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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

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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.