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Absolute isotopic composition and atomic weight of erbium

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Abstract

Calibrated mass spectrometric measurements on highly enriched isotopes of erbium in the form of oxides of well-defined purity were carried out by using a thermal ionization mass spectrometer, yielding an absolute isotopic composition of 0.139(3) at. % ^{162}Er, 1.601(2) at. % ^{164}Er, 33.503(24) at. % ^{166}Er, 22.869(6) at. % ^{167}Er, 26.978(12) at. % ^{168}Er, and 14.910(24) at. % ^{170}Er, and the atomic weight of erbium as 167.2591(9) with an uncertainty given on the basis of 95% confidence limit. No isotopic fractionation was found in terrestrial normal erbium materials. (Int J Mass Spectrom 177 (1998) 131–136) © 1998 Elsevier Science B.V.

Keywords: Erbium; Isotopic abundance; Atomic weight

1. Introduction

The current atomic weight of erbium A_r(Er) = 167.26(3) was recommended in 1969 [1], the value within the parentheses denoting the uncertainty of the last figure (such notation is to be used throughout this article). The present investigation aims at obtaining a new value for A_r(Er) by means of calibrated mass spectrometric measurement by using highly enriched isotopes, ^{166}Er and ^{168}Er. Hereby the possible isobaric interference is shown in Table 1 [2], from which we can see that any contamination of $^{168}_{70}$Yb in $^{168}_{68}$Er during the process of electromagnetic mass separation must be negligible.

As erbium has six stable isotopes, it is necessary to measure the five isotopic ratios. Calibration with a pair of major isotopes will yield one correction factor, namely $K_{168/166}$. The other four factors can be derived through the exponential rule.

2. Experimental

2.1. Purification of the isotopic materials

Isotopic materials of $^{166}Er_2O_3$ (Sample A) and $^{168}Er_2O_3$ (Sample B) were supplied by the Isotec Inc. (A. Matheson). They were labeled as 96.21 at. % ^{166}Er and 97.25 at. % ^{168}Er, respectively. A VG Plasmaquad mass spectrometer was used to detect chemical impurities. The results are shown in Tables 2 and 3. In the latter, the cationic impurities detected as elements are reconsidered as oxides, thus the total oxide impurities in these samples were 72.13 and 73.96 $\mu g\ g^{-1}$ Er_2O_3 respectively. Therefore, the

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Table 1
Isobaric interferences

Mass no.	162	164	166	167	168	170
Element (natural abundance, at. %)	Dy (25.5) Er (0.14)	Dy (28.2) Er (1.16)	Er (33.6)	Er (22.95)	Er (26.8) Yb (0.13)	Er (14.9) Yb (3.05)

chemical purity was both 99.993%, or was assessed as 99.99 ± 0.02%.

Samples A and B were each dissolved in 1.6 mol L^{-1} HNO_3 (all chemicals used in this work were either analytical or guaranteed reagents, and water was bidistilled), by using two separate sets of glassware to prevent mutual contamination. The solution was treated with oxalic acid. The hydrated oxalate was ignited at 800 °C in a muffle furnace. Although erbium oxide is much less basic among rare earths, it is still advisable to pass a current of nitrogen (previously dried in solid NaOH tower to remove any trace of water vapor and CO_2) to the bottom of the furnace to carry away the decomposition products, H_2O and CO_2, which are also present in the air. After cooling, the crucible was transferred into a desiccator containing solid NaOH. This process ensured the absence of these anionic impurities in Er_2O_3 [3]. The yield was 95%.

2.2. Preparation of two standard solutions

About 135 mg of each purified isotopic oxide, $^{166}Er_2O_3$ (A) or $^{168}Er_2O_3$ (B), was carefully weighed on a microbalance with calibrated weights. The balance permits estimation to 1 μg, and the precision is 0.02 mg. The weight pertained to the difference between the weighing bottle containing the sample and after it from which a portion of the sample had been emptied into a small beaker. All weighings were corrected for air buoyancy. The weighed sample was dissolved in 1.6 mol L^{-1} HNO_3 in the beaker and transferred into a volumetric flask by means of a dropper, and another dropper was used to rinse the beaker with the acid. Such a procedure was repeated 15 times. The solution was weighed with the same care, and the weight was accurate to 0.1 mg. All the data are shown in Table 4.

Solutions A and B were analyzed once more for the cationic impurities by the VG Plasmaquad with the result that the total impurity including Al and Fe was about 0.01% in either sample, thus confirming the above assessment of the chemical purity as 99.99%.

2.3. Mass spectrometric measurement

A thermal ionization mass spectrometer of Finnigan MAT-261 model, whose principal specifications were given in a previous article of ours [4], was used to measure the five isotopic ratios of erbium in samples A, B, mixes, and terrestrial materials. The instrument was equipped with a multicollector system of five Faraday cups and a secondary electron multiplier detector, controlled by an on-line HP-9836 computer. The thermal ionization ion source contained 13 inserts for filaments to accommodate the same number of samples to be measured in a single experiment. Double filament technique was adopted in this work. Rhenium filaments were first cleaned and degassed in vacuum. Then the sample filament

Table 2
Impurities below the detection limit in both samples ($\mu g\ g^{-1}$ Er_2O_3)

<0.5	Ce	La	Pr	Eu	Gd	Tb	Lu	Hf	Ta	Re	Ti	Bi	Th	U		
<1	Li	Be	V	Co	Ga	Ge	Y	Nb	Zr	Mo	Cd	In	Sb	Te	Cs	Ba
<2	Tm															
<5	As															
<10	Se															

Table 3
Cationic impurities (μg g^{-1} Er_2O_3)

Element	In sample A	In sample B
Ti	2.34	3.5
Cr	1.08	1.1
Mn	1.54	2.54
Ni	0.6	1.63
Cu	17.6	9.6
Zn	<1	10.8
Sr	1.70	2.9
Sn	10.3	3.2
Nd	0.74	<0.5
Sm	<0.5	1.6
Dy	16.3	13.4
Ho	1.77	1.30
Yb	2.3	3.8
Pb	3.2	6.1

was loaded with a tiny drop of the nitrate solution containing about 8 μg Er, and it was dried by passing a current. After the filament inserts were put into the basic instrument and the vacuum reached 10^{-8} mbar, the ionization filament was heated with a current gradually increased to 5 ~ 5.5 Å. The sample filament was heated with a current increased very slowly to about 2 Å, whence the ion peak of ^{166}Er was monitored as the pilot signal to adjust the parameters of the lens system in the ion source to get the optimum ion beam of about 10^{-11} Å.

The measurement of four isotopic ratios of ^{164}Er/^{166}Er, ^{167}Er/^{166}Er, ^{168}Er/^{166}Er, and ^{170}Er/^{166}Er was performed automatically by using five Faraday cups to collect simultaneously the five ion beams from ^{164}Er through to ^{170}Er, whereas the ratio $R_{162/166}$ was measured by means of scanning the peak height of ^{162}Er and ^{166}Er. Because the isotopic abundance of ^{162}Er in nature is very low, the procedure, though simple, will not effect the final evaluation of the atomic weight.

Table 4
Standard solutions A and B

Sample	A	B
Compound	$^{166}Er_2O_3$	$^{168}Er_2O_3$
Purity (%)	99.99	99.99
Weight (mg)	139.663	130.131
Net weight (mg)	139.649	130.118
Weight of solution (g)	54.35671	47.29713

Table 5
Isotopic ratios of erbium in samples A and B

Sample	A	B
$R_{164/166}$	0.000691(29)	0.0387(15)
$R_{167/166}$	0.028947(7)	1.9278(9)
$R_{168/166}$	0.0075602(46)	156.082(98)
$R_{170/166}$	0.0017145(13)	0.6391(12)

The on-line HP-9836 computer with ingenious software was used to monitor the various electric parameters of the ion source and adjust the cup positions to attain optimum coincidence of ion-peak shapes through matching the computer graphs so that the ion beam of each isotope could be normalized to 100% scale. This procedure ensured the complete collection of the ion beam in cup in order to make precise measurement. In short, the loading technique, the heating current, as well as the measuring program, were kept identical in measuring all samples so that the fractionation effect due to mass discrimination remained the same.

In the measurement of samples A and B, the ^{162}Er peak was absent. Fifty readings of each of the four isotopic ratios with automatic reduction of background were recorded for six replicate loadings of each sample. The results are listed in Table 5, which shows that both samples have an error of 0.062% in the value of $R_{168/166}$. All calculations for the error of the computer-recorded data are based on 95% confidence limit.

An algebraic calculation of these isotopic ratios yields the isotopic composition of samples A and B as given in Table 6. These data are essential to calculat-

Table 6
Isotopic composition (at. %) of samples A and B

Sample	A	B
^{162}Er	0	0
^{164}Er	0.0665	0.0242
^{166}Er	96.2545	0.6262
^{167}Er	2.7863	1.2073
^{168}Er	0.7277	97.7421
^{170}Er	0.1650	0.4002

Table 7
Isotopic concentration of standard solutions

Sample	A	B
Atomic weight	165.978049	167.914802
$ErO_{1.5}$ mol weight	189.977149	191.913902
Total μmol Er	735.083	678.002
At. % ($^{166}Er + ^{168}Er$)	96.9822	98.3683
μmol ($^{166}Er + ^{168}Er$)	0.712900	0.666939
μmol ($^{166}Er + ^{168}Er$) g^{-1} solution	13.11522 (C_A)	14.10104 (C_B)

ing the concentration of the standard solutions A and B, that is, C_A and C_B, in terms of μmol ($^{166}Er + ^{168}Er$) g^{-1} solution as shown in Table 7.

2.4. The mixed standard solutions

Portions of solutions A and B were accurately weighed and thoroughly mixed to form eight mixed solutions as shown in Table 8. The weight is denoted by W_A and W_B, respectively. Three replicates of each solution were measured for the isotopic ratio $R_{168/166}$. Results are shown in the fourth column of the table. For each mixed standard solution the correction factor $K_{168/166}$ for mass discrimination can be calculated by means of the following formula:

$$K = \frac{W_A C_A (R_A - R_{AB}) - W_B C_B (R_{AB} - R_B)}{W_B C_B R_A (R_{AB} - R_B) - W_A C_A R_B (R_A - R_{AB})}$$

the derivation of which was given in our previous article [5]. As regards, the calculation for K (denoting $K_{168/166}$) in the eight mixed standard solutions, R_A and R_B (denoting $R_{168/166obs.}$ in Table 5) as well as C_A and C_B, are all constant, whereas R_{AB} (denoting $R_{168/166obs.}$ in Table 8) as well as W_A and W_B, are all variable. Thus, we obtain eight values of $K_{168/166}$ with 1.00338(27) as the mean as shown in the last column of Table 8.

Table 8
Observed $R_{168/166}$ of mixed standard solutions and the correction factor $K_{168/166}$

Sample	Weight of solution A W_A (mg)	Weight of solution B W_B (mg)	$R_{168/166}$	$K_{168/166}$
1	1166.477	662.613	0.61458(15)	1.003364
2	1063.194	865.532	0.87640(73)	1.002949
3	1137.164	842.450	0.79826(48)	1.003404
4	1167.329	1041.649	0.95855(23)	1.003864
5	1112.438	783.173	0.75950(22)	1.002927
6	1120.133	902.565	0.86723(15)	1.003347
7	1138.485	824.254	0.78018(12)	1.003742
8	642.408	1825.744	2.99787(106)	1.003424
Mean				1.00338
Error				0.00027

As C_A and C_B have been calculated from uncorrected R_A and R_B, respectively (Table 5), an iterative calculation based on KR_A instead of R_A, and KR_B instead of R_B yields new values C'_A and C'_B, which when used in the above formula for K will yield a new K′. But K′ differs from K by less than 0.00002, a difference much smaller than the error 0.00027.

2.5. Terrestrial erbium samples

Erbium samples from mineral and trade products were collected for isotopic analysis:
Sample I. Rare earth adsorption kaolinite, a mineral of extensive deposit in South Jiangxi Province, China. 99.9999% Er_2O_3 was extracted therefrom by the Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun. It was separated by means of reverse extraction chromatography, and contained other rare oxides of less than 0.88 $\mu g\ g^{-1}$.
Sample II. 99.99% Er_2O_3, supplied by the Institute of Rare Earths, Baotao, Inner Mongolia, China.
Sample III. 99.997% $ErCl_3 \cdot 6H_2O$ containing 0.002% Tm, Aldrich Co., USA.
Sample IV. 99.99+% Er_2O_3, Acros Co., USA.
Sample V. Er metal, 99.9% pure, containing 0.1% (Ho + Tm), Fluka Co., Switzerland.

Table 9
Deviation from the exponential rule of normalization

Nickel [6]	Operator 1	Operator 2
$K_{62/60}$	1.015663(183)	1.014676(267)
$K_{60/58}$	1.015900(188)	1.014842(365)
$(K_{62/60} \cdot K_{60/58})^{1/2}$	1.01578	1.01476
Deviation	0.00012	0.00008

Table 10
Observed isotopic ratios of erbium in mineral and chemicals (corrected)

Sample	$R_{162/166}$	$R_{164/166}$	$R_{167/166}$	$R_{168/166}$	$R_{170/166}$
I	0.0041385	0.0477330	0.682393	0.804845	0.444663
II	0.0041534	0.0477771	0.682730	0.805496	0.444795
III	0.0041862	0.0477971	0.682759	0.805570	0.445514
IV	0.0040878	0.0478133	0.682661	0.805379	0.445352
V	0.0041370	0.0478028	0.682480	0.805023	0.444900

Four replicates of each sample in the form of nitrate solution were measured for the five isotopic ratios. The observed ratios are corrected by the corresponding factors, which are calculated from $K_{168/166} = 1.00338$ according to the exponential rule of normalization as follows:

$$K_{162/166} = K_{168/166}^{-2} = 0.99328$$

$$K_{164/166} = K_{168/166}^{-1} = 0.99663$$

$$K_{167/166} = K_{168/166}^{1/2} = 1.00169$$

$$K_{170/166} = K_{168/166}^{2} = 1.00676$$

Regarding the exponential rule for the normalization of related K′s, very little information can be found in the literature. In the case of nickel [6], which involves four isotopic ratios, the $K_{62/60}$ and $K_{60/58}$ are considered as shown in Table 9 (from which it can be noted that a very small deviation from the exponential rule exists by an amount about 0.01%, which is considered as negligible).

With the five factors given above, the observed isotopic ratios are corrected, and the corrected ratios are listed in Table 10, where the calculated errors are not shown.

2.6. Absolute isotopic composition and the atomic weight of erbium

From the five corrected isotopic ratios given in Table 10, we can calculate the absolute isotopic composition of erbium in these samples as shown in Table 11, in which each of the six isotopes has a mean value (at. %) listed with the corresponding error. Consequently, we can assess the absolute isotopic composition of erbium as follows:

0.139(3) at. % ^{162}Er

1.601(2) at. % ^{164}Er

33.503(24) at. % ^{166}Er

22.869(6) at. % ^{167}Er

26.978(12) at. % ^{168}Er

14.910(24) at. % ^{170}Er

Furthermore, from the isotopic composition and the corresponding isotopic mass [7], the atomic weight of erbium can be calculated for the five samples as follows:

Sample	A_r(Er)
I	167.2588(21)
II	167.2589(25)
III	167.2595(16)
IV	167.2594(14)
V	167.2589(13)
Mean	167.2591_0
Error	0.0003_9

Table 11
Isotopic composition of erbium (at. %)

Sample	^{162}Er	^{164}Er	^{166}Er	^{167}Er	^{168}Er	^{170}Er
I	0.13870	1.59975	33.51462	22.87015	26.97406	14.90272
II	0.13914	1.60060	33.50138	22.87239	26.98523	14.90125
III	0.14020	1.60080	33.49156	22.86666	26.97981	14.92097
IV	0.13693	1.60163	33.49755	22.86746	26.97821	14.91821
V	0.13962	1.60179	33.50821	22.86868	26.97490	14.90780
Mean	0.1387	1.6009	33.5027	22.8691	26.9784	14.9102
Error	0.0014	0.0010	0.0104	0.0026	0.0051	0.0103

Table 12
Summary of the calculation of the atomic weight of erbium

Value	167.25910
Mass spectrometric analytical error, $2S_m$	±0.00039
Limit of error in chemical analysis, $2S_c$	±0.00055
Possible bias in separated isotope ratio, B	±0.00021
Possible bias in isotopic mass, B_n	±0.000004
Overall limit of error, $\pm[2(S_m^2 + S_c^2)^{1/2} + B + B_n]$	±0.00089

The overall limit of error for the atomic weight of erbium is shown in Table 12. So, we have

$$A_r(\mathrm{Er}) = 167.2591(9)$$

on the basis of 95% confidence limit. Similar consideration of the overall limit of error for the absolute isotopic composition has already been given above.

3. Conclusion

Since 1941 the atomic weight of erbium has been determined by various authors making mass spectrometric measurement of the five isotopic ratios, yielding results as shown in Table 13. The new value found in this work is superior to all the others, because it originates from the calibrated mass spectrometric measurement and has a significantly improved uncertainty.

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Table 13
Atomic weight values of erbium found by various authors

Year	A_r(Er)	Author	Note	Reference
1941	167.248(7)	Wahl		[8]
1950	167.262(7)	Hayden et al.		[9]
1950	167.264(6)	Leland		[10]
1966	167.247(7)	Komori et al.		[11]
1981	167.257(2)	Holliger and Devillers		[12]
1994	167.2577(2)[a]	Chang and Gao		[13]
1998	167.2591(9)	This work	Calibrated	

[a] Calculated from raw data.

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