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Absolute isotopic composition and atomic weight of samarium

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Abstract

Gravimetric synthetic mixtures prepared from highly enriched isotopes of samarium in the form of oxides of well defined purity were used to calibrate a thermal ionization mass spectrometer. Measurements on natural samarium samples yielded an absolute isotopic composition 3.08(1) at.% ^{144}Sm, 15.02(5) at.% ^{147}Sm, 11.25(3) at.% ^{148}Sm, 13.83(4) at.% ^{149}Sm, 7.35(2) at.% ^{150}Sm, 26.74(3) at.% ^{152}Sm, and 22.73(5) at.% ^{154}Sm, and the atomic weight of samarium as 150.363(8) both with an uncertainty given on the basis of 95% confidence limit. No isotopic fractionation was found in terrestrial samarium materials. (Int J Mass Spectrom 218 (2002) 167–172)

Keywords: Samarium; Isotopic abundance; Atomic weight; Mass spectrometry

1. Introduction

The current atomic weight of samarium $A_r(\mathrm{Sm}) = 150.36(3)$ was recommended in 1979 [1], the value within the parentheses denoting the uncertainty of the last figure (such notation is to be used throughout this paper). In 1997 Chang and Qiao reported a higher value as 150.366(1) [2], and their given isotopic composition was considered as the best measurement [3]. In this work we used the separated isotopes of samarium to carry out a calibrated mass spectrometric measurement in order to obtain an accurate value of $A_r(\mathrm{Sm})$.

This work concerns the last one of the ten elements studied as a project by our research group starting in 1990. The nine elements having been reported are indium [4], iridium [5], antimony [6], europium [7], cerium [8], erbium [9], germanium [10], dysprosium [11], and zinc [12]. All these new values of $A_r(\mathrm{E})$'s have been recommended by the IUPAC Commission on Atomic Weights and Isotopic Abundances. The value of iridium $A_r(\mathrm{Ir}) = 192.217(3)$ is a joint contribution by Walczyk and Heumann [13] working with negative ion $\mathrm{IrO_2}^-$ and by us measuring the positive ion Ir^+.

Samarium is a heptanuclidic element with interfering isobars shown in Table 1. The method and technique of finding its atomic weight are similar to those described in our papers on $A_r(\mathrm{Er})$ [9] and $A_r(\mathrm{Dy})$ [11].

2. Experimental

2.1. *Separated isotopes*

Separated isotopes of 96.9 at.% ^{152}Sm (sample A) and 98.9 at.% ^{154}Sm (sample B) were purchased from

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Table 1
Interfering isobars of samarium

	Mass number						
	144	147	148	149	150	152	154
Element (natural abundance, at.%)	Nd (23.8) Sm (3.1)	Sm (15.0)	Nd (5.76) Sm (11.3)	Sm (13.8)	Nd (5.64) Sm (7.4)	Sm (26.7) Gd (0.2)	Sm (22.7) Gd (2.18)

Isotech Inc. (A. Matheson), USA Co. In order to remove the possible presence of anionic impurities CO_2 and water vapor and also to decrease cationic impurities, each sample was dissolved in dilute nitric acid (guaranteed reagent) and the resulting clear solution was treated with oxalic acid. The precipitated samarium oxalate hydrate after filtration, washing, and drying was ignited at 800 °C in a muffle furnace, to whose base a current of dried nitrogen was passed to remove the decomposed product, CO_2, and water vapor. So we obtained the two purified isotopes in the form of oxides (yield 98.5%), which were analyzed for most impurities by using VG-Plasmaquard mass spectrometer, besides Na, K, Mg, Ca, Fe, and Al by the method of emission spectra. Results are shown in Table 2. It is to be noted that the significant presence of Eu in sample A of $^{152}Sm_2O_3$ is probably due to the collection cage for the beam of ^{152}Sm being contaminated by ^{151}Eu and ^{153}Eu present in the raw material of Sm during feeding the electromagnetic mass separation machine. However, these two Eu isotopes do not interfere with the $^{152}Sm^+$ measurement.

Other impurities were found below the detection limit. Those below 10 $\mu g\,g^{-1}$ were: Ho, Er, Tm, Zn, and Ge; those below 5 $\mu g\,g^{-1}$ were: Pr, Tb, Dy, Yb, Lu, Y, Th, U, Ti, V, Cr, Mn, Co, Ni, Cu, Ga, Rb, Sr, Zr, Nb, In, Sn, Ba, Al, Fe, Ca, Mg, K, and Na; those below 1 $\mu g\,g^{-1}$ were La and Ce. After an allowance of 200 $\mu g\,g^{-1}$ Sm is made for undetected impurities, the chemical purity of samples A and B can be assessed as 99.51(2)% and 99.95(2)%, respectively.

Table 2
Impurities in samples A and B (microgram per gram Sm)

Impurity	In sample A	In sample B
Nd	7.2	<5
Eu	4370	64
Gd	99	15
Mo	221	179
Cd	<5	55

2.2. Primary solutions A and B

About 220 mg each of samples A and B was accurately weighed and dissolved in 1.6 mol L^{-1} HNO_3. The weighing technique including the correction for air buoyancy and the transference of the solution from the beaker to the volumetric flask were the same as those described in our previous paper [6]. Results are shown in Table 3.

2.3. Mass spectrometric measurement

The measurement of the six isotopic ratios for seven samarium isotopes was performed on an automatic magnetic sector thermal ionization multicollector Finnigan MAT-262 mass spectrometer. It is provided with five Faraday cups, a secondary electron multiplier with an ion counter and a retarding potential quadrupole (RPQ). The 23 cm radius, 90° magnetic

Table 3
Primary solutions A and B

	Sample	
	A	B
Compound	$^{152}Sm_2O_3$	$^{154}Sm_2O_3$
Purity (%)	99.51	99.95
Weight (mg)	227.333	228.586
Net weight (mg)	226.219	228.472
Weight of solution (g)	34.49189	36.92591

sector mass analyzer has an asymmetric, extended geometry design that gives a mass dispersion equivalent to that of a 64 cm radius sector using standard geometry. As the ion beams enter and leave the magnetic field at oblique angles, the focusing also occurs in the *z*-direction and improves transmission efficiency. The ion source and the collector slits are 0.20 and 0.82 mm, respectively. The working resolution is 500 (10% valley definition).

Double filament inserts were utilized in this work. The sample and ionization filaments made of rhenium (each 8 mm long, 0.7 mm wide and 0.04 mm thick) were set at a distance of 0.7 mm parallel to each other. Both filaments were first cleaned and degassed under vacuum by heating with a current of 5.5 A for 1.5 h. After the sample filament was loaded at its center with a tiny drop of a nitrate solution containing 8 μg Sm, it was dried by a current of 1.6 A for about 10 min. Then the ion source with the filament inserts was mounted in the mass spectrometer, which was then evacuated down to 10^{-8} mbar. After the ionization filament was heated with a current gradually increasing to 5.5 A for 18 min, the sample filament was heated with a current increasing very slowly to 2.0 A, whence the ion peak of the major isotope of samarium was monitored as the pilot signal to adjust the ion–lens system of the ion source to get the greatest possible ion beam. So stable emission of Sm^+ ions could be attained and the major isotope of samarium had an ion current of about 10^{-11} A, which could be retained almost for 1 h.

Five Faraday cups were employed for the simultaneous collection of $^{154}Sm^+$, $^{152}Sm^+$, $^{150}Sm^+$, $^{149}Sm^+$, and $^{148}Sm^+$ ions, respectively. $^{147}Sm^+$ and $^{144}Sm^+$ were determined by the peak jump method. The RPQ system enabled the precise measurement of low abundant ions in the two separated samarium isotopes. The on-line computer is Legend 586 LX-P5/100 PCI system with the color graphics software package written in HT BASIC (version 4.4). It monitored the various electric parameters in the ion source and adjusted the cup's position to attain optimum coincidence of peak shapes through matching the computer graphs. In this way the peak of each ion beam could be normalized to the 100% scale. Such a procedure ensured the almost perfect positioning of the cups to include each ion beam completely. In short, the loading technique, the heating current, as well as the measuring program were kept identical during the measurement of all samples in this work so that the fractionation effect due to mass discrimination was minimized.

Table 4
Measured isotopic ratios of samples A and B, each six replicates (1s)

	Sample	
	A	B
$^{144}Sm/^{152}Sm$	0.000461(1)	0.01002(82)
$^{147}Sm/^{152}Sm$	0.002390(5)	0.05031(30)
$^{148}Sm/^{152}Sm$	0.002808(3)	0.05710(23)
$^{149}Sm/^{152}Sm$	0.003634(3)	0.08479(13)
$^{150}Sm/^{152}Sm$	0.004594(3)	0.08284(20)
$^{154}Sm/^{152}Sm$	0.018251(10)	118.252(34)

For each loading 50 ratios were recorded with automatic reduction of the background. Measurement was repeated as several replicates for each sample. In the case of samples A and B results are shown in Table 4.

From these data the isotopic composition of samples A and B can be readily obtained as shown in Table 5. The $^{154}Sm/^{152}Sm$ ratios in samples A and B are as follows:

$$R_{A(154/152)} = 0.01825, \quad R_{B(154/152)} = 118.2521.$$

Then the isotopic composition of ^{152}Sm and ^{154}Sm in primary solutions A and B can be calculated as shown in Table 6, where the data of the atomic mass of samarium nuclides [14] are used to calculate the atomic weight.

Table 5
Isotopic composition of samples A and B (atomic percent)

Isotope	A	B
144	0.0447	0.0084
147	0.2315	0.0421
148	0.2720	0.0478
149	0.3521	0.0709
150	0.4451	0.0693
152	96.8863	0.8365
154	1.7683	98.9250

Table 6
Isotopic composition of primary solutions A and B

	Sample	
	A	B
Atomic weight	151.907657	153.892452
$SmO_{1.5}$, molecular weight	175.906757	177.891552
Total micromole Sm	1286.0165	1284.3330
Atomic percent ($^{152}Sm + ^{154}Sm$)	98.6546	99.7615
Micromole ($^{152}Sm + ^{154}Sm$)	1268.7145	1281.2699
Micromole ($^{152}Sm + ^{154}Sm$) per gram solution	36.78298 (C_A)	34.69840 (C_B)

2.4. *Mixed solutions AB and the correction factor $K_{154/152}$*

Portions of the primary solutions A and B were accurately weighed and thoroughly mixed to form a series of five mixed solutions AB. The respective weights W_A and W_B are shown in columns 2 and 3 of Table 7.

Then the isotopic ratio $R_{154/152}$ of each mix was measured. Results are shown in the fourth column of Table 7.

By applying the following formula [6]

$$K_{154/152} = \frac{W_A C_A (R_A - R_{AB}) - W_B C_B (R_{AB} - R_B)}{W_B C_B R_A (R_{AB} - R_B) - W_A C_A R_B (R_A - R_{AB})},$$

where W_A, W_B and $R_{AB(154/152)}$ are given in Table 7 for each mix, whereas $R_{A(154/152)}$ and $R_{B(154/152)}$ being calculated from Table 4 as shown above, and C_A and C_B given in Table 6 are all constants for each mix, we can calculate a series of five values of $K_{154/152}$ with the mean 1.00674(67).

Since the values of C_A and C_B are calculated from R_A and R_B, the latter, if replaced by KR_A and KR_B, will cause C_A and C_B to have new values. Thereby a new iterative $K_{154/152}$ is obtained as 1.00663. The other K's can be calculated from $K_{154/152}$ by the relation: $\Delta K = 0.00331_5$ per atomic mass unit. All the K's are as follows:

$K_{144/152}$	0.97348
$K_{147/152}$	0.98343
$K_{148/152}$	0.98674
$K_{149/152}$	0.99006
$K_{150/152}$	0.99337
$K_{154/152}$	1.00663

2.5. *Terrestrial samples of samarium*

Five samples of samarium were collected from China, the US and Japan respectively. They are: (1) Rare earth adsorption kaolinite, Jiangxi, China,

Table 7
Measured $R_{154/152}$ of mixed solutions (three replicates) and the correction factor $K_{154/152}$ (1s)

Mixed solution number	Weight of solution A (W_A (mg))	Weight of solution B (W_B (mg))	$R_{154//152}$	$K_{154/152}$
1	607.289	642.448	1.00988(18)	1.00767
2	861.824	720.378	0.80452(6)	1.00584
3	682.475	693.119	0.97164(80)	1.00647
4	1059.270	960.309	0.86972(7)	1.00686
5	1187.742	970.153	0.78594(7)	1.00687
Mean				1.00674(67)

Table 8
Measured isotopic ratios of samarium in natural samples (five replicates, 1s)

Sample	^{144}Sm/^{152}Sm	^{147}Sm/^{152}Sm	^{148}Sm/^{152}Sm	^{149}Sm/^{152}Sm	^{150}Sm/^{152}Sm	^{154}Sm/^{152}Sm
1	0.11825(19)	0.57059(59)	0.42629(36)	0.52216(33)	0.27728(88)	0.84487(30)
2	0.11843(9)	0.57086(29)	0.42646(17)	0.52233(15)	0.27764(6)	0.84477(18)
3	0.11828(22)	0.57075(67)	0.42638(40)	0.52225(36)	0.27618(39)	0.84493(38)
4	0.11867(4)	0.57188(11)	0.42705(7)	0.52288(7)	0.27657(36)	0.84424(8)
5	0.11860(16)	0.57167(49)	0.42693(29)	0.52276(27)	0.27637(47)	0.84426(26)
Mean	0.11845(14)	0.57115(43)	0.42662(26)	0.52248(24)	0.27681(43)	0.84461(24)
Corrected	0.115306	0.561685	0.420965	0.517284	0.274970	0.850212

Table 9
Summary of the calculation of the isotopic composition and atomic weight of samarium (sample 1)

Parameter	Value	Mass spectrometric analytical error $2S_{\mathrm{m}}$, $\pm 10^{-4}$	Possible error in chemical analysis $2S_{\mathrm{c}}$, $\pm 10^{-4}$	Possible bias in separated isotope ratio B, $\pm 10^{-4}$	Overall limit of error[a] $2(S_{\mathrm{m}}^2 + S_{\mathrm{c}}^2)^{1/2} + B$, $\pm 10^{-4}$
Isotopic ratio					
^{144}Sm/^{152}Sm	0.115117	3.29	0.35	0.48	3.78
^{147}Sm/^{152}Sm	0.561134	9.99	1.67	2.31	12.44
^{148}Sm/^{152}Sm	0.420634	5.99	1.25	1.73	7.85
^{149}Sm/^{152}Sm	0.516973	5.54	1.53	2.12	7.86
^{150}Sm/^{152}Sm	0.275438	8.01	0.81	1.12	9.18
^{154}Sm/^{152}Sm	0.850468	5.76	2.47	3.43	9.69
Atomic percent					
^{144}Sm	3.0782	115	16.0	22.1	138
^{147}Sm	15.0045	421	77.0	106.8	535
^{148}Sm	11.2476	276	57.5	79.8	362
^{149}Sm	13.8237	290	70.4	97.7	396
^{150}Sm	7.3651	289	37.4	51.9	343
^{152}Sm	26.7397	273	57.1	79.2	358
^{154}Sm	22.7412	384	113.9	158	558
Atomic weight	150.3641	9.21[b]	1.28	1.77	11.07
		21.08[b]	3.85	5.34	26.77
		11.04[b]	2.30	3.19	14.47
		8.70[b]	2.11	2.93	11.88
		5.78[b]	0.75	1.04	6.86
		7.69[b]	2.28	3.17	11.19

[a] For the uncertainty in the value of atomic weight, an item $B_{\mathrm{n}} = 3 \times 10^{-6}$ (possible bias in isotopic mass) is added.

[b] The six components pertain to the six ratios.

Table 10
Atomic weight values of samarium by various authors

Year	Atomic weight	Author	Note	Reference
1981	150.361(2)	Holliger and Devillers		[16]
1981	150.3656	Wasserburg et al.	Spike	[17]
1997	150.366(1)	Chang and Qiao	Single sample	[2]
2002	150.3628(76)	This work	Calibration	

99.9999% Sm_2O_3 prepared by Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, (2) 99.99% $Sm_2(SO_4)_3 \cdot 8H_2O$, Aldrich, USA, (3) 99.99% Sm_2O_3, Shin-Etsu Chemical Co., Japan, (4) 99.99% Sm_2O_3, Baotou Rare Earth Research Institute, China, and (5) 99.9% Sm_2O_3, containing <0.02% each of Pr, Nd, Eu, Gd, and Y oxides, and 0.01% Fe, Si, and Ca oxides, Shanghai Chemical Reagents Corp., China.

Each sample was dissolved in $1.6\,\mathrm{mol\,L^{-1}}$ HNO_3 to form the loading solution. The measured isotopic ratios for each sample are shown in Table 8.

2.6. Absolute isotopic composition and atomic weight of samarium

The final error analysis for the absolute isotopic composition and atomic weight of samarium is carried out for each terrestrial sample as shown in Table 9, where only the data of sample 1 are listed for convenience. The mean absolute isotopic composition of samarium (2s) is as follows:

$$\begin{aligned}
3.083(13)\,\text{at.\%}\ &{}^{144}\text{Sm}\\
15.017(50)\,\text{at.\%}\ &{}^{147}\text{Sm}\\
11.254(34)\,\text{at.\%}\ &{}^{148}\text{Sm}\\
13.830(37)\,\text{at.\%}\ &{}^{149}\text{Sm}\\
7.351(24)\,\text{at.\%}\ &{}^{150}\text{Sm}\\
26.735(32)\,\text{at.\%}\ &{}^{152}\text{Sm}\\
22.730(52)\,\text{at.\%}\ &{}^{154}\text{Sm}
\end{aligned}$$

The atomic weight of samarium (2s) is (1) 150.3641(82), (2) 150.3633(70), (3) 150.3641(80), (4) 150.3610(70), and (5) 150.3615(76). Therefore the mean atomic weight of samarium is

$$A_r(\text{Sm}) = 150.3628(76).$$

It is to be noted that the A_r(Sm) will be 150.3626(76), if the other K's are derived from $K_{154/152}$ by the exponential rule. So the difference is insignificant. On the other hand, if the measured K has not been corrected by iteration, the value of A_r(Sm) will increase by 0.0004.

3. Conclusion

The atomic weight of samarium measured by various authors since 1948 was reviewed by IUPAC Commission on Atomic Weights and Isotopic Abundances [15]. Recent measurements since the recommendation of the current value in 1979 are listed in Table 10. Evidently, the A_r(Sm) found in this work is superior to all others, as it originates from a calibrated measurement using gravimetric synthetic mixtures of separated isotopes of samarium.

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