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Thermal ionization mass spectrometry of molybdenum isotopes

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Abstract

A simple and reliable analytical technique for molybdenum isotope abundance determinations by thermal ionization mass spectrometry, capable of realizing precise data from submicrogram amounts of material, is described. This method was specifically designed for molybdenum fission product and double-beta decay studies, for which only nanogram amounts of sample are available. The molybdenum isotope composition of a high purity molybdenum metal rod, four off-the-shelf reagents, and five molybdenites from different regions were analyzed. No significant isotope abundance variations were observed. The molybdenum isotope abundances determined were compared to current International Union of Pure and Applied Chemistry (IUPAC) isotope composition and atomic weight data. (Int J Mass Spectrom 197 (2000) 253–261) © 2000 Elsevier Science B.V.

Keywords: Molybdenum; Mass spectrometry; Isotopic composition; Fractionation; Molybdenites

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1. Introduction

Molybdenum has an atomic number of 42 and seven stable isotopes, ^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo. Isotopes of molybdenum are formed by the r process (^{100}Mo), s process (^{96}Mo), both r and s processes (^{95}Mo, ^{97}Mo, and ^{98}Mo), and p process (^{92}Mo) [1]. In addition, ^{96}Mo is produced by the double-beta decay of ^{96}Zr. Double-beta decay is a relatively rare decay process, and the transmutation of one element to another of $Z + 2$ occurs with the emission of either two or no neutrinos, depending on whether the neutrino has nonzero mass. Isotopes of molybdenum are located near the peak of the lower mass hump of uranium fission yields, and the determination of molybdenum fission products can provide information on nuclear structure. Molybdenum is an essential micronutrient for both plants and animals, and is present at concentrations ranging from ppb to ppm levels. High sensitivity stable isotope tracer studies can play an important role in the study of molybdenum metabolism and biogeochemical processes [2, 3]. The stable isotope dilution technique can be used to measure the elemental abundance of molybdenum in biological, meteoritic, and geological samples. Molybdenum isotope abundance ratios are measured effectively by thermal ionization mass spectrometry, where the ionization of molybdenum occurs at or near the surface of a hot metallic filament. Sensitive molybdenum isotope abundance measurements are limited by several factors including (1) the high ionization potential of molybdenum (7.1 eV), (2)

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the evaporation of molybdenum compounds before ionization occurs, and (3) possible isobaric interference from zirconium at m/q 92, 94, and 96, and from ruthenium at m/q 100.

The first comprehensive investigation of molybdenum isotope abundances by thermal ionization mass spectrometry was by Murthy in 1963 [4]. Murthy [4] published molybdenum isotope abundance data for three terrestrial samples and eight iron meteorites. Microgram quantities of molybdenum were analyzed with precisions of 0.6% $(2s)$ from MoS_2 deposited on tantalum filaments. Murthy [4] measured a $^{92}Mo/^{100}Mo$ isotope abundance ratio of 1.54, which, for historical reasons to be discussed, is the basis of the current International Union of Pure and Applied Chemistry (IUPAC) recommended molybdenum isotope abundances [5]. Wetherill, in 1964 [6], measured molybdenum isotope abundance data from meteoritic iron samples with precisions of better than 1% by depositing 15 μg of molybdenum as MoS_2 on rhenium filaments. A double spike methodology was employed to correct for the time and mass dependent fractionation that occurred during the analysis. No significant differences in molybdenum isotope abundances were observed among eight different iron meteorites. Wetherill [6] normalized the measured isotope abundance data to $^{92}Mo/^{100}Mo = 1.540$, as determined by Murthy [4]. Moore and co-workers [7] reported a method for high accuracy molybdenum concentration measurements of standard reference materials using a ^{100}Mo spike by isotope dilution techniques. Molybdenum ion current intensities greater than 5×10^{-12} A were obtained from 40 μg of molybdenum deposited on zone refined rhenium filaments and heated to 1760 °C. The molybdenum sample was prepared as ammonium molybdate and reduced to molybdenum metal on the surface of the filament in the presence of H_2 gas. Ratios were normalized to a $^{92}Mo/^{100}Mo$ of 1.5400 to allow their measurements to be compared to previous data, including those from Wetherill [6]. Isotope abundance ratios were determined with precisions of 1‰ $(2s)$. The data from Moore et al. [7] are the basis for the IUPAC recommended molybdenum isotope abundances [5].

More recently, Lu and Masuda [8,9] have reported molybdenum isotope abundance data with internal precisions of 0.03‰ (95% confidence limit) measured using a single Faraday cup collector. Twenty micrograms of molybdenum were loaded with 1 M nitric and boric acids on the outgassed side filaments of a triple rhenium filament assembly. The filaments were heated initially to 2 A over 5 min and to 3 A over 3 h. A ^{96}Mo ion current as high as 2×10^{-12} A was maintained for 5 h. Isotope abundance data were normalized to a $^{94}Mo/^{98}Mo$ of 0.3802 that was based on their average measured ratios for Aldrich 99.999% pure MoO_3. The spectrum was scanned prior to data acquisition, and it was determined that isobaric interference from zirconium and ruthenium could be neglected. Lee and Halliday [10] have also reported high precision molybdenum isotope abundance data obtained with a magnetic sector inductively coupled plasma (ICP) multicollector mass spectrometer. A solution of 1–2 ppm molybdenum metal was analyzed, and precisions of 0.03‰ $(2s)$ were achieved. Molybdenum isotope abundance ratios were normalized to a $^{94}Mo/^{98}Mo$ of 0.38315 based on data from Moore et al. [7]. The presence or absence of zirconium and ruthenium isobaric interference was not discussed. Kawashima and co-workers [11] measured molybdenum isotope abundance ratios from 10 ng of molybdenum from a molybdenum atomic absorption standard using a Daly detection system. The molybdenum sample was converted to MoO_2Cl_2 and deposited on specially prepared rhenium filaments coated with a rhenium–platinum slurry. A mixture of ascorbic acid and ammonium iodide was deposited with the molybdenum sample to reduce the Mo(VI) to Mo(III), which was less volatile and ionized more efficiently. Kawashima et al. [11] corrected for the presence of zirconium isobars by monitoring the $^{90}Zr/^{95}Mo$ ratio during the analysis. All data were normalized to $^{100}Mo/^{95}Mo$ of 0.6049 from Moore et al. [7]. The measurements were comparable to Moore et al. [7] within their analytical uncertainty of ±0.5‰ $(1s)$.

This article reports on a simple method for precise molybdenum isotope abundance measurements from submicrogram amounts of sample. Efficient and reliable data were obtained from sample sizes ranging from 20 ng to 2 μg molybdenum deposited on single rhenium filaments, and measured on Daly and multiple Faraday cup detectors, respectively. In this article, only data obtained from amounts of molybdenum greater than 1 μg are reported. However, measurements from the analysis of 20 ng of molybdenum, for double-beta decay investigations, yielded data of similar precision (article in preparation). High purity molybdenum metal, off-the-shelf molybdenum laboratory reagents, and a selection of molybdenites (MoS_2) were analyzed to determine the extent of molybdenum isotope abundance variations. The molybdenum isotope abundance ratios determined in this study are an improvement over earlier data for several reasons. First, the possibility of isobaric interference from zirconium and ruthenium was checked before and after each analysis and found to be negligible. Second, the mass dependent fractionation corrections were based on isotope abundance ratios determined in this study, and were not dependent on previous uncalibrated measurements. Third, attempts were made to demonstrate that the data were free of instrumental bias (within analytical uncertainties).

2. Experimental

The molybdenum metal solution was prepared from a 99.993% pure molybdenum metal rod from Johnson Matthey Chemicals Limited (Westdeptford, NJ) (JMC 726 Laboratory No. S-8555). The molybdenum metal was lightly cleaned in HNO_3, washed in water, weighed, and dried. The sample was then dissolved in a 3:1 mixture of ultra high purity HCl: HNO_3 in acid cleaned PFA Savillex vials. The solution was evaporated to dryness, redissolved in 11 M HCl, and evaporated to dryness. The residue was taken up in 4 M HCl to a molybdenum concentration of 1 μg molybdenum per milligram of solution, ready for deposition on rhenium filaments.

Off-the-shelf reagents included molybdenum powder (BDH, Victoria, Australia, Lot No. 118 8062), molybdic acid (Mallinckrodt, Phillipsburg, NJ), ammonium molybdate (Analar BDH, Lot No. 326520), and molybdenum trioxide (Univar Ajax Chemicals, NSW, Australia). Molybdenite samples were obtained from Westonia (Western Australia), Spencers Brook (Western Australia), Bencubbin (Western Australia), Kingsgate (New South Wales, Australia), and from an unspecified location in India. The samples were dissolved in 3:1 mixtures of ultra high purity HCl and HNO_3 in thoroughly cleaned PFA Savillex vials. The dissolved molybdenum solutions were evaporated to dryness, redissolved in 11 M HCl, and evaporated to dryness. The residue was redissolved in 4 M HCl to obtain molybdenum concentrations of 1 μg molybdenum per milligram of solution. Molybdenum from the molybdenite samples was isolated by ion exchange chemistry. The samples were loaded in 4 M HCl on anion exchange resin (Dowex AG 1-X8, 100–200 mesh) and molybdenum was eluted with two column volumes of 0.5 M HCl. The eluate was evaporated to dryness, redissolved in 0.5 M HCl, and loaded on cation resin (Dowex AG 50W-X8, 200–400 mesh). With this molarity of HCl, the cation resin retained iron and uranium, but not molybdenum. The separated molybdenum was collected and evaporated slowly to dryness under an infrared heat lamp. All chemical extractions were carried out under a laminar flow hood with HEPA filtered air.

Molybdenum samples were mixed with 4 microlitres of ascorbic acid dissolved in 4 M HCl (20 mg ascorbic acid per gram of solution). The solution was deposited on outgassed single rhenium filaments and dried with 1.4 A filament current. The filament was heated to 2 A at which point the deposit fumed and became black. Three microlitres of a silica–gel suspension were deposited on the filament and dried. Finally, the filament was heated to a dull red colour for 5 s. The ascorbic acid in 4 M HCl was prepared immediately prior to sample deposition because solutions older than 24 h were much less effective at enhancing molybdenum ion production.

Molybdenum isotopic ion currents were measured on a VG354 thermal ionization mass spectrometer equipped with nine moveable Faraday cup detectors and an axial Daly detector. Seven of the Faraday cup collectors were arranged to collect the seven molybdenum isotopes simultaneously. A strict heating and analytical procedure was followed to ensure that all

Table 1
Raw and fractionation-corrected Mo isotope abundance data for the Mo metal rod using the multiple Faraday cup collectors. Uncertainties in parentheses are the standard errors at the 95% confidence level

Sample	92/95	94/95	96/95	97/95	98/95	100/95
1	0.92848 (86)	0.58003 (24)	1.04864 (37)	0.60145 (43)	1.5217 (15)	0.60799 (98)
2	0.9230 (12)	0.58044 (17)	1.04815 (27)	0.60075 (63)	1.5191 (15)	0.6064 (13)
3	0.92804 (80)	0.58015 (27)	1.04876 (26)	0.60154 (33)	1.5226 (12)	0.60851 (70)
4	0.92840 (91)	0.58047 (14)	1.04897 (40)	0.60168 (44)	1.5226 (16)	0.6085 (11)
5	0.93038 (79)	0.58084 (24)	1.04829 (36)	0.60062 (35)	1.5195 (12)	0.60654 (77)
6	0.9290 (14)	0.58024 (36)	1.04856 (51)	0.60124 (51)	1.5210 (21)	0.6076 (14)
7	0.9270 (12)	0.57965 (32)	1.04910 (45)	0.60190 (51)	1.5238 (20)	0.6094 (13)
8	0.9278 (17)	0.58008 (70)	1.04893 (62)	0.60171 (66)	1.5230 (26)	0.6089 (17)
9	0.92672 (99)	0.57973 (26)	1.04926 (32)	0.60219 (43)	1.5246 (14)	0.60991 (92)
10	0.92888 (92)	0.58034 (27)	1.04873 (34)	0.60118 (45)	1.5215 (16)	0.60785 (99)
11	0.9306 (14)	0.58063 (30)	1.04797 (46)	0.60058 (59)	1.5188 (21)	0.6061 (14)
12	0.9294 (14)	0.58038 (29)	1.04841 (45)	0.60106 (59)	1.5205 (20)	0.6073 (14)
Average	0.92872 (70)	0.58025 (22)	1.04865 (25)	0.60133 (33)	1.52155 (120)	0.60792 (76)
Fractionation corrected[b]	0.92872 (14)	0.58025 (12)	1.04865 (5)	0.60133 (5)	1.52155[a]	0.60791 (3)

[a] Normalizing ratio is taken to be exact.

[b] Each sample was corrected for mass fractionation before this average was calculated.

samples were analyzed under identical conditions, and resulted in consistent and predictable behaviour for the different samples. The filament was heated to 1300 °C over 3 min and left to stabilize for 2 min. The temperature was then increased to 1400 °C and left for 5 min. At this temperature, low molybdenum ion currents could be measured with the Daly detector. The filament temperature was increased to 1500 °C, 1550 °C, and 1600 °C, with a pause of 5 min after each increment. Isotope abundance ratios were acquired after waiting for 5 min at 1600 °C to allow the ion beam to stabilize. The filament temperature was not adjusted during the analysis. Typically, 1 μg of molybdenum on the filament produced ion current intensities of 10^{-12} A that were sustained over several hours. The ^{90}Zr ion current was monitored before and after the measurements, and it was always less than 0.1% of the ^{98}Mo ion current intensity. Isobaric interference from ruthenium was checked by monitoring the ion current at m/q 99. No ruthenium isotopes were observed for any of the samples. There was an occasional ion current measured approximately 0.5 u above ^{100}Mo that appeared at low temperatures (~1300 °C), but decayed before 1600 °C.

3. Results and discussion

Twelve filaments, each loaded with 2 μg of molybdenum from the molybdenum metal rod, were analyzed. A total of 150 ratios for each sample were collected in 15 blocks of 10 ratios, and the data are given in Table 1. The spread in the measured ratios was the result of mass and time dependent fractionation, and the ratios were corrected using the average measured ^{98}Mo/^{95}Mo ratio of 1.52155 according to an exponential law [Eq. (1)] [12]. The ^{98}Mo/^{95}Mo isotope abundance ratio was chosen as the internal reference because these two molybdenum isotopes have the largest relative mass difference, free from zirconium and ruthenium isobaric interference

$$\left(\frac{{}^{x}\mathrm{Mo}}{{}^{95}\mathrm{Mo}}\right)_{\mathrm{corrected}} = \left(\frac{{}^{x}\mathrm{Mo}}{{}^{95}\mathrm{Mo}}\right)_{\mathrm{measured}} \cdot \left(\frac{({}^{98}\mathrm{Mo}/{}^{95}\mathrm{Mo})_{\mathrm{measured}}}{({}^{98}\mathrm{Mo}/{}^{95}\mathrm{Mo})_{\mathrm{standard}}}\right)^{\ln(x/95)/\ln(98/95)} \quad (1)$$

The averages of the fractionation corrected ratios of the 12 molybdenum metal rod samples are presented in Table 1. The fractionation corrected isotope abundance ratios measured for the four off-the-shelf re-

Table 2
Fractionation corrected isotope abundance ratios of off-the-shelf molybdenum reagents and molybdenites (MoS_2) measured using the multiple Faraday collectors. Uncertainties in parentheses are at the 95% confidence level

Sample	92/95	94/95	96/95	97/95	98/95	100/95
India MoS_2	0.92904 (42)	0.58037 (34)	1.04887 (5)	0.60129 (36)	1.52155	0.60798 (7)
Kingsgate MoS_2	0.92984 (52)[a]	0.58116 (43)[a]	1.04883 (22)	0.60120 (23)	1.52155	0.60782 (14)
Bencubbin MoS_2	0.92864 (121)	0.58069 (90)	1.04848 (28)	0.60097 (15)	1.52155	0.60792 (10)
Edna May MoS_2	0.92906 (35)	0.58061 (25)	1.04876 (30)	0.60120 (27)	1.52155	0.60790 (2)
Spencers Brook MoS_2	0.92881 (35)	0.58018 (7)	1.04854 (2)	0.60133 (9)	1.52155	0.60791 (6)
Mo powder	0.92877 (25)	0.58014 (11)	1.04851 (13)	0.60136 (31)	1.52155	0.60797 (26)
Molybdic acid	0.92890 (14)	0.58018 (22)	1.04871 (12)	0.60103 (9)	1.52155	0.60788 (9)
Molybdenum trioxide	0.92886 (52)	0.58037 (40)	1.04866 (24)	0.60139 (19)	1.52155	0.60792 (35)
Ammonium paramolybdate	0.92862 (1)	0.58008 (2)	1.04849 (3)	0.60133 (1)	1.52155	0.60791 (8)
Average of all molybdenite and off-the-shelf regents	0.92884 (13)	0.58033 (18)	1.04865 (12)	0.60123 (11)	1.52155	0.60791 (4)
Difference from Mo metal rod (‰)	+0.1	+0.1	0.0	−0.2		0.0

[a] ^{92}Mo and ^{94}Mo isotope abundances were affected by the presence of Zr and these data were not used in the calculation of the average.

agents and molybdenites are given in Table 2. A minimum of two replicate analyses of each sample were performed. The averages of the isotope abundance ratios of off-the-shelf reagents and molybdenites were calculated and compared to those for the molybdenum metal rod. No natural molybdenum isotope abundance variations were observed. Because it was demonstrated that there were no significant differences in the isotope abundances measured among the different molybdenum samples, the fractionation-corrected data for the molybdenum metal, off-the-shelf reagents, and molybdenites were combined to obtain a laboratory value for molybdenum isotope abundance ratios (Table 3).

It is worth noting that there is the possibility for isotope fractionations to be caused by the purification of a metal to better than 99% by multiple recrystallization (e.g. zone refining). Lighter isotopes could be preferentially volatilized from the melt leaving the purified metal relatively enriched in the heavier isotopes. These effects have been observed with gallium [13]. This was not the case with molybdenum.

Although the data in Table 3 were measured with high precision, the accuracy of isotope abundances cannot be assessed if the magnitudes of instrumental and analytical biases are unknown [14,15]. An assessment of the accuracy requires the measurement of certified isotope abundance reference materials, of which there are none for molybdenum. Hence, an indication of the accuracy of isotope abundance measurements was sought by analyzing strontium in the National Institute of Standards and Technology reference material SRM 987. Normalized ^{87}Sr/^{86}Sr isotope abundance ratios were within ±0.5‰ of the certified value measured over a range of ^{87}Sr ion currents from 10^{-12}–10^{-14} A. An advantage of molybdenum isotope abundance measurements is that the molybdenum isotope abundances are all the same order of magnitude. Hence, small nonlinearities in the measurement system will not have a significant effect on

Table 3
Combined Mo isotope abundance ratios determined from Mo metal rod, off-the-shelf reagents, and molybdenites. Uncertainties in parentheses are at the 95% confidence interval

92/95	94/95	96/95	97/95	98/95	100/95
0.92877 (9)	0.58028 (9)	1.04865 (6)	0.60129 (6)	1.52155	0.60791 (2)

Table 4
Comparison of peak jump and multicollector Mo isotope abundance ratios[a] for the laboratory standard fractionation corrected to ^{98}Mo/^{95}Mo = 1.52155. Uncertainties in parentheses are at the 95% confidence interval

	92/95	94/95	96/95	97/95	98/95	100/95
Multicollector[b]	0.92877 (9)	0.58028 (9)	1.04865 (6)	0.60129 (6)	1.52155	0.60791 (2)
Peak jump	0.92890 (43)	0.58031 (20)	1.04839 (31)	0.60120 (34)	1.52155	0.60800 (31)
Difference (‰)	+0.1	0.0	−0.2	−0.2		0.1

[a] Faraday collector used.
[b] Data from Table 3.

the measured ratios. In addition to biases introduced by nonlinear detectors and amplifiers, differences in individual cup efficiencies and associated electronics could affect data collected on the multicollector Faraday cup array. Therefore, strontium isotopic ion currents from SRM 987 were measured using three adjacent collectors covering all nine Faraday cups. Normalized ^{87}Sr/^{86}Sr isotope abundance ratios measured over the multicollector array were all within ±0.3‰ of the certified value. In addition, six samples of 2 μg molybdenum each were also measured using the axial Faraday collector in a peak-jumping mode and compared to those measured by the multicollector array. The average normalized ratios are given in Table 4 and no significant differences were observed.

Mass and time dependent fractionations will affect measured isotope abundance ratios such that the lighter isotopic species are evaporated preferentially from the hot filament. As a result, the ratios measured at the beginning of an analysis will be preferentially enriched in the lighter isotope. As the analysis proceeds, the measured isotope abundance ratio will become relatively enriched in the heavier isotopes. High precisions for replicate measurements can be achieved if the analytical conditions are repeated exactly from filament to filament, and the ratios are measured over the same period in the lifetime of the sample. Total evaporation and simultaneous integration of the isotopic ion currents of interest can overcome the effect of mass and time dependent fractionation [16,17]. In this manner, the total charge measured will reflect the isotope composition of the entire sample, provided there has not been a significant loss of the lighter isotopes before ionization occurred. The temporal behaviour of molybdenum isotope abundance ratios was investigated by analyzing molybdenum isotopic ion currents from the first appearance of Mo$^+$ until the molybdenum ion currents were no longer measurable with the multicollector Faraday cup array. Four samples of 1 μg molybdenum were heated to 1600 °C at 200 mA/min, and data were taken immediately once this filament temperature was attained. The filament temperatures were not adjusted during the analysis. The ^{98}Mo/^{95}Mo isotope ratio and ^{95}Mo ion current intensity from one of the four samples are plotted as a function of time in Fig. 1. The ion current decreased exponentially during the analysis. The ^{98}Mo/^{95}Mo isotope ratio increased steadily during the first 50 min of the analysis, remained stable within analytical requirements over the next 50 min, and became more scattered as the ion current intensity (and signal to noise ratio) decreased.

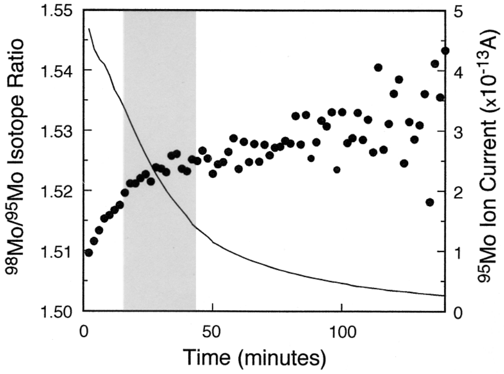

Fig. 1. ^{95}Mo ion current and ^{98}Mo/^{95}Mo isotope abundance ratio plotted as a function of time during the total evaporation of a 1 μg sample. The shaded region indicates the period during which data were collected for the results presented in Tables 1 and 2. Filled circles indicate ^{98}Mo/^{95}Mo isotope abundance ratio. Straight line indicates ^{95}Mo ion current.

Table 5
Results of total evaporation of Mo metal rod for four different analyses measured using the multiple Faraday cup collectors. Uncertainties in parentheses are at the 95% confidence interval

Sample	92/95	94/95	96/95	97/95	98/95	100/95
1	0.9290	0.5804	1.0493	0.6014	1.5220	0.6081
2	0.9290	0.5808	1.0488	0.6019	1.5222	0.6079
3	0.9275	0.5803	1.0491	0.6020	1.5240	0.6098
4	0.9297	0.5805	1.0480	0.6013	1.5199	0.6070
Average	0.9288 (29)	0.5805 (6)	1.0488 (19)	0.6016 (13)	1.5220 (54)	0.6082 (35)
Difference (‰)[a]	0.0	+0.4	+0.2	+0.5	+0.3	+0.4

[a] Compared with the Mo isotope abundance ratios in Table 3.

The integrated molybdenum isotope abundance ratios were calculated by taking a weighted average of the blocks of 10 ratios. The weighting was determined by the fraction of the total ^{95}Mo ion current collected during the particular block. The data are summarized in Table 5, and are within 0.5‰ of the ratios determined by following the procedure described earlier. The results of this total evaporation experiment are not intended to replace the data listed in Tables 1 and 2, but rather to indicate that there is good agreement with the high precision data determined in this study.

The present data were compared to earlier molybdenum isotope abundance ratios determined by Wetherill [6], Moore et al. [7], Lu and Masuda [8,9], Lee and Halliday [10], and Kawashima et al. [11]. Data from the other authors are presented relative to ^{95}Mo in Table 6. The uncertainties quoted by these authors were propagated to arrive at an uncertainty for the resultant ratio relative to ^{95}Mo. No uncertainty is given with the ^{100}Mo/^{95}Mo from Kawashima et al. [11] because the ratios from their study were all normalized to ^{95}Mo. The isotope abundance ratios are plotted in Fig. 2 as differences in parts per thousand from the molybdenum isotope abundance ratios measured in this study (Table 3).

The data from Wetherill [6] and Moore et al. [7] are much less precise than more recent isotope abundance measurements. However, the molybdenum isotope abundance ratio data from Moore et al. [7] have remained the "best" measurement [5] because there has not yet been convincing evidence that the more recent, precise data are also more accurate. The isotope abundances measured by Lee and Halliday [10] are in very good agreement with the present data, although they fall along a different slope reflecting different extents of mass dependent fractionation. The latter were normalized using the ^{100}Mo/^{95}Mo ratio determined by Moore et al. [7] and no raw data were provided. Lu and Masuda [8,9] did not assume a normalizing ratio, and based their fractionation correction on their average measured value for ^{94}Mo/^{98}Mo. Isotope abundance ratios determined by Lu and Masuda [8,9] agree well with the present data, except they are fractionated by 0.6‰ per mass unit with enrichment in the heavier isotopes. Lu and Masuda [8,9] heated the samples for 3 h at 3 A prior to data

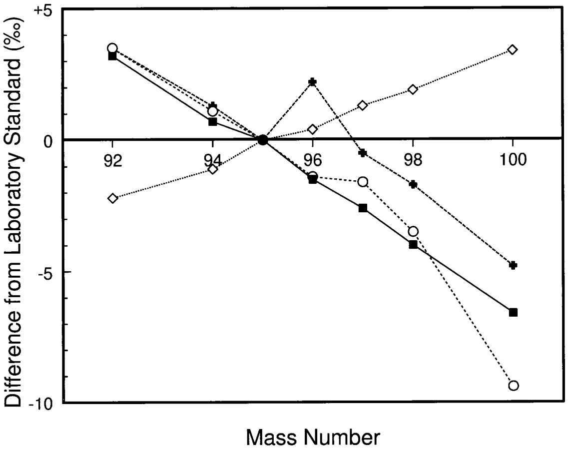

Fig. 2. Comparison of Mo isotope abundance ratios determined by others to those determined in this study, expressed as differences in parts per thousand (‰) from the data in Table 3. All ratios are relative to ^{95}Mo. Crosses, Wetherill [6]; open circles, Moore et al. [7]; open diamonds, Lu and Masuda [9]; filled squares, Lee and Halliday [10].

Table 6
Comparison of raw Mo isotope abundance ratios (reported with respect to ^{95}Mo) measured by other authors

Sample	92/95	94/95	96/95	97/95	98/95	100/95	Normalization
This study[a]	0.92877 (9)	0.58028 (9)	1.04865 (6)	0.60129 (6)	1.52155[c]	0.60791 (2)	Own
Murthy[b] [4]	0.928 (6)	0.577 (3)	1.048 (6)	0.598 (4)	1.524 (9)	0.602 (4)	Own
Wetherill [6]	0.932 (3)	0.581 (2)	1.051 (3)	0.601 (3)	1.519 (5)	0.605 (2)	Murthy [4]
Moore et al. [7][a]	0.9319 (13)	0.58090 (80)	1.0472 (10)	0.60038 (82)	1.5162 (21)	0.60219 (83)	Wetherill [6]
Lu and Masuda [9][a]	0.92677 (3)	0.57961 (1)	1.04906 (3)	0.60209 (2)	1.52447 (3)	0.60999 (2)	Own
Lee and Halliday [10][b]	0.93169 (5)	0.58067 (2)	1.04710 (5)	0.59979 (3)	1.51552 (5)	0.60390 (2)	Moore et al. [7]
Kawashima et al. [11][b,d]	0.93191 (15)	0.58063 (61)	1.04667 (43)	0.60051 (39)	1.51630 (56)	0.6049[c]	Moore et al. [7]

[a] Uncertainties in parentheses are at the 95% confidence interval.
[b] Uncertainties in parentheses are 2s mean.
[c] Normalizing ratio is taken to be exact.
[d] Data measured by Daly detector.

collection (compared to 25 min for the present method), and this may explain the relative enrichment in the heavier isotopes compared to this study. It is significant to note that only Murthy [4], Lu and Masuda [8,9], and the present study have obtained molybdenum isotope abundance data independently, without normalization to earlier measurements.

The abundances of the seven molybdenum isotopes were calculated based on the average measured isotope abundance ratios given in Table 3 and are presented in Table 7. The atomic weight of molybdenum was calculated based on the atomic masses compiled by Audi and Wapstra [18], and is compared to molybdenum atomic weights determined by Moore et al. [7], Lu and Masuda [9], and current IUPAC data [5]. The results from Kawashima et al. [11] and Lee and Halliday [10] were not included in the comparison because they were derived from isotope abundance ratios normalized to results from Moore et al. [7] and are not independent measurements. It should be noted that there are no calibrated measurements of molybdenum isotope abundances and no accurate value can be confidently assigned to the atomic weight.

4. Conclusions

A method for molybdenum isotope abundance determinations by thermal ionization mass spectrometry was developed capable of realizing data with precisions better than ±0.5‰ (95% confidence interval) from 1 μg of molybdenum. This level of sensitivity and precision is essential in order to investigate molybdenum isotope abundances and concentrations (measured by isotope dilution mass spectrometry) in carbonaceous chondrite meteorites, fission product, and double-beta decay studies. The method results in both reproducible ion current intensity and mass fractionation during the analysis. The molybdenum isotope abundances measured for five molybdenites and four off-the-shelf chemicals were found to be identical within analytical uncertainty. Molybdenum in the molybdenites was separated from the dissolved minerals by ion exchange techniques to eliminate possible intereferences. No natural isotope abundance fractionations resulting from mass dependent processes were observed.

There are no calibrated molybdenum isotope reference materials. Therefore, the accuracy of measurements made with the mass spectrometer was assessed by measuring the National Institute of Standards and Technology strontium standard SRM 987 over a range of ion currents. To ensure that individual cup biases did not affect the measured isotope abundance ratios, measurements made with the multicollector array were compared to the data collected in a peak-jumping mode. The data obtained by static and dynamic methods were identical within analytical uncertainty. The mass dependent fractionation of molybdenum isotope abundance ratios was examined

Table 7
Atomic weight of Mo based on isotope abundance data from this study and other authors

Isotope	Mass (u) Audi and Wapstra [18]	Atom % This study	Atom % Lu and Masuda [9]	Atom % Moore et al. [7]	Atom % IUPAC [5]
^{92}Mo	91.906810	14.769 (1)	14.7294 (4)	14.84 (2)	14.84 (35)
^{94}Mo	93.905087	9.228 (1)	9.2112 (2)	9.25 (1)	9.25 (12)
^{95}Mo	94.905841	15.9022 (4)	15.8932 (2)	15.927 (5)	15.92 (13)
^{96}Mo	95.904678	16.676 (7)	16.6729 (4)	16.678 (5)	16.68 (2)
^{97}Mo	96.906020	9.5618 (7)	9.5692 (3)	9.56 (1)	9.55 (8)
^{98}Mo	97.905407	24.1959 (6)	24.2287 (4)	24.148 (2)	24.13 (31)
^{100}Mo	99.907476	9.6671 (4)	9.6947 (3)	9.59 (1)	9.63 (23)
	Atomic weight of Mo (u)	95.9377 (1)	95.94150 (2)	95.930 (1)	95.93 (1)

by collecting molybdenum ion currents until total evaporation of the sample. The molybdenum isotope abundance ratios determined by integrating the molybdenum isotopic ion currents over the measurable lifetime of the sample were comparable to those measured over a shorter period.

The molybdenum isotope abundance ratios determined in this study represent an improvement over previous results for several reasons. First, the present method did not require complicated sample deposition procedures, and the behaviour of the sample during the analysis was consistent from filament to filament (i.e. intensity and stability of the ion current, fractionation during analysis). Second, the possibility of zirconium and ruthenium isobaric interference was checked before each analysis, and found to be negligible. Third, the ratio used for fractionation corrections was based on measured data, and was not assumed from previous uncalibrated measurements. Finally, the accuracy of the measured isotope abundance ratios was assessed by investigating the linearity and relative efficiencies of the collector array, and the temporal behaviour of the molybdenum isotope abundance ratios.

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