Isotopic Analysis of Molybdenum by Surface Ionization Mass Spectrometry and a Carbonization Technique

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A technique to increase and stabilize the ion production of molybdenum and some other elements has been developed in their isotopic analysis by single-filament surface ionization mass spectrometry. A mixture of the element (5–100 μ g, dilute sulfuric acid solution) and five to ten as much glycerol (5 v/v % aqueous solution purified by ion exchange) was mounted on a ribbon filament and was charred in air to slightly wet tar, and then heated in the mass spectrometer ion source under a vacuum of $\sim 5 \times 10^{-7}$ Torr to appropriate temperatures by slowly increasing the filament current. As the filament material, rhenium ribbon was suitable for Mo and Hf, and tantalum ribbon for Cr samples. The sample coated in the form of oxo-compounds was reduced possibly through intermediate or direct carbonization during mass spectrometry and the sample pretreatment outside or inside the instrument was shortened. Stable ion currents of 10^{-13} to 10^{-11} A for Mo^+ , Hf^+ , and Cr^+ ions were obtained and found to be usable in routine isotopic analysis.

1. Introduction

In the isotopic analysis of the elements by surface ionization mass spectrometry, many techniques have been proposed to increase the ion production of the elements. Studier *et al.*¹⁾ studied the uranium ion production by reducing the *in vacuo* prebaked rhenium and tungsten filaments with benzene atmosphere and carbonizing the filaments before sample deposition. Fenner²⁾ described the ion increase by the treatment of a uranyl nitrate sample mounted on a canoe-type single rhenium ribbon with a 0.3 Torr hydrogen-oxygen mixture or by the deposition of the nickel thin layer onto the uranium sample. Fenner and his coworkers³⁾ have also used the technique reported by Studier *et al.* for the uranium isotopic analysis of submicrogram amounts of samples. Crouch and Tuplin⁴⁾ used the hydrogen reduction treatment of molybdenum trisulfide samples on rhenium filaments for

“terrestrial” molybdenum isotope analyses by an instrument equipped with a Faraday cup collector. The similar techniques for molybdenum samples have been applied in the precision isotope ratio measurement work by Stevens⁵⁾ and by Moore *et al.*⁶⁾. Walker⁷⁾ has used the hydrogen reduction in determining rhenium in microgram amounts of rhenium-tungsten alloys by isotope dilution mass spectrometry. The techniques for realizing the thermal ion production of the elements of high ionization potentials and of the elements difficult to analyze because of their evaporation profiles were reviewed by Crouch and Tuplin⁸⁾.

This paper describes a technique to produce enhanced ion intensities of molybdenum by adding organic materials to the sulfuric acid solution of molybdenum and making tar on a ribbon filament by preheating in air and measuring isotopic ratios of molybdenum with reasonable relative standard deviations by

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surface ionization mass spectrometry. Ion intensities of hafnium and chromium were also substantially increased by the same technique.

2. Experimental

2.1 Apparatus and Materials

Isotopic analyses were made on a modified DuPont (CEC) 21-702B single focusing, 30 cm radius, 90 degree sector, surface ionization mass spectrometer. A Faraday cup ion collector, followed with vibrating reed electrometers (Varian/Cary Model 401 for a single ion collector and Takeda-TR-84M for a 50 % transmission grid total ion monitor) and a paper strip chart recorder (Leeds & Northrup, Speedomax G-2), was utilized as the measuring system. The detection limit of ion currents for this system was $\sim 1 \times 10^{-15}$ A by using an input resistor of 1×10^{11} ohms. Mass spectra scanning was performed by changing the magnetic field at a constant ion accelerating voltage (7 kV). Peak top signals were recorded over a period of 30 second.

Fused silica beakers and polypropylene bottles were used because of low alkali metal and molybdenum blanks. Hydrochloric acid and water were purified by double distillation in a silica apparatus. Sulfuric and nitric acids were of "precision analysis grade", and hydrofluoric acid of "transistor grade".

Natural molybdenum solutions were prepared by dissolving separately molybdenum metal wire (0.1 mm diameter) and sheet (1 mm thickness). These metals were 99.97 % pure (major impurity: 30 to 50 ppm Fe, Tokyo Tungsten Co., Tokyo). Approximately 0.3 g of the wire and 1 g of the sheet were mechanically cleaned and then washed with acetone and ethanol. Metals were rinsed with water and dried at 55°C before weighing and transferring to silica beakers. After dissolving metals in dilute sulfuric acid with small amounts of hydrochloric and nitric acids (a few drops of

hydrofluoric acid was also added), the solutions were evaporated to fumes of sulfuric acid, and then diluted to concentrations of 2 N sulfuric acid and of ~ 5 mg Mo/g soln., and transferred to polypropylene bottles.

Spike molybdenum solution was prepared by dissolving ~ 50 mg of ^{96}Mo isotope (96 % ^{96}Mo , MoO_3 , Oak Ridge National Laboratory, USA) similarly.

Filament materials used were mostly rhenium ribbons (0.025×0.75 mm, Chase Brass & Copper Co., Waterbury, Conn., USA) and they were baked in a vacuum of $\sim 1 \times 10^{-6}$ Torr and at the filament current of ~ 5.5 A for 2 to 6 hours under an electrical potential field, prior to mass spectrometry. Approximately same sized tantalum ribbons (Fansteel Metallurgical Corp., Ill., USA) were used in several trial runs.

Organic materials added as "reducing" or "carbonizing" agents to sulfuric acid solutions of molybdenum and some elements were a 5 v/v % aqueous solution of glycerol and a 5 w/v % aqueous solution of sucrose. The alkali and alkaline earth elements in these solutions were removed by passing through a cation-exchange resin (Diaion SK #1, 100~200 mesh, Mitsubishi Kasei Co., Tokyo) in silica columns. A 5 w/v % benzene solution of naphthalene (reagent grade, without further purification) was also prepared.

Metal carbides used were micron-fine powders and coated on the filament as freshly prepared water suspension. Molybdenum carbide powder (99.9 % Mo_2C , $3.3 \sim 4.0 \mu\text{m}$, Mitsuwa Chemicals Co., Osaka) was identified as $\beta\text{-Mo}_2\text{C}$ (ASTM Powder Diffraction File No. 11-680) by X-ray diffraction.

An optical microscope equipped with a camera (Union NUM-1 metallurgical microscope) was used for observing the filament surfaces after mass spectrometry.

2.2 Procedure

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Five to 25 μg of molybdenum was mounted with a disposable tip microsyringe (Eppendorf microliter pipet) on a rhenium filament and heated in air by passing of electric currents of 1.4 to 1.6 A to fumes of sulfuric acid. If nitric, hydrochloric and hydrofluoric acids were considerably present, they inhibited the formation of rigid carbonized films on the filament surfaces. These acids were removed by fuming. Then 25 to 250 μg of organic materials (5 to 10-fold amount of molybdenum) was dropped onto the filament and charred in air to slightly wet tar. The filament was loaded into the mass spectrometer ion source and evacuated down to 5×10^{-7} Torr. Molybdenum metal ion current was produced by increasing the filament current in steady increments. After 50 to 70 minutes the $^{98}\text{Mo}^+$ ion currents of 10^{-13} to 10^{-11} A were obtained at the filament currents of 3.5 to 4.8 A.

Isotopic analyses of samples containing less abundant isotopes (spike isotope and spiked dilution analysis) were carried out with 20 to 50 μg of molybdenum.

Raw isotopic ratios were calculated on eight to ten ratios for each $^{(92+i)}\text{Mo}/^{96}\text{Mo}$ ratio ($i=0, 2, 3, 5, 6$, and 8) at several ion intensities and filament current-time sequences. Normalization to a value of $^{92}\text{Mo}/^{100}\text{Mo} = 1.5400^9$ was made to compare the observed isotopic ratios with previously reported values when "natural" isotopic molybdenum samples were analyzed.

3. Results and Discussion

3.1 Filament Material and Organic

Additive; Chemistry of the Technique

Rhenium and tantalum ribbons were examined as filament materials. Burning-off of tantalum filaments at the filament currents of less than 4 A occurred frequently when large amounts of sodium and potassium were pre-

sent. Rhenium filaments were burnt off at the filament currents of less than 4.5 A when considerable amounts of rubidium ($^{88}\text{Mo}^+ / ^{39}\text{K}^+ / ^{85}\text{Rb}^+ \sim 100/1/1000$) were present. But the Mo^+ ion currents obtained with tantalum ribbons were erratic even in the presence of very small amounts of alkali elements. Possibly, this disturbance is caused by the formation of tantalum carbide (TaC)¹⁰.

The rhenium ribbon has larger crystal grains than the tantalum one, as shown in Figs. 1a and 1b. These large crystal grains may cause the differences of ionization efficiency in different filaments. However, the rhenium ribbon was thermally and chemically more resistive than the tantalum one, and was suitable for filaments.

Blank molybdenum ion currents of $1 \sim 2 \times 10^{-14}$ A were detected at the filament currents of 5 to 5.5 A for both unbaked rhenium and tantalum ribbons. For the latter, $^{93}\text{Nb}^+$ ion signals of smaller than 2×10^{-14} A were also observed. After baking under a vacuum of $\leq 1 \times 10^{-6}$ Torr at the filament currents of 5 to 5.5 A for 2 to 6 hours, these blank ion currents decreased to $1 \sim 5 \times 10^{-15}$ A at ≥ 5 A, and smaller than 1×10^{-15} A at < 5 A. Mo^+ blank ion currents observed for the filaments on which glycerol and sulfuric acid had been coated were similar to the above. Accordingly, the filament currents during measurements were controlled below the prebaking currents.

Organic materials that reduce or carbonize oxygen-containing compounds of molybdenum to the metal or carbides, or their mixture were selected from purification easiness and chemical composition (carbon content, cyclic or non-cyclic). When glycerol, sucrose, and naphthalene were added, they were carbonized by high temperature heating in vacuum and in the presence of sample elements, and Mo^+ ion currents obtained were nearly the same. But high alkali metal impurity in sucrose, and

Fig. 1 (a). Photomicrographs of an unbaked rhenium ribbon filament (the upper one) and the rhenium ribbon filament (the lower one) baked in a vacuum of 5×10^{-7} Torr and at 5.5 A ($\sim 2200^\circ\text{C}$) for 120 minutes.

Fig. 1 (b). Photomicrographs of an unbaked tantalum ribbon filament (the upper one) and the tantalum ribbon filament (the lower one) baked in a vacuum of 5×10^{-7} Torr and at 6 A ($\sim 2200^\circ\text{C}$) for 10 minutes, and then at 5 A ($\sim 1800^\circ\text{C}$) for 120 minutes.

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formation of large carbon particles with naphthalene that inhibited the fine and uniform distribution of the sample onto the filament surface, were less advantageous than glycerol. Ethylene glycol was not suitable because of formation of a flaky carbon film.

Inorganic carbonaceous materials such as SiC and WC powders were not suitable because of impurities, e. g., zirconium and niobium in SiC. Mo^+ ion signals obtained with these materials were erratic and corrosion of the filaments was observed after the mass spectrometry.

In the chemical determination of molybdenum, some organic or inorganic precipitates containing molybdenum are oxidized to the oxides by heating and igniting them in air. Usually the oxide is molybdenum trioxide that sublimes at $780\sim 795^\circ\text{C}$ ^(11,12). The reduction of molybdenum trioxide by hydrogen proceeds rather slowly for completeness and above 600°C the sublimation of the trioxide becomes appreciable⁽¹³⁾. It was necessary to heat a molybdenum trisulfide sample ($\sim 5\text{ }\mu\text{g}$ of molybdenum) on the rhenium filament for 12 hours up to 1400°C to decompose it to fine particles of metallic molybdenum⁽¹⁴⁾. $^{98}\text{Mo}^+$ ion currents obtained by this treatment was $\sim 10^{-14}\text{ A}$ at the filament temperature of 1600°C .

The chemical reaction of graphite powder and molybdenum trioxide in a 50 to 50 wt% mixture under dry nitrogen atmosphere has been studied thermogravimetrically and optical microphotographically by McKee⁽¹⁵⁾. He observed the presence of MoO_2 and small amounts of Mo_4O_{11} and Mo_2C in addition to MoO_3 in the residue from heating the mixture (300 mg) to 1100°C . Although we have little knowledge of the $\text{MoO}_3\text{-C}$ system of micrograms size in vacuum, the formation of molybdenum carbide or molybdenum metal in real samples might be considered from the formation of lamp carbon or slightly graphitized carbon in high temperature reactions of organic materials or carbons catalyzed by metals^(16,17).

Observation of the surfaces of filaments used in the mass spectrometry by an optical microscope has revealed the differences of carbon particles that were formed from various organic materials added to the molybdenum samples. The parts photographed were approximately 2 mm apart from the center of the filament (the length of the flattened part of the filament that was coated with the sample solution was $\sim 8\text{ mm}$). The upper part of Fig. 2 shows the fine carbon particles formed from the mixture of $20\text{ }\mu\text{g}$ of molybdenum and $250\text{ }\mu\text{g}$ of glycerol at a slow heating up to

Fig. 2. Fine carbon particles on the rhenium ribbon filament (the upper side) formed from the mixture of $20\text{ }\mu\text{g}$ of molybdenum and $250\text{ }\mu\text{g}$ of glycerol. The mixture was loaded on the filament and charred in air and then heated up to 4.4 A ($\sim 1760^\circ\text{C}$) for 10 minutes in a vacuum of $3\times 10^{-7}\text{ Torr}$. Rates of heating from 0 to 3 A and 3 to 4.4 A were 0.2 A/3 min and 0.1 A/3 min , respectively. $^{98}\text{Mo}^+$ ion currents observed at $3.98\sim 4.05\text{ A}$ were $\sim 5\times 10^{-13}\text{ A}$.

Fig. 3. Coalesced carbon particles on the rhenium ribbon filament formed from the mixture of 100 μg of molybdenum (96 % enriched ^{96}Mo) and 1 mg of naphthalene. The mixture was coated on the filament and charred in air and then heated up to 5.3 A ($\sim 2100^\circ\text{C}$) for 25 minutes in a vacuum of 1×10^{-7} Torr. Rates of heating from 0 to 3 A and 3 to 5.3 A were 0.2 A/3 min and 0.1 A/3 min, respectively. $^{96}\text{Mo}^+$ ion currents observed at 4.4, 4.8, and 5.4 A were 1.5×10^{-12} , 1.8×10^{-11} , and 2×10^{-11} A, respectively.

Fig. 4. Fine and coalesced carbon particles on the rhenium ribbon filament formed from the mixture of 20 μg of molybdenum and 250 μg of unpurified sucrose. The mixture was loaded on the filament and charred in air and then heated up to 5.2 A ($\sim 2100^\circ\text{C}$) for 20 minutes in a vacuum of 1×10^{-7} Torr. Rates of heating from 0 to 3 A and 3 to 5.2 A were 0.2 A/3 min and 0.1 A/3 min, respectively. $^{96}\text{Mo}^+$ ion currents observed at 4.6, 4.7, and 5.2 A were 8.5×10^{-13} , 1.5×10^{-12} , and 1.0×10^{-12} A, respectively.

4.4 A. Coalesced carbon particles were seen when the mixture of 100 μg of molybdenum and 1 mg of naphthalene was slowly heated up to 5.3 A (Fig. 3). Enamel-like brightening and coexistence of large and small carbon particles were observed when the mixture of 20 μg of molybdenum and 250 μg of unpurified sucrose was heated up to 5.2 A (Fig. 4).

Appearance very similar to Fig. 1 (a) (the lower photograph) was observed when the sulfuric acid solution of molybdenum was heated. The sudden change in the Mo^+ ion intensities frequently observed with sucrose and naphthalene might be caused by flaking-off of the carbon particles containing¹⁶⁾ the metal species.

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Ion production profiles observed for carbide powder samples, with or without glycerol, were very similar to those experienced in the proposed technique.

3.2 Relative Isotopic Ratios of Molybdenum in Samples

The relative isotopic ratios of molybdenum in molybdenum wire and sheet, and in Mo₂C samples are shown in Table 1. Individual isotopic ratios in each sample and analytical runs gave relative standard deviations of 0.1~0.5 % for 8 to 10 peak sets. Tabulated ratios were calculated on the peaks recorded about the middle of the measuring periods of time. Ion intensities calculated for the wire sample were $\sim 5 \times 10^{-13}$ A, and those for the sheet and carbide samples were $\sim 1.5 \times 10^{-12}$ A on $^{98}\text{Mo}^+$,

respectively. Even though more intense ion currents were observed in over the half of analytical runs, these sizes of the ion currents have been reproducible and could be stably kept for a long period of time ($n \sim n \times 10$ hours). Slightly nonlinear variations in raw isotopic ratios observed in early stages of sample evaporation may due to many unsolved parameters including the evaporation rates of different sizes of the samples^{14, 18)}, chemical and physical changes of surface layers of the filaments with coated samples and additives during mass spectrometry⁸⁾, etc., but the average ratios are considered satisfactory.

The relative isotopic ratios obtained in the present work and by other workers are shown in Table 2. The ratios were calculated by

Table 1. Relative isotopic ratios of molybdenum in molybdenum metal and Mo₂C powder samples.

Sample and Anal. No.	Relative isotopic ratios of molybdenum ^{a)}					
	92/96	94/96	95/96	97/96	98/96	100/96
Mo wire ^{b)}						
1	0.8887	0.5549	0.9566	0.5724	1.4464	0.5771
2	0.8890	0.5543	0.9521	0.5732	1.4489	0.5773
3	0.8892	0.5532	0.9559	0.5727	1.4425	0.5774
Mo sheet ^{c)}						
1	0.8884	0.5544	0.9534	0.5729	1.4459	0.5769
2	0.8885	0.5528	0.9551	0.5722	1.4470	0.5769
3	0.8886	0.5520	0.9538	0.5714	1.4481	0.5772
4	0.8886	0.5540	0.9544	0.5730	1.4521	0.5772
β -Mo ₂ C powder ^{d)}						
1	0.8900	0.5553	0.9553	0.5746	1.4493	0.5779
2	0.8900	0.5545	0.9540	0.5730	1.4456	0.5780
3	0.8874	0.5530	0.9535	0.5740	1.4457	0.5763
Average and	0.8888	0.5538	0.9544	0.5729	1.4472	0.5772
Std. dev.	0.0007 ₇	0.0010 ₄	0.0013 ₃	0.0009 ₆	0.0026 ₁	0.0004 ₉

a) Averaged ratios for 8 to 10 peak sets. Observed ratios were normalized to a value of $^{92}\text{Mo}/^{100}\text{Mo}=1.5400$.

b) 99.97 % molybdenum wire (0.1 mm ϕ , Tokyo Tungsten Co., Tokyo). Amounts of the sample were 5, 10, and 20 μg of molybdenum in the analysis number order.

c) 99.97 % molybdenum sheet (1 mm, Tokyo Tungsten Co., Tokyo). Amounts of the sample were 25 to 30 μg of molybdenum.

d) 99.9 % Mo₂C powder (3.3~4.0 μm , Mitsuwa Chemicals Co., Osaka). Approximately 50 μg of Mo₂C was coated as freshly prepared water suspension.

b, c, d). Concerning the ion currents observed and chemical procedures, see the text.

Table 2. Comparison of relative isotopic ratios of molybdenum^{a)}.

Isotopic ratio	Wetherill ^{b)}	This work (average)	NBS SRM ^{c)} (average)	ANL reference ^{d)} sample
92/96	0.8868	0.8888	0.8897	0.8897
	(1.0000)	1.0023	1.0033	1.0033)
94/96	0.5528	0.5538	0.5545	0.5551
	(1.0000)	1.0018	1.0031	1.0041)
95/96	0.9515	0.9544	0.9547	0.9552
	(1.0000)	1.0030	1.0034	1.0039)
97/96	0.5718	0.5729	0.5730	0.5730
	(1.0000)	1.0019	1.0021	1.0021)
98/96	1.4453	1.4472	1.4472	1.4483
	(1.0000)	1.0013	1.0013	1.0021)
100/96	0.5757	0.5772	0.5777	0.5777
	(1.0000)	1.0026	1.0035	1.0035)
Ratio of ratio:		1.0022	1.0028	1.0032
Standard deviation:		0.0006 ₁	0.0008 ₉	0.0008 ₉

^{a)} Figures in parentheses are the ratios of ratios that were calculated on taking the values obtained by a double spiking technique^{b)} as unity.

^{b, c, d)} See references 9), 6), and 5), respectively.

assuming the isotopic ratios obtained by a double spiking technique⁹⁾ as unity. Agreements between the ratios are fairly good.

Isotopic ratios for the 96 % enriched ⁹⁶Mo spike are shown in Table 3. The results indicate effectiveness of the technique that enables to analyze smaller abundance isotopes with increased ion currents. ⁹⁶Mo⁺ ion currents obtained at the filament currents of 4.6 to 4.8 A were ~ 0.8 to 3×10^{-11} A with 20 to 50 μ g of molybdenum.

3.3 Application to Other Elements

Application of the proposed technique to other elements has shown a substantial increase in the ion current intensities of hafnium and chromium (both in a sulfuric acid solution). Table 4 shows the observed isotopic ratios for Hf metal and 82 % enriched ¹⁷⁹Hf isotope sample. Ion currents of $1 \sim 5 \times 10^{-12}$ A (¹⁷⁹Hf⁺) were obtained at the filament currents of 5.3 to 5.5 A after depositing 20 to 50 μ g of Hf ("natural", sulfuric acid solution) on the single

Table 3. Observed isotopic ratios of molybdenum in the 96 % enriched ⁹⁶Mo spike.

Anal. No.	Observed isotopic ratios of molybdenum ^{a)}					
	92/96	94/96	95/96	97/96	98/96	100/96
1	0.00210	0.00236	0.01024	0.01046	0.00938	0.00191
2	0.00208	0.00236	0.00999	0.01048	0.00944	0.00192
3	0.00212	0.00239	0.01000	0.01047	0.00939	0.00191
Average and	0.00210	0.00237	0.01008	0.01047	0.00940	0.00191
Std. dev.	0.00002 ₉	0.00001 ₇	0.00014	0.00001 ₉	0.00003 ₂	0.00000 ₆

^{a)} In each analysis ~ 50 μ g of molybdenum (sulfuric acid solution) was coated on the rhenium filament with 0.5 mg of glycerol. Calculated for the ⁹⁶Mo⁺ ion currents of $0.8 \sim 3 \times 10^{-11}$ A that were obtained at the filament currents of 4.6 $\sim$ 4.8 A.

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Table 4. Observed isotopic ratios of hafnium in hafnium metal and 82 % enriched ^{179}Hf isotope (HfO_2) sample.

Sample and Anal. No.	Observed isotopic ratios of hafnium				
	174/179	176/179	177/179	178/179	180/179
Hf metal ^{a)}					
1	0.01124	0.3818	1.3566	1.9988	2.5821
2	0.01142	0.3790	1.3512	1.9948	2.5825
Average and range	0.01133	0.3804	1.3539	1.9968	2.5823
	0.00009	0.0014	0.0027	0.0020	0.0002
82 % ^{179}Hf (HfO_2) ^{b)}					
1	0.00055	0.00205	0.01838	0.06402	0.1303
2	0.00043	0.00211	0.01863	0.06410	0.1298
3	— ^{c)}	— ^{c)}	0.01897	0.06322	0.1296
Average and Std. dev.	0.00049	0.00208	0.01866	0.06378	0.1299
	0.00006 ^{d)}	0.00003 ^{d)}	0.00030	0.00049	0.0004

^{a)} Hf metal sponge of 98.5 % purity (Nippon Kogyo Co., Tokyo). Twenty to 50 μg of hafnium (sulfuric acid solution) was coated on a rhenium filament with 0.5 mg of glycerol. $^{179}\text{Hf}^+$ ion currents obtained at the filament currents of 5.3~5.5 A were $0.5\sim 1\times 10^{-12}$ A.

^{b)} Obtained from Oak Ridge Nat. Lab. Fifty to 100 μg of hafnium (sulfuric acid solution) was coated on a rhenium filament with 0.5~1 mg of glycerol and heated to the filament currents of 5.6~6.0 A. Obtained $^{179}\text{Hf}^+$ ion currents were $2\sim 3\times 10^{-12}$ A at ~ 5.8 A and $1\sim 2\times 10^{-11}$ A at ~ 6 A.

^{c)} Not measured.

^{d)} Range.

rhenium filament with 0.25 to 0.5 mg of glycerol. The use of rhenium ribbons, instead of the tungsten ones that were used previously in the hafnium oxide sample-triple tungsten filament technique¹⁹⁾, was enough to obtain the increased ion currents at lower temperatures and eliminated the correction for tungsten isotope peaks that interfered with the measurement of hafnium.

Very stable ion currents ($^{52}\text{Cr}^+$) of $\sim 3\times 10^{-12}$ and $\sim 3\times 10^{-11}$ A were obtained at the filament currents of ~ 3.1 and ~ 3.3 A, respectively, when approximately 100 μg of Cr_3C_2 powder (99 % Cr_3C_2 , 3~6 μm , Mitsuwa Chemicals Co., Osaka) was coated on the rhenium filament with 0.5 mg of glycerol and 10 μl of 10 v/v % sulfuric acid. When 5 to 10 μg of Cr (dilute hydrochloric acid solution) were mounted on the rhenium filament and heated at the filament currents of 2.2~2.9 A, $^{52}\text{Cr}^+$ ion currents of $1\sim 3\times 10^{-13}$ A were detected but were very erratic and rapidly decreased. However, rather

stable $^{52}\text{Cr}^+$ ion currents of 1×10^{-12} A could be obtained when the rhenium filament was replaced by a tantalum one and 10 μg of Cr (dilute sulfuric acid solution) was loaded with 0.1 mg of glycerol and 10 μg of boron (pure borax solution) and heated at the filament current of ~ 2.5 A. Table 5 shows the raw isotopic ratios of chromium in chromium metal and Cr_3C_2 powder samples that were observed by the proposed technique. Since it has been reported that no natural variations in the isotopic composition of commercial chromium sources exist²⁰⁾, the agreement between the present data and the NBS values²⁰⁾ shows the adequacy of the technique.

Iron is one of the elements that catalyze graphitization of organic carbons²¹⁾. Twelve to 20 μg of iron (dilute sulfuric acid solution) were coated on the rhenium filament with 1.5 mg of glycerol and heated to 5 A. $^{56}\text{Fe}^+$ ion current of 5×10^{-14} A was maintained for a

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Table 5. Observed isotopic ratios of chromium in chromium metal and Cr_3C_2 powder samples.

Sample	Anal.	Observed isotopic ratios of chromium ^{a)}			
	No.	50/52	53/52	54/52	(⁵² Cr ⁺ ion signal)
Cr metal ^{b)}					
	1	0.05199	0.1127	0.02785	(∼1×10 ⁻¹² A)
		0.00012	0.0003 ₇	0.00028	
Cr ₃ C ₂ powder ^{c)}					
	2	0.05189	0.1132	0.02816	(∼3×10 ⁻¹² A)
		0.00018	0.0003 ₆	0.00014	
	3	0.05194	0.1134	0.02819	(∼3×10 ⁻¹¹ A)
		0.00012	0.0002 ₇	0.00007 ₄	
Average and		0.05194	0.1131	0.02807	
std. dev.		0.000050	0.00036	0.00019	
NBS corrected ratios and 95 % C. L. on ratio determination ^{d)}		0.051859	0.113386	0.028222	
		0.000029	0.000032	0.000019	

^{a)} Averaged ratios and std. dev. (1 sigma) for 8~12 peak sets.

^{b)} 99.9 % chromium metal (Yokosawa Chemicals Co., Tokyo). Ten μg of chromium (dilute sulfuric acid solution) was loaded on the single tantalum filament with 0.1 mg of glycerol and 10 μg of boron (pure borax solution). The filament current was ~ 2.5 A.

^{c)} Approximately 100 μg of Cr_3C_2 powder (~ 98.6 % Cr_3C_2 , $3\sim 6$ μm , Mitsuwa Chemicals Co., Osaka) was coated on the single rhenium filament with 10 μl of water and 0.5 mg of glycerol.

^{d)} Ref. 21).

period of 20 to 30 minutes. After the mass spectrometry, thick but fragile carbon films were observed on the filament surface.

Tungsten ion currents ($^{184}\text{W}^+$) of $1\sim 2 \times 10^{-14}$ A were detected for 20 to 30 minutes when a carbide sample (~ 10 μg of tungsten, 99 % WC, 0.75 μm , Mitsuwa Chemicals Co., Osaka) with 0.5 mg of glycerol was heated up to 5.2~5.7 A (filament rhenium ion signals $\sim 5 \times 10^{-12}$ A).

Calcium ion currents ($^{40}\text{Ca}^+$) of 5×10^{-13} and 1×10^{-11} A at the filament currents of 3.20 and 3.35 A, respectively, were obtained for ~ 5 μg of calcium (nitrate) samples coated on the tantalum single filament with 0.1 mg of glycerol and 10 μl of 10 v/v % sulfuric acid. But the obtained ion currents were erratic.

Platinum is one of the most difficult elements to ionize by thermal ionization because of its high elemental ionization potential (I_{Pt} :

~ 9.0 eV)²³⁾. To an aliquot of the *aqua regia* solution of platinum in a silica beaker, a small amount of sulfuric acid was added and heated to fumes of sulfuric acid. Approximately 40 μg of platinum was mounted on the rhenium ribbon with 0.5 mg of glycerol. By increasing the filament currents from 0 to 6.2 A in a regular rate during 160 minutes, no detectable ion current for Pt^+ ions was found. Carbon film or particle was not apparent on the filament surface after the mass spectrometry.

Approximately 10 μg of 50 % enriched ^{235}U (dilute nitric acid solution), 10 μl of 10 v/v % sulfuric acid, and 0.5 mg of glycerol were coated on the single rhenium filament. Ion currents of $^{235}\text{UO}^+$ observed at the filament currents of 4.3 and 5.0 A were $\sim 1.5 \times 10^{-13}$ and $\sim 2 \times 10^{-14}$ A, respectively, while the metallic ion was detected at more elevated filament

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currents: $^{235}\text{U}^+$ ion currents obtained at the filament currents of 5.3 and 5.9 A were $\sim 5 \times 10^{-13}$ and $\sim 5 \times 10^{-15}$ A, respectively. These sizes of ion currents may correspond to those obtained for the single graphite filament ionization of uranium²⁴⁾. After the mass spectrometry, fibrous and fine carbon particles were observed on the filament surface.

4. Conclusion

A simple and effective technique for routine isotopic analysis of molybdenum is mainly described. Sulfuric acid solutions of molybdenum were loaded on the single rhenium filament with organic additive and reduction or carbonization of oxo-compounds of molybdenum proceeded during mass spectrometric analysis. Pretreatment of the samples outside or inside the ion source was shortened. The technique is useful for analyzing microgram amounts of molybdenum with a relative standard deviation of $\leq 0.5\%$. The technique can be applied to determination, by isotope dilution mass spectrometry, of several % of molybdenum in nickel-base heat resisting alloys²⁵⁾

Application to other elements and chemistry of the technique will be further investigated.

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