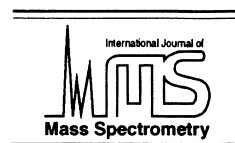




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# Absolute isotopic composition and atomic weight of dysprosium

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## Abstract

Gravimetric synthetic mixtures of highly enriched isotopes of  $^{162}\text{Dy}$  and  $^{164}\text{Dy}$  in the form of oxides of well defined purity were used to calibrate a thermal ionization mass spectrometer. Measurements on five natural samples of dysprosium yielded an absolute isotopic composition of 0.056 (2) at. %  $^{156}\text{Dy}$ , 0.095(2) at. %  $^{158}\text{Dy}$ , 2.329(12) at. %  $^{160}\text{Dy}$ , 18.889 (28) at. %  $^{161}\text{Dy}$ , 25.475(24) at. %  $^{162}\text{Dy}$ , 24.896(28) at. %  $^{163}\text{Dy}$  and 28.260(36) at. %  $^{164}\text{Dy}$ , and the atomic weight of dysprosium as 162.4995(17) with an uncertainty given on the basis of 95% confidence limit. No isotopic fractionation was found in terrestrial normal dysprosium materials. (Int J Mass Spectrom 207 (2001) 13–17) © 2001 Elsevier Science B.V.

**Keywords:** Dysprosium; Isotopic abundance; Atomic weight; Mass spectrometry

## 1. Introduction

The current atomic weight of dysprosium  $A_r(\text{Dy})=162.50$  (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  $A_r(\text{Dy})$  by means of calibrated mass spectrometric measurement using samples with highly enriched isotopes,  $^{162}\text{Dy}$  and  $^{164}\text{Dy}$ . Hereby the possible isobaric interference is shown in Table 1 [2], for which we used natural samples of dysprosium containing less than 0.003% of each gadolinium or erbium isobar as impurity in the determination of the absolute isotopic composition of dysprosium.

The experimental procedure of this calibrated mass spectrometric measurement to determine the atomic weight of dysprosium was almost exactly the same as that for erbium [3], both as rare earth elements.

## 2. Experimental

### 2.1. Purification of the isotopic materials

Isotopically enriched materials of  $^{162}\text{Dy}$  (sample A) and  $^{164}\text{Dy}$  (sample B) were purchased from the Isotec Inc. (A. Matheson, USA). Their nominal enrichments were 94.4 at. %  $^{162}\text{Dy}$  and 96.0 at. %  $^{164}\text{Dy}$ , each 200 mg of Dy. Besides the certified impurities given by the company for the first seven elements listed in Table 2, we analyzed for other impurities by using a VG Plasmaquad, and the results are also shown in this table. On the other hand, the

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Table 1  
Isobaric interference

Mass no.	156	158	160	161	162	163	164
Element	Gd (20.47)	Gd (24.84)	Gd (21.86)				
(natural abundance, at. %)	Dy (0.06)	Dy (0.10)	Dy (2.34)	Dy (18.9)	Dy (25.5) Er (0.14)	Dy (24.9)	Dy (28.2) Er (1.61)

following 20 elements were found to be below the detection limit  $<5 \mu\text{g g}^{-1} \text{Dy}_2\text{O}_3$ : Pr, Nd, Sm, Gd, Tb, Tm, Th, U, Ti, V, Cr, Mn, Co, Ni, Ge, Rb, Zr, Nb, Mo, and In. Further, in order to remove any possible absorbed  $\text{CO}_2$  and water vapor, the two samples were purified through oxalate precipitation, and the oxalate hydrate was ignited at  $800^\circ\text{C}$  in a muffle furnace, in which a current of dry nitrogen was passed to the furnace bottom to remove these two gases as the decomposition product. Therefore, the purity of samples A and B was assessed as 99.89(2)% and 99.87(2)%, respectively after an allowance of  $200 \mu\text{g g}^{-1} \text{Dy}_2\text{O}_3$  was made for those impurities below the detection limit.

Table 2  
Impurities ( $\mu\text{g compound g}^{-1} \text{Dy}_2\text{O}_3$ )

Element	In sample A	In sample B
K	60	20
Na	430	160
Ca	70	200
Fe	20	20
Al	50	70
Si	30	40
Pb	50	120
Cu	18.8	10.2
Zn	33.6	22.4
Cd	13.7	$<5$
Sn	12.7	10.3
Ga	$<5$	36.3
Sr	3.6	2.7
Ba	11.4	53.9
Y	8.8	9.6
La	2.3	6.9
Ce	1.7	5.2
Eu	2.6	10.2
Ho	$<5$	240
Er	17.1	82.3
Yb	$<5$	20.5
Lu	50.2	$<5$

## 2.2. Preparation of the standard solutions

The purified samples of A and B,  $^{162}\text{Dy}_2\text{O}_3$  and  $^{164}\text{Dy}_2\text{O}_3$  respectively, were dissolved in  $1.6 \text{ mol L}^{-1} \text{HNO}_3$  (guaranteed reagent). Careful manipulation and weighing including the correction for air buoyancy have been described in [3]. Results are shown in Table 3.

## 2.3. Isotopic composition of samples A and B

A thermal ionization mass spectrometer of Finnigan MAT-261 model was used to measure the six isotopic ratios of dysprosium for samples A and B. The measuring technique was the same as in the case of erbium [3]. Peaks of  $^{156}\text{Dy}$  and  $^{158}\text{Dy}$  were not detected. Results are shown in Table 4. From those observed ratios the isotopic composition can be calculated and is listed in Table 5.

## 2.4. Isotopic concentration of standard solutions A and B

The calculation for the isotopic concentration for the two standard solutions is shown in Table 6.

Table 3  
Standard solutions A and B

Sample	A	B
Compound	$^{162}\text{Dy}_2\text{O}_3$	$^{164}\text{Dy}_2\text{O}_3$
Purity (%)	99.89	99.87
Weight (mg)	158.870	162.205
Net weight (mg)	158.695	161.994
Weight of solution (g)	39.559 07	39.580 97

Table 4  
Measured isotopic ratios of samples A and B, each 5 replicates (1s)

Sample	A	B
$^{164}\text{Dy}/^{162}\text{Dy}$	0.009 258 4(76)	114.706(107)
$^{163}\text{Dy}/^{162}\text{Dy}$	0.040 423 (19)	3.386 6(32)
$^{161}\text{Dy}/^{162}\text{Dy}$	0.015 747 6(48)	0.641 18(12)
$^{160}\text{Dy}/^{162}\text{Dy}$	0.000 371 5(14)	0.076 12(53)

### 2.5. Mixed standard solutions and the correction factor $K_{164/162}$

Portions of the standard solutions A and B were combined to form eight mixed standard solutions as shown in Table 7. The isotopic ratio  $R_{164/162}$  was measured for each mix, and these ratios are listed in Table 7

Then the correction factor  $K_{164/162}$  can be obtained by applying the following formula [3]:

$$K_{164/162} = \frac{W_A C_A (R_A - R_{AB}) - W_B C_B (R_{AB} - R_B)}{W_B C_B R_A (R_{AB} - R_B) - W_A C_A R_B (R_A - R_{AB})}$$

where  $R_A$ ,  $R_B$ , and  $R_{AB}$  observed for the mix all pertain to  $R_{164/162}$ , that is,  $R_A = 0.009258$ ,  $R_B = 114.71$  (see Table 4), whereas  $C_A$  and  $C_B$  are given in Table 6.

Results of calculation are shown in Table 7. So we obtain the mean  $K_{164/162} = 1.00504(98)$ , which differs from unity only by 0.5%, thus exempting an iterative calculation. Application of the exponential rule enables to find the correction factors for other isotopic ratios as follows:

$$K_{156/162} = K_{164/162}^{-3} = 0.985\ 03$$

Table 5  
Isotopic composition (at. %) of samples A and B

Sample	A	B
$^{156}\text{Dy}$	0	0
$^{158}\text{Dy}$	0	0
$^{160}\text{Dy}$	0.0349	0.0635
$^{161}\text{Dy}$	1.4775	0.5352
$^{162}\text{Dy}$	93.8262	0.8347
$^{163}\text{Dy}$	3.7927	2.8266
$^{164}\text{Dy}$	0.8687	95.7400

Table 6  
Isotopic concentration of standard solutions A and B

Sample	A	B
Atomic weight	161.966 718	163.865 520
$\text{DyO}_{1.5}$ , mol weight	185.965 818	187.864 620
Total $\mu\text{mol Dy}$	853.356	862.291
at. % ( $^{162}\text{Dy} + ^{164}\text{Dy}$ )	94.694 9	96.574 7
$\mu\text{mol } (^{162}\text{Dy} + ^{164}\text{Dy})$	808.084	832.755
$\mu\text{mol } (^{162}\text{Dy} + ^{164}\text{Dy}) \text{ g}^{-1} \text{ soln.}$	20.427 28 ( $C_A$ )	21.039 28 ( $C_B$ )

$$K_{158/162} = K_{164/162}^{-2} = 0.990\ 00$$

$$K_{160/162} = K_{164/162}^{-1} = 0.994\ 99$$

$$K_{161/162} = K_{164/162}^{-1/2} = 0.997\ 49$$

$$K_{163/162} = K_{164/162}^{1/2} = 1.002\ 52$$

$$K_{164/162} = 1.005\ 04$$

### 2.6. Terrestrial samples of dysprosium

Five dysprosium samples were collected from China, Japan, and USA for isotopic analysis: (1) Bastnaesite, Inner Mongolia, China, 99.99%  $\text{Dy}_2\text{O}_3$ , prepared by Baotou Rare Earth Research Institute; (2) Rare earth adsorption kaolinite, Jiangxi, China, 99.9999%  $\text{Dy}_2\text{O}_3$ , prepared by Changchun Institute of Applied Chemistry; (3) 99.999%  $\text{Dy}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , Aldrich, USA; (4) 99.99%  $\text{Dy}_2\text{O}_3$ , Shin-Etsu Chemical

Table 7  
Measured  $R_{164/162}$  of mixed standard solutions (3 replicates) and the correction factor  $K_{164/162}$  (1s)

Mix no.	Weight of solution A $W_A$ (mg)	Weight of solution B $W_B$ (mg)	$R_{164/162}$	$K_{164/162}$
1	994.060	697.940	0.724 64	1.005 096
2	400.738	683.379	1.729 15	1.006 482
3	755.634	766.171	1.039 63	1.004 980
4	868.014	878.761	1.037 67	1.005 367
5	750.776	816.314	1.115 05	1.003 485
6	477.680	613.781	1.311 17	1.005 536
7	617.626	430.101	0.718 52	1.005 550
8	669.356	888.167	1.355 46	1.003 800
Mean				1.005 04(98)

Table 8

Measured isotopic ratios of dysprosium in natural samples (5 replicates, 1s)

Sample	$^{164}\text{Dy}/^{162}\text{Dy}$	$^{163}\text{Dy}/^{162}\text{Dy}$	$^{161}\text{Dy}/^{162}\text{Dy}$	$^{160}\text{Dy}/^{162}\text{Dy}$	$^{158}\text{Dy}/^{162}\text{Dy}$	$^{156}\text{Dy}/^{162}\text{Dy}$
1	1.103 57(54)	0.974 71(25)	0.743 48(20)	0.091 906(50)	0.003 769(12)	0.002 187(7)
2	1.103 36(81)	0.974 77(58)	0.743 52(42)	0.091 876(88)	0.003 762(6)	0.002 267(22)
3	1.104 40(70)	0.975 03(30)	0.743 08(27)	0.091 810(69)	0.003 777(22)	0.002 258(24)
4	1.103 60(81)	0.974 79(35)	0.743 38(31)	0.091 883(77)	0.003 773(22)	0.002 186(7)
5	1.103 91(56)	0.974 84(25)	0.743 26(19)	0.091 848(46)	0.003 775(6)	0.002 282(16)

Co., Japan; (5) 99.9%  $\text{Dy}_2\text{O}_3$ , containing the three interfering isobars of gadolinium each as  $<0.002\%$ , Shanghai Chemical Reagents Corp., China. Each sample was dissolved in  $1.6 \text{ mol L}^{-1} \text{HNO}_3$  to form the loading solution, which contained  $4 \mu\text{g } \mu\text{L}^{-1} \text{Dy}$ . The measured isotopic ratios for each sample are shown in Table 8.

## 2.7. Absolute isotopic composition and the atomic weight

The final error analysis for the absolute isotopic composition and atomic weight of each terrestrial dysprosium sample is carried out as shown in Table 9,

Table 9

Summary of the calculation of the isotopic abundance and atomic weight of dysprosium (sample 1)

Parameter	Value	Mass spectrometric analytical error $2S_m, \pm 10^{-4}$	Possible error in chemical analysis $2S_c, \pm 10^{-4}$	Possible bias in separated isotope ratio $B, \pm 10^{-4}$	Overall limit of error $2(S_m^2 + S_c^2)^{1/2} + B, \pm 10^{-4}$
Isotopic ratio					
$^{156}\text{Dy}/^{162}\text{Dy}$	0.002 154	0.076	0.0127	0.0083	0.085
$^{158}\text{Dy}/^{162}\text{Dy}$	0.003 731	0.146	0.0218	0.0143	0.162
$^{160}\text{Dy}/^{162}\text{Dy}$	0.091 446	0.772	0.532	0.350	1.29
$^{161}\text{Dy}/^{162}\text{Dy}$	0.741 61	3.12	4.31	2.82	8.14
$^{163}\text{Dy}/^{162}\text{Dy}$	0.977 17	4.05	5.64	3.70	10.7
$^{164}\text{Dy}/^{162}\text{Dy}$	1.109 13	9.06	6.39	4.19	15.3
at. %					
$^{156}\text{Dy}$	0.054 9	7.57	1.26	0.83	8.5
$^{158}\text{Dy}$	0.095 1	14.5	2.17	1.42	16.1
$^{160}\text{Dy}$	2.329 7	64.8	44.7	29.3	108
$^{161}\text{Dy}$	18.893 5	103	142	93.0	268
$^{162}\text{Dy}$	25.476 1	112	110	71.9	229
$^{163}\text{Dy}$	24.894 4	104	144	94.6	272
$^{164}\text{Dy}$	28.256 3	204	144	94.1	344
Atomic weight					
	162.499 4	0.454 <sup>b</sup>	0.0757	0.0496	0.51
		0.582 <sup>b</sup>	0.0867	0.0568	0.65
		1.30 <sup>b</sup>	0.894	0.587	2.16
		1.03 <sup>b</sup>	1.42	0.930	2.68
		1.04 <sup>b</sup>	1.45	0.948	2.73
		4.08 <sup>b</sup>	2.88	1.89	6.88

<sup>a</sup> For the uncertainty in the value of atomic weight, an item  $B_n = 4 \times 10^{-6}$  (possible bias in isotopic mass) is added.

<sup>b</sup> The six components pertain to the six ratios.

Table 10

Atomic weight values of dysprosium by various authors

Year	Atomic weight	Author	Note	Reference
1949	162.499(3)	Inghram et al.		[5]
1950	162.50(1)	Leland		[6]
1957	162.495(4)	Collins et al.		[7]
1966	162.492(7)	Komori et al.		[8]
1981	162.498(2)	Holliger and Devillers		[9]
1996	162.500(2)	Chang and Gao	Subst. calibrated <sup>a</sup>	[10]
2000	162.4995(17)	This work	Calibrated	

<sup>a</sup>  $K_{151/153}$  of Eu = 0.9957(16) was used for bias correction.

where only the data of sample (1) are listed for convenience.

The mean absolute isotopic composition of dysprosium (2s) is as follows: 0.056 (2) at. %  $^{156}\text{Dy}$ , 0.095 (2) at. %  $^{158}\text{Dy}$ , 2.329 (12) at. %  $^{160}\text{Dy}$ , 18.889 (28) at. %  $^{161}\text{Dy}$ , 25.475 (24) at. %  $^{162}\text{Dy}$ , 24.896 (28) at. %  $^{163}\text{Dy}$ , and 28.260 (36) at. %  $^{164}\text{Dy}$ .

The atomic weight of dysprosium (2s) is (1) 162.4994(16), (2) 162.4992(18), (3) 162.4998(18), (4) 162.4995(17), and (5) 162.4995(16).

Therefore, the mean atomic weight of dysprosium is  $A_r(\text{Dy})=162.4995(17)$ .

### 3. Conclusion

A comparison of all the known values of the atomic weight of dysprosium obtained by various authors is shown in Table 10. The value of this work is superior to all the others, since it originates from a calibrated measurement with gravimetric synthetic mixtures of separated isotopes.

### Acknowledgement

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