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Isotope ratio measurements of dysprosium by multiple collection inductively coupled plasma mass spectrometry

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Abstract

Isotope ratio measurements for four natural dysprosium samples were performed by multiple collection inductively coupled plasma mass spectrometry (MC-ICP-MS). Instrumental mass discrimination was corrected by internal normalization using the ratio $^{161}\mathrm{Dy}/^{163}\mathrm{Dy} = 0.75872$, derived from recently published thermal ionization mass spectrometry (TIMS) measurements in dysprosium with isotopic calibrated composition. This ratio was chosen because of absence of isobaric interference at 161 and 163 mass numbers. The exponential correction equation was applied. The corrected ratios, recalculated for comparison, relative to ^{162}Dy are: $^{164}\mathrm{Dy}/^{162}\mathrm{Dy} = 1.109151(17)$, $^{163}\mathrm{Dy}/^{162}\mathrm{Dy} = 0.977088(6)$, $^{161}\mathrm{Dy}/^{162}\mathrm{Dy} = 0.741336(4)$, $^{160}\mathrm{Dy}/^{162}\mathrm{Dy} = 0.091377(8)$, $^{158}\mathrm{Dy}/^{162}\mathrm{Dy} = 0.0036868(37)$ and $^{156}\mathrm{Dy}/^{162}\mathrm{Dy} = 0.0020954(74)$. The precision measurement shown in brackets is two standard deviations calculated from 90 measurements. The mean values are in very good agreement with the absolute values obtained by TIMS. The precision is by at least one order of magnitude better comparing to TIMS measured precision. The calculated atomic weight of dysprosium, based on the mass spectrometric analytical error only is 162.4997(1), in very good agreement with recently published TIMS value of 162.4995(8). The overall limit of error for the TIMS value is 17×10^{-4}. (Int J Mass Spectrom 216 (2002) 177–184) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dysprosium; Isotope ratio determination; Multiple collection ICP-MS; Isotopic abundance; Atomic weight

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1. Introduction

Dysprosium is a rare-earth element comprising seven isotopes in the 156–164 mass range. The ^{156}Dy and ^{158}Dy isotopes are the minor ones with abundance below 0.1%, ^{160}Dy has an abundance of 2.3% and ^{161}Dy–^{164}Dy between 19 and 28%. The element has a relatively low ionization potential of 5.93 eV, therefore it is easily analyzed by thermal ionization mass spectrometry (TIMS). The TIMS isotope ratio measurements till 1996 were reviewed by Platzner [1]. Recently, the absolute isotopic composition and the atomic weight of dysprosium were determined using gravimetric synthetic mixtures prepared from highly enriched ^{162}Dy and ^{164}Dy isotopic samples [2]. In TIMS, the sample purity is of utmost importance as the most abundant ^{156}Gd and ^{158}Gd interfere with the minor Dy isotopes, and the minor ^{162}Er and ^{164}Er isotopes are isobaric with the major ^{162}Dy and ^{164}Dy isotopes. The highest gadolinium impurity level in one of the samples, determined by two different ICP-MS techniques, was 35–44 ppm. No erbium was found in all our dysprosium samples. The non-interfering mono-isotopic ^{159}Tb isotope was observed in some

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of the samples at a level of <60 ppm. TIMS and also multiple collection inductively coupled plasma mass spectrometry (MC-ICP-MS) isotope ratio measurements may further be obscured by isobaric CeO^+ and rare-earth oxide ions, namely the corresponding NdO^+ and SmO^+ ions. When an ICP ion source is applied, the oxide formation can be significantly reduced by replacing the more frequently used Meinhard nebulizer by the desolvating microconcentric Aridus type nebulizer. Two further types of interferences should be kept in mind when ICP ionization is applied, namely argide (MAr^+), (M = Cd, Sn, Sb, Te) and hydride (DyH^+) ions. The eventual formation of interference ions with any nebulizer type must be experimentally verified and quantified, as will be shown further on. An important advantage of ICP-MS over TIMS is the possibility to correct ionic interferences by direct subtraction of their intensity as has been demonstrated previously [3,4]. A further advantage of MC-ICP-MS is the simultaneous ion beam collection which effectively eliminates the effects of plasma fluctuations, plasma and instrumental drifts on the measured isotopic ratios. In a single collector ICP instrument, where consecutive ion beam measurement is applied, the plasma fluctuations increase the measurement uncertainty. This effect is expected to increase as the duration of a measurement cycle is larger, (i.e., the number of isotopes in the sample is larger). The plasma and instrumental drifts may heavily affect both the measurement uncertainty and the data accuracy.

The MC-ICP-MS technique is successfully applied in this work. The possibility to measure isotope ratios in selected rare-earth elements (Nd, Sm) with high precision and high accuracy has been demonstrated since the early applications of the MC-ICP-MS system [5]. The aim of this work is to verify the capability of the MC-ICP-MS system to measure high precision and high accuracy dysprosium isotope ratios. Reducing the measurement uncertainty of an isotope ratio measurement increases the option of revealing smaller and smaller isotope effects of natural processes. It will be shown that the improved precision allowed to distinguish between differences in ratio values of the dysprosium minor isotopes, attributing them to presence of impurities, rather than to natural fractionation of the lighter isotopes.

2. Experimental

2.1. The mass spectrometers

(1) The multiple collector ICP mass spectrometer is a double-focusing instrument of Nier–Johnson geometry made by Nu Instruments, UK. The unique feature of this machine is the use of a fixed multiple-collector array. The ion beams are targeted to the chosen collectors by the use of a variable dispersion ion-optical arrangement. The resolving power of the instrument is about 300. At optimized conditions, the ion peak has a trapezoid shape with a width of 0.3 and 0.48 μm at the top and 10% height, respectively. The Aridus microconcentric nebulizer (CETAC, USA) was used. Further details were described elsewhere [3]. Instrumental operating conditions were as given in Table 1.

Table 1
Operating conditions used for MC-ICP-MS

RF power	1300 W
Ar cooling gas flow rate	13 L/min
Ar auxiliary gas flow rate	~1 L/min (optimized daily)
Ar nebulizer gas flow rate	~0.6 L/min (optimized daily)
Interface cones	Nickel
Acceleration voltage	4 kV
Ion-lens setting	Optimized for maximum intensity
Mass resolution	~300
Mass analyzer pressure	$<2 \times 10^{-9}$ mbar
Detection system	12 Faraday cups and three electron multipliers
Nebulizer	Aridus microconcentric, CETAC Technologies, NE, USA
Ar sweep gas flow rate	~3.5 L/min (optimized daily)
Spray chamber temperature	70 °C
Desolvator temperature	160 °C
Sample flow rate	0.08 mL/min
Typical ^{163}Dy sensitivity	9 V/(mg/L)
Sampling mode	1 run = 3 blocks of 10 × 10 s
No. of runs/sample	3

(2) The Elan 6000 (Perkin-Elmer, Canada) quadrupole-based ICP-MS equipped with an ion counting system and the Meinhard nebulizer was used for impurity detection in the Dy samples. The sensitivity of this instrument was 27,000 cps for the ^{156}Dy isotope (0.056%) in a 1 mg/L Dy solution with an instrumental blank of 10–20 cps.

2.2. Materials

Four dysprosium samples from the following sources were used for isotopic analysis: (1) Aldrich, USA, (atomic absorption standard); (2) Merck, Darmstadt, Germany, Dy_2O_3; (3) Johnson Matthey Chemicals, UK, Dy_2O_3; (4) "Unknown", this sample is a solution of analytical Dy_2O_3 which lost its manufacturer's label, most probably BDH, UK. Samples 1–3 were prepared by dissolving dysprosium oxide equivalent to 100 mg Dy in 10 mL 0.1 N ultra pure nitric acid, and finally adjusted to 0.5 mg/L Dy. Commercial samples 1–3 were used to allow future comparison isotope ratio measurements of pure, well-defined materials by other laboratories. Sample 4 was incorporated in this study because of the availability of a pure Dy material. The element concentration has also been adjusted to 0.5 mg/L in 0.1 N HNO_3. Geological samples were not used to avoid the time consuming chemical separation and purification, which was not the aim of the present work.

2.3. Interference measurements

(1) *Hydrides*. The DyH^+ ion intensity was estimated by measuring hydride formation in a pure lanthanum, cerium free solution using the MC-ICP-MS. This element has two isotopes ^{138}La and ^{139}La with relative abundance of 0.09 and 99.9%, respectively.

(2) *Oxides*. The oxides of cerium, neodymium and samarium are isobaric with dysprosium isotopes. Traces of these elements in the sample solutions were determined with the Elan 6000 ICP-MS. The extent of oxide formation was determined in pure Ce, Nd and Sm solutions with the MC-ICP-MS.

(3) *Argides*. Argide molecular ions (MAr^+) of cadmium, tin, antimony and tellurium are also isobaric with dysprosium isotopes. The sample solutions were tested for traces of these elements (Elan 6000) and solutions of the pure elements studied with the MC-ICP-MS for argide formation.

(4) *Gadolinium*. The concentration of this element was determined by direct measurement of the $m/z = 155$ ion intensity relatively to ^{156}Dy using the Elan 6000. At this mass only the ^{155}Gd isotope exists. The relevant interfering ions are summarized in Table 2.

2.4. Analytical procedures

The sample solutions were introduced into the plasma via the Aridus microconcentric nebulizer. A final ratio result comprises the acquisition of 3 data runs, each of 3 blocks of 10 ratio measurements, i.e., 90 ratios are accumulated. The total time for 1 run is ∼9 min, which include the ion intensity and zero measurements and the duration of peak centering between each block. Therefore, the element consumption per sample is ∼1.1 μg. Between each run the nebulizer is washed with pure 0.1 N nitric acid solution The mean ratio values quoted in Section 3 is the mean of the means of 3 runs and the uncertainty is $\pm 2\sigma$.

Seven out of 12 Faraday collectors were used in this work, in the simultaneous data collection mode of operation. Isotope ^{160}Dy was adjusted to the "axial" collector, ^{161}Dy, ^{162}Dy, ^{163}Dy and ^{164}Dy to the high-1, high-2, high-3 and high-4 collectors, respectively, and ^{158}Dy and ^{156}Dy to the low-2 and low-3 collectors, respectively. Two mass units dispersion (low-2 and low-3 collectors) is because of an ion count collector placed between them. The zero measurements are made at half masses from 163.5 on high-4 to 155.5 on low-3 collectors by deflecting the electrostatic analyzer potential.

Table 2
Interferences to dysprosium isotopes from isobaric rare-earth elements, hydrides, oxides and argides

Mass number						
156	158	160	161	162	163	164
Dysprosium atoms						
Dy (0.06)[a]	Dy (0.10)	Dy (2.34)	Dy (18.9)	Dy (25.5)	Dy (24.9)	Dy (28.2)
Possible atomic interferences						
Gd (20.5)	Gd (24.8)	Gd (21.9)		Er (0.14)		Er (1.61)
Possible molecular interferences						
Hydrides						
			DyH	DyH	DyH	DyH
Oxides						
CeO	CeO					
	NdO	NdO	NdO	NdO		NdO
		SmO			SmO	SmO
Argides						
CdAr						
SnAr	SnAr	SnAr		SnAr		SnAr
			SbAr		SbAr	
		TeAr		TeAr	TeAr	TeAr

[a] Natural atom abundance (%).

3. Results and discussion

3.1. Sample purity and spectral interference

3.1.1. Hydrides

In a cerium free (no ^{142}Ce of 11.1% abundance was detected) lanthanum solution, $^{139}\mathrm{LaH}^+/^{139}\mathrm{La}^+ = 5.8 \times 10^{-6}$ was observed. This value is the upper limit of LaH$^+$ formation because traces of the more abundant ^{140}Ce (88.5%) would contribute to the ion current at $m/z = 140$. The direct hydride determination using the abundant ^{164}Dy (28.2%) isotope is a dubious alternative, because the $^{164}\mathrm{DyH}^+/^{164}\mathrm{Dy}^+$ ratio may be affected by trace amounts of the mono isotopic ^{165}Ho. The same consideration applies to the $^{165}\mathrm{HoH}^+/^{165}\mathrm{Ho}^+$ ratio, the $^{165}\mathrm{HoH}^+$ hydride is isobaric with the most abundant (33.4%) ^{166}Er isotope. In a recent measurement of uranium hydride, $^{235}\mathrm{UH}^+/^{235}\mathrm{U}^+ \sim 2 \times 10^{-7}$ has been observed [6]. It should be noted that $^{235}\mathrm{UH}^+/^{235}\mathrm{U}^+ \sim 5 \times 10^{-6}$ was observed in natural uranium, (essentially free of ^{236}U isotope) when a MC-ICP-MS with a Meinhard nebulizer was used [7]. Cerium free lanthanum has been chosen because absolutely pure rare-earth element samples are extremely exceptional.

3.1.2. Oxides

Traces of cerium, neodymium and samarium had been detected in the Aldrich sample at the following levels: $\mathrm{Ce/Dy} = 9 \times 10^{-5}$, $\mathrm{Nd/Dy} = 3 \times 10^{-5}$ and $\mathrm{Sm/Dy} = 2 \times 10^{-5}$. In the JMC sample the trace levels were $\leq 1 \times 10^{-5}$, $\leq 1 \times 10^{-5}$ and $\leq 1 \times 10^{-6}$, respectively. The CeO$^+$/Ce$^+$, NdO$^+$/Nd$^+$ and SmO$^+$/Sm$^+$ ratios measured with the MC-ICP-MS and Aridus nebulizer were $<1 \times 10^{-4}$, 2×10^{-4} and 2×10^{-4}, respectively. Only ^{140}Ce (88.5%) and ^{142}Ce (11.1%) oxides are isobaric with the two minor ^{156}Dy and ^{158}Dy isotopes. A ≤ 1 mV ^{140}Ce ion current was observed in the Aldrich sample. Therefore, the CeO$^+$ ion current will contribute to the ^{156}Dy ion current ($\sim$5 mV) $<10^{-4}$ mV, which will affect the $^{156}\mathrm{Dy}/^{162}\mathrm{Dy}$ ratio (Table 5, line 1) by $<10^{-4}/2350$ or $\leq 40 \times 10^{-7}$, ($^{162}\mathrm{Dy} = 2350$ mV). This contribution is within the $\pm 2\sigma$ measurement uncertainty of $^{156}\mathrm{Dy}/^{162}\mathrm{Dy} = 0.0021245(55)$, and therefore may be neglected. All the other isobaric oxides described above will affect the measured Dy isotope ratios by $<4 \times 10^{-7}$ and therefore are negligible.

3.1.3. Argides

Tin and antimony traces were observed only in Aldrich sample. A 200 μg/L tin sample yielded a 700 mV ^{120}Sn (32.8%) ion intensity and 300 cps ^{120}Sn^{40}Ar intensity. The conversion factor for the MC-ICP-MS is $1000\,\text{mV} = 62 \times 10^{6}$ cps, therefore tin argide formation is at a level of $\text{SnAr}^{+}/\text{Sn}^{+} = 7 \times 10^{-6}$. The ^{120}Sn ion intensity in the 0.5 mg/L Dy Aldrich solution was ~1 mV, which contributes 7×10^{-6} mV at $m/z = 160$. The measured ^{160}Dy ion intensity was 210 mV, therefore $^{120}\text{Sn}^{40}\text{Ar}/^{160}\text{Dy} \sim 7 \times 10^{-6}/210 = 3.3 \times 10^{-8}$, and thus argide contribution at this mass can be neglected. The most pronounced effect of SnAr will be at $m/z = 156$ where relatively to mass 160 the expected ^{116}Sn (14.4%) ion intensity would be ~0.44 mV and the ^{156}Dy ion intensity 5.2 mV. Therefore, $^{116}\text{Sn}^{40}\text{Ar}/^{156}\text{Dy} \sim 0.44 \times 7 \times 10^{-6}/5.2 = 6 \times 10^{-7}$. Using similar calculation, it may be concluded that the ^{162}Dy (25.5%) ion intensity is not affected by ^{122}Sn^{40}Ar, therefore the estimated contribution of ^{116}Sn^{40}Ar to the ratio $^{156}\text{Dy}/^{162}\text{Dy} = 0.0021245(55)$ given in Table 5, line 1, may be estimated as 6×10^{-7} well within the experimental error. The observed SbAr^{+}/Sb^{+} ratio was about the same as SnAr^{+}/Sn^{+} but the Sb/Sn ratio in the Aldrich sample is $\sim 10^{-2}$, excluding any possible SbAr interference at $m/z = 161$ and 163.

3.1.4. Gadolinium

Traces of this element were detected in the Aldrich sample. In a 1 mg/L Dy solution at $m/z = 155$ a Gd blank subtracted ion count yielded 350 cps and at $m/z = 156$ the Dy ion count was 30,000 cps. Accounting for the isotopic abundance of each isotope, the Gd elemental impurity was calculated as $\text{Gd}/\text{Dy} = 44 \times 10^{-6}$. In the JMC sample at the same conditions, the ^{155}Gd blank subtracted ion count yielded 20 cps (twice the blank count), corresponding to $\text{Gd}/\text{Dy} \sim 1.2 \times 10^{-6}$.

3.2. Dysprosium isotope ratio measurements

The measured data were normalized to $^{161}\text{Dy}/^{163}\text{Dy} = 0.75872$ calculated from the isotopic abundance values of Chang et al. [2] and applying the exponential correction equation [3,8]. The corrected values are presented for comparison reasons relatively to ^{162}Dy as in [2]. We assume that the ion current observed at mass no 162 corresponds to the ^{162}Dy isotope only. Erbium has a minor interfering isotope at mass no 162 (0.14%). The major isotope is ^{166}Er (33.6%), no measurable ion intensity was observed at this mass number in all the studied samples.

In Table 3 the mass discrimination corrected isotope ratios in JMC dysprosium are given. The given mean value is the mean of the 3 runs. The quoted precision $\pm 2\sigma$ represent measurement uncertainties. This set of data was chosen because it represents our purest (without isobaric interference) isotopic dysprosium sample.

The uncertainty of the mass spectrometric measurement presented in this work reveals at least one order of magnitude improved precision for the isotope ratio values as compared to the TIMS data given by Chang et al. [2]. This is shown in Table 4 for the Aldrich commercial sample, as this is the only common one

Table 3
Mass discrimination corrected isotope ratios in Johnson Matthey Chemicals dysprosium (uncertainty: $\pm 2\sigma$)[a]

	Isotope ratio					
	164/162	163/162	161/162	160/162	158/162	156/162
Run 1	1.109148(22)	0.977090(12)	0.741337(9)	0.091373(3)	0.0036886(22)	0.0020978(21)
Run 2	1.109163(19)	0.977090(12)	0.741338(9)	0.091381(4)	0.0036870(18)	0.0020911(31)
Run 3	1.109143(21)	0.977085(9)	0.741334(7)	0.091376(3)	0.0036849(28)	0.0020972(23)
Mean	1.109151(17)	0.977088(6)	0.741336(4)	0.091377(8)	0.0036868(37)	0.0020954(74)

[a] $(^{161}\text{Dy}/^{163}\text{Dy}) = 0.75872$ was used for fractionation correction [2].

Table 4
Uncertainty comparison (precision given as $\pm 2\sigma$) of MC-ICP-MS and TIMS measured isotope ratios for dysprosium in Aldrich commercial sample

	Isotope ratio					
	164/162	163/162	161/162	160/162	158/162	156/162
Chang et al. [2][a]	1.10997(140)	0.97749(60)	0.74121(54)	0.091350(138)	0.003739(44)	0.002224(48)
This work[b]	1.10915(2)	0.97712(1)	0.74136(1)	0.091406(5)	0.003725(6)	0.002125(6)

[a] Measured by TIMS, calculated from [2] Table 8, sample 3.

[b] Measured by MC-ICP-MS, taken from Table 5.

among the five samples studied by Chang et al. and the four studied in this work. For clarity reason, the TIMS data were corrected for mass fractionation, using the correction factors given in [2].

Table 5 summarizes the mass discrimination corrected isotope ratios studied in this work. Inspecting this table reveals excellent agreement in between the samples regarding the $^{164}\text{Dy}/^{162}\text{Dy}$, $^{163}\text{Dy}/^{162}\text{Dy}$ and $^{161}\text{Dy}/^{162}\text{Dy}$ ratios. The $^{158}\text{Dy}/^{162}\text{Dy}$ and $^{156}\text{Dy}/^{162}\text{Dy}$ ratios show a 1.0 and 1.4% difference between the lowest (JMC) and the highest (Aldrich) values, respectively. Assuming that these ratio increments are due to gadolinium impurities, ^{158}Gd (most abundant, -24.8% isotope) and ^{156}Gd (third abundant, -20.5% isotope). In calculating the possibility of Gd impurity we assume equal ICP ionization efficiency of Gd and Dy. The difference in the two $^{158}\text{Dy}/^{162}\text{Dy}$ ratios is attributed to $^{158}\text{Gd}/^{162}\text{Dy} = 3.68 \times 10^{-5}$. The measured ^{162}Dy ion intensity is 2350 mV, therefore the ion intensity of $^{158}\text{Gd} = 0.086$ mV and the total ion intensity of Gd $= 0.086/0.248 = 0.35$ mV. In the same way, the total ion intensity of Dy $= 2350/0.255 = 9216$ mV, (the ^{162}Dy isotope abundance is $\sim$25.5%). Finally, Gd/Dy $= 0.35/9216 = 38 \times 10^{-6}$, i.e., $\sim 20 \times 10^{-12}$ g Gd/g in the 0.5×10^{-6} g Dy/g solution, used in these measurements. When applying the same calculation for the $^{156}\text{Dy}/^{162}\text{Dy}$ and $^{160}\text{Dy}/^{162}\text{Dy}$ ratios we obtain Gd/Dy $= 37 \times 10^{-6}$ and 34×10^{-6}, respectively, which is in good agreement with the value derived from the $^{158}\text{Dy}/^{162}\text{Dy}$ ratio. Taking in account the Gd determination with the Elan 6000 ICP-MS quadrupole, the Gd/Dy ratio in the Aldrich sample is in the range of (35–44) $\times 10^{-6}$. It should be noted that the Dy sample #5 studied by Chang et al. also contained about 20 ppm Gd. This is clearly seen on the enhanced $^{156}\text{Dy}/^{162}\text{Dy}$ ratio. We may therefore conclude that the corrected isotope ratios for the JMC sample are the true or at least the closest to true ratios, provided the normalization factor $^{161}\text{Dy}/^{163}\text{Dy} = 0.75872$ used in this work is the true value of this ratio.

Table 5
Mass discrimination corrected isotope ratios for dysprosium in various commercial samples[a]

	Isotope ratio					
	164/162	163/162	161/162	160/162	158/162	156/162
Aldrich[b]	1.109152(23)	0.977119(14)	0.741360(11)	0.091406(5)	0.0037246(60)	0.0021245(55)
Merck	1.109154(16)	0.977079(16)	0.741329(11)	0.091382(4)	0.0036967(32)	0.0021024(15)
JMC	1.109151(17)	0.977088(6)	0.741336(4)	0.091377(8)	0.0036868(37)	0.0020954(74)
Unknown	1.109133(34)	0.977086(24)	0.741337(24)	0.091339(8)	0.0037133(41)	0.0021169(54)
Mean[c]	1.109148(21)	0.977093(35)	0.741341(27)	0.091376(55)	0.0037054(330)	0.0021098(272)

[a] $(^{161}\text{Dy}/^{163}\text{Dy}) = 0.75872$ was used for fractionation correction [2].

[b] Each ratio value in lines 1–4 represents the mean of 3 runs of 30 measurements.

[c] The mean ratios are mean ratio values for the four different samples.

Table 6
Isotope abundance in dysprosium (at.%) (uncertainty: ±2σ)

	^{164}Dy	^{163}Dy	^{162}Dy	^{161}Dy	^{160}Dy	^{158}Dy	^{156}Dy
Chang et al. [2]	28.260(36)	24.896(28)	25.475(24)	18.889(28)	2.329(12)	0.095(2)	0.056(2)
This work (JMC)	28.2596(6)	24.8954(4)	25.4791(6)	18.8887(3)	2.3288(1)	0.0946(2)	0.0539(2)

Table 7
Atomic weight values of dysprosium by various authors (uncertainty: ±2σ)

Year	Atomic weight	Author	Method	References
1949	162.499(3)	Inghram et al.	TIMS	[9]
1950	162.50(1)	Leland	TIMS	[10]
1957	162.495(4)	Collins et al.	TIMS	[11]
1966	162.492(7)	Komori et al.	TIMS	[12]
1981	162.498(2)	Hollinger and Devillers	TIMS	[13]
1996	162.500(2)	Chang and Gao[a]	TIMS	[14]
2001	162.4995(17)	Chang et al.[b]	TIMS	[2]
2001	162.4995(8)[c]	Chang et al.	TIMS	[2]
2002	162.4997(1)[c]	This work[d]	MC-ICP-MS	

[a] $(^{151}\text{Eu}/^{153}\text{Eu}) = 0.9957(17)$ was used for bias correction.
[b] The mass spectrometer was calibrated with highly enriched ^{162}Dy and ^{164}Dy isotopes.
[c] Analytical measurement uncertainty (±2σ) only.
[d] $(^{161}\text{Dy}/^{163}\text{Dy}) = 0.75872$ was used for fractionation correction [2].

3.3. *Atomic weight of dysprosium*

Several isotope ratio measurements of dysprosium were reported in literature [2,9–14]. From Table 5 and the above mentioned discussion, it may be assumed that the JMC sample has the closest isotopic composition to the true value, thus we used the results given in Table 3 for the isotope abundance and atomic weight calculations. The calculated isotope abundance from the present work compared to Chang et al. [2] is shown in Table 6 and a summary of atomic weights of Dy is given in Table 7. It should be noted that our uncertainties in Table 6 represent only the MC-ICP-MS measurement precision, whereas the TIMS data shown for comparison represent the overall limit of error. The mass spectrometric measurement uncertainty in the TIMS study accounts for about half of the reported overall limit of error.

4. Conclusions

In this work we present the first published dysprosium isotope ratio measurements using the MC-ICP-MS technique. The data are in very good agreement with recently published TIMS study, revealing an at least one order of magnitude better measurement precision. Further advantages of the MC-ICP-MS technique are time saving and simplicity of sample preparation and shorter data acquisition periods. Five samples were studied by Chang et al. [2] and four in this work, all of commercial origin. One of them in each study was from the same manufacturer, (Aldrich). No natural isotopic variations could be detected in these samples. We attributed the increase in the isotope ratios of minor dysprosium isotopes in the Aldrich sample to the presence of trace gadolinium isobaric interferences. The data agreement between the JMC and Merck samples is very good. We recommend considering one of these materials as a candidate for isotopic reference material, preferably the JMC, because of its slightly higher purity.

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