr values obtained by the conventional method (200 ng Cr). The sample number *x*–*y* means *y*th measurement of sample *x*. The bold line and the dotted lines are the certified value and its uncertainties (2 S.D.), respectively [6]. It is clear that, from the 1st to the 3rd measurement, the ^{50}Cr/^{52}Cr decreased due to the mass fractionation effect. All isotope ratios are summarized in Fig. 2. Each data is the averaged value of the 10 samples and the errors are the experimental error of 2 S.E. The number typed in the abscissa means *y*th measurement. The clear mass fractionation effect can be seen in each isotope ratio. For the sample amount, 50 ng Cr is small to attain and maintain the adequate ion beam current. This would result in the large errors. The 1st measurement with 200 ng Cr shows the isotope ratio close to the certified value, but the measured isotope ratio deviates from the certified value over time. This means that the data acquisition in measurement of isotope ratios of 200 ng Cr should be initiated immediately after the ion beam is stabilized. On the other hand, the 1st measurement with 500 ng Cr is considered to be slightly premature. The isotope ratios obtained by the 2nd measurements are more accurate. From the 1st to the 3rd measurement, the isotope ratios are identical with the certified values within the experimental errors. As shown in Fig. 2, however, the mass fractionation effect occurs clearly through these measurements. This effect limits gathering precise and accurate data. The suppression of the mass fractionation effect is necessary for attaining better reproducibility.

3.2. Precision and accuracy of the isotopic analysis of chromium with the total evaporation technique

Fig. 3 shows the raw data of the chromium isotope ratios obtained by the total evaporation method. Since the ion current was integrated for each isotope in the total evaporation measurement, one measurement gives no analytical error such as standard error of more than two measured isotope ratios (runs), as obtained in the conventional method. Hence, we evaluated the reproducibility as an experimental error. Measurement results with 2 S.E. are shown in Table 1. The certified values [6] of NIST-SRM979 by conventional method are shown together with 2 S.D. Our previous data [7] (500 ng Cr, total evaporation method) are also shown.

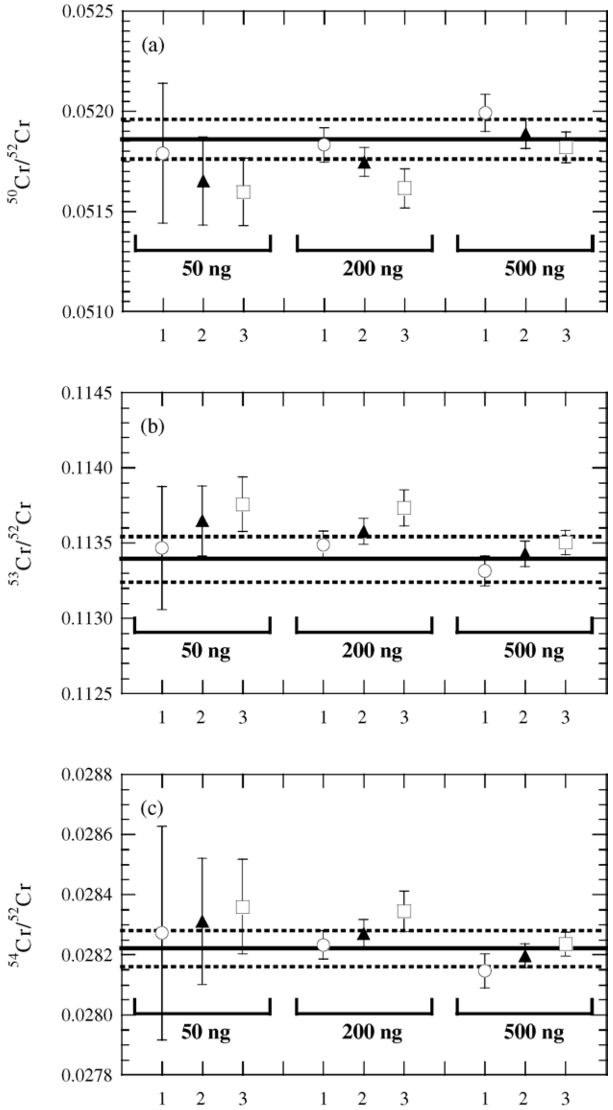

Fig. 2. Chromium isotope ratios measured by the conventional method: (a) ^{50}Cr/^{52}Cr, (b) ^{53}Cr/^{52}Cr, and (c) ^{54}Cr/^{52}Cr. The errors are 2 S.E. of 10 samples.

High reproducibility of the present isotopic analysis can be seen in Table 1. For three type samples (50 ng, 200 ng, and 500 ng Cr), each isotope ratio, ^{m}Cr/^{52}Cr, shows the same value within experimental error of 1 S.E. The amount of sample on the filament is one of factors to enhance the mass fractionation effect in the conventional method. However, with the total evaporation technique, the chromium isotope ratio is not affected by the change in the sample amount. This high reproducibility indicates that in point of the internal error (reproducibility) during a short experimental period, the standard error can be minimized by measuring more samples.

Table 1
Measurement results of NIST-SRM979

	^{50}Cr/^{52}Cr	^{53}Cr/^{52}Cr	^{54}Cr/^{52}Cr
Certified value [6]	0.051859 ± 0.000100	0.113386 ± 0.000145	0.028222 ± 0.000059
This study (50 ng Cr) ($n = 17$)	0.051716 ± 0.000024	0.113621 ± 0.000023	0.028292 ± 0.000012
This study (200 ng Cr) ($n = 13$)	0.051703 ± 0.000036	0.113622 ± 0.000037	0.028294 ± 0.000019
This study (500 ng Cr) ($n = 20$)	0.051710 ± 0.000047	0.113613 ± 0.000049	0.028289 ± 0.000024
Previous study [7] ($n = 8$)	0.051647 ± 0.000105	0.11368 ± 0.00011	0.028321 ± 0.000058

n: number of measurements. The errors are 2 S.D. (certified value) and 2 S.E. (our data).

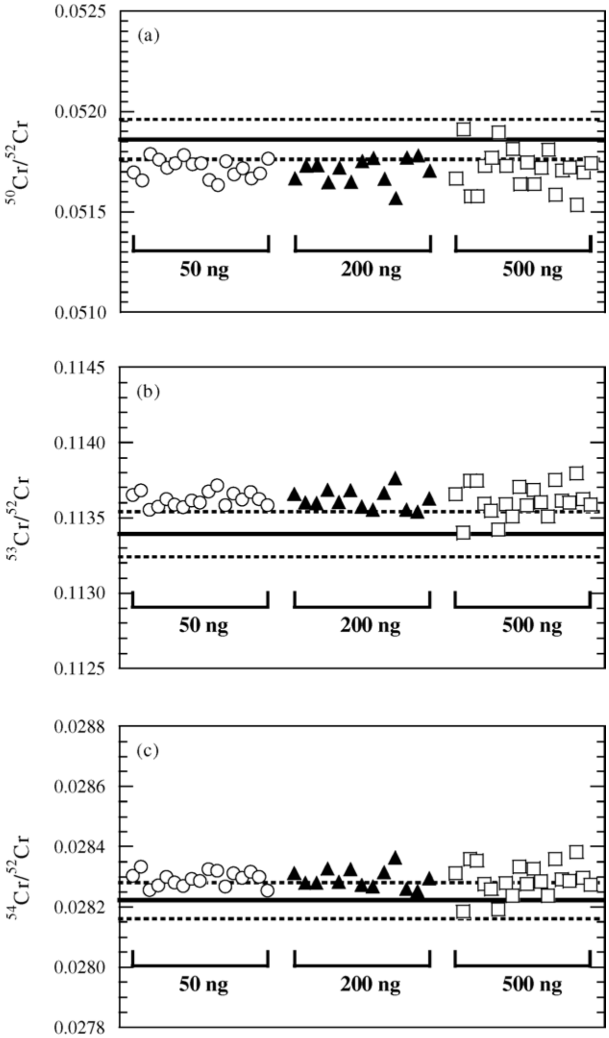

Fig. 3. Chromium isotope ratios measured by the total evaporation method: (a) ^{50}Cr/^{52}Cr, (b) ^{53}Cr/^{52}Cr, and (c) ^{54}Cr/^{52}Cr.

The present results show good agreement with our previous result [7] within the experimental errors of 1–2 S.E. This proves the small external error of the isotopic analysis of chromium with the total evaporation technique.

Our results are identical with the certified values within the experimental errors of 2–3 S.D. Though there is a good conformation, the absolute values of our data are slightly shifted from the certified values which suggests an enrichment of heavy isotopes. Since the total evaporation method is the fractionation bias-free measurement, the difference would not be due to the mass fractionation effect. The origin of this bias could not be clarified in this study. This may become clear by measuring isotope ratios of a mixture of chromium monoisotopes, whose isotopic composition is certified by weight, with the total evaporation technique.

For chromium, it is difficult to describe that the total evaporation method is the absolute measurement of the isotope ratio. As well as the conventional method, the total evaporation method requires an external correction by the reference material. However, once the bias is set, an extremely small internal error will be obtained. Furthermore, the reliable results can be obtained without the experienced technique required for the conventional method.

3.3. Effect of the coexisting elements to the isotopic analysis of chromium

As shown in Table 2, the isotope ratios without Zn, $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{init}}$, show agreement with those with Zn, $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{init+Zn}}$, within the experimental errors of 2 S.E. (but disagreement within 1 S.E.). $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{init}}/([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{init+Zn}}$ was shown in Fig. 4. Fig. 4 shows an isotope fractionation, whose magnitude is larger than 1 S.E. This isotope fractionation suggests a mass-dependent isotope effect. Adding a certain amount of zinc on the filament results in an enrichment of the light isotopes of chromium. Even if the coexisting zinc enhances the mass fractionation effect of chromium and/or changes the

Table 2
Measurement results of chromium isotopes (APL)

	^{50}Cr/^{52}Cr	^{53}Cr/^{52}Cr	^{54}Cr/^{52}Cr
200 ng Cr	0.051791 ± 0.000028	0.113558 ± 0.000033	0.028266 ± 0.000016
200 ng Cr + 40 ng Zn	0.051828 ± 0.000030	0.113529 ± 0.000030	0.028250 ± 0.000017

The errors are 2 S.E.

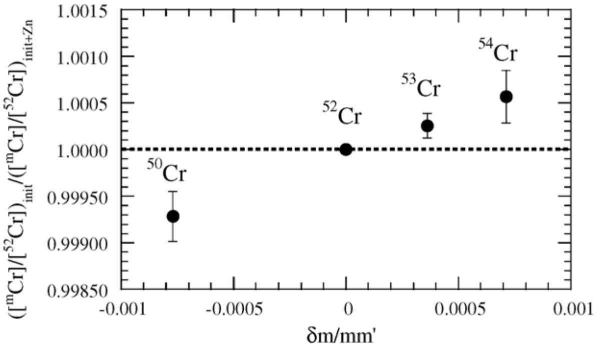

Fig. 4. Effect of the coexistent zinc on the isotopic analysis of chromium. Chromium isotope ratios were measured by the total evaporation method. $\delta m/mm' = (m - 52)/52m$. The errors are 1 S.E. (see Table 2).

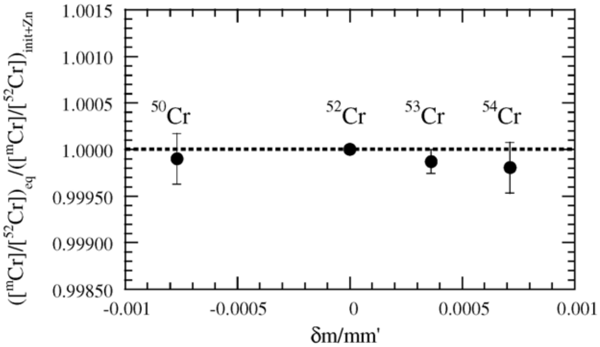

Fig. 5. Isotope fractionation of chromium in a pyrometallurgical bi-phase extraction. Chromium isotope ratios were measured by the total evaporation method. The errors are 1 S.E. (see Tables 2 and 3).

Table 3
Measurement results of chromium isotopes (bi-phase extraction)

200 ng Cr + ca. 40 ng Zn	
^{50}Cr/^{52}Cr	0.051823 ± 0.000029
^{53}Cr/^{52}Cr	0.113514 ± 0.000030
^{54}Cr/^{52}Cr	0.028244 ± 0.000015

The errors are 2 S.E.

ionization efficiency of chromium, these effects should be canceled out by the total evaporation technique. Zinc should be evaporated from the filament earlier than chromium. Assuming zinc changes the ionization efficiency and the mass fractionation effect of chromium by the end of its evaporation, this may result in the isotope fractionation. Further investigations for the effects of coexisting elements are required for understanding the isotope fractionation in the isotopic analysis with the total evaporation method.

3.4. Application of the total evaporation method to the study of isotope fractionation of chromium

As an actual case, an isotope fractionation in a chemical exchange system was studied by using the total evaporation method. For the pyrometallurgical bi-phase extraction, the detailed information can be seen elsewhere [5]. The extraction equilibrium is:

$$2\mathrm{CrCl_3(in\ LiCl–KCl)} + 3\mathrm{Zn(in\ Zn)} \leftrightarrow 2\mathrm{Cr(in\ Zn)} + 3\mathrm{ZnCl_2(in\ LiCl–KCl)} \quad (1)$$

The equilibrium constant is isotopically different between isotopes. If the difference is detectable, the chromium isotope ratios in both phases should be shifted from their original.

The isotope ratios of chromium in the equilibrated LiCl–KCl phase, $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{eq}}$, with 2 S.E. were shown in Table 3. $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{eq}}/([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{init+Zn}}$ was calculated and shown in Fig. 5. The errors are the experimental errors of 1 S.E. As shown in Fig. 5, the isotope fractionation in the reaction (1) is negligibly small. This means that the isotopic change in the equilibrium constant was very small to observe by the single stage experiment. If the $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{eq}}$ was not compared with $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{init+Zn}}$ but with the $([^{m}\mathrm{Cr}]/[^{52}\mathrm{Cr}])_{\mathrm{init}}$, the isotopic difference may have been attributed to the isotope fractionation of the reaction (1). In order to use the total evaporation method for the accurate isotopic analysis of chromium, the purification of chromium is essential.

4. Conclusions

The total evaporation technique is the strong tool for the isotopic analysis of chromium. High measurement reproducibility is obtained, and the measurement is not affected by the sample amount on the filament. However, the coexisting zinc results in the isotope fractionation of chromium in the total evaporation method.

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