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Absolute measurements of neodymium isotopic abundances and atomic weight by MC-ICPMS

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Abstract

Gravimetric synthetic mixtures prepared from highly enriched isotopes of neodymium in the form of oxides of well-defined purity were used to calibrate a multicollector inductively coupled plasma mass spectrometry (MC-ICPMS). Measurements on natural neodymium samples yielded an absolute isotopic composition 27.147(20) at.% ^{142}Nd, 12.182(21) at.% ^{143}Nd, 23.803(14) at.% ^{144}Nd, 8.297(6) at.% ^{145}Nd, 17.190(13) at.% ^{146}Nd, 5.755(8) at.% ^{148}Nd, 5.626(10) at.% ^{150}Nd, and the atomic weight of neodymium as 144.2409(17) both with an uncertainty given on the basis of 95% confidence limit. No isotopic fractionation was found in terrestrial neodymium materials. Thermal ionization mass spectrometry (TIMS) analyses were carried on the same samples measured by MC-ICPMS and the essentially identical results were obtained, both for the abundances and the atomic weights.

Keywords: Neodymium; Isotopic abundance; Atomic weight; MC-ICPMS

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1. Introduction

The current atomic weight of neodymium A_r(Nd) = 144.24 was recommended in 1962. In the report, CAWIA recommended A_r(Nd) = 144.24 based on the average of the isotopic abundance measurements by Inghram et al. [1] and Walker and Thode [2] with atomic masses by Everling et al. [3]. In 1969, CAWIA evaluated the uncertainty $U[A_r$(Nd)] to be 0.03.

Atomic weights of many elements have been determined by calibrated thermal ionization mass spectrometry (TIMS) such as Dy [4] and Sm [5]. Multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) is a new type mass spectrometry for isotopic measurement. Its precision can be comparative to TIMS, but the observed values must be corrected for accurate measurement. Optimum concentration of the sample, torch position, nebulizer gas flow rate, collision gas flow rate and ion lens system were researched. The present investigation aims at obtaining a new value for A_r(Nd) by means of calibrated MC-ICPMS measurement using highly enriched isotopes, ^{142}Nd and ^{144}Nd. As neodymium is a hepta-isotopic element, it is necessary to measure the six isotopic ratios. Calibration with a pair of major isotopes will yield one correction factor, namely $K_{144/142}$. The other five correction factors can be derived through the exponential rule.

2. Experimental

2.1. Instrumentation

All measurements of the isotopic abundance ratios were performed using the GV Micromass IsoProbe single focussing MC-ICPMS. The instrument was operated in an air temperature (20 ± 2 °C) stabilised clean (class 1000) laboratory. Before the measurements were started, the instrument was stabilised for 2 h under normal working conditions until the temperature sensor within the mass spectrometer indicated constant values of ±2 K. The air temperature in the room was monitored during the measurements to detect any

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Table 1
Analytically relevant operating parameters of GV Micromass IsoProbe MC-ICPMS

Parameter	Value
RF power (W)	1350
Accelerating voltage (V)	6000
Plasma Ar gas flow (L min^{-1})	13.5
Auxiliary Ar gas flow (L min^{-1})	1.05
Nebulizer Ar gas flow (L min^{-1})	1.085
Sampling cone material	Ni
Mass resolving power (10% valley), $m/\Delta m$	450
Nebulizer type	Ar
Typical sample uptake rate (μL min^{-1})	200
Air temperature in clean hood for instrument (°C)	20 ± 2

unacceptable deviation from the target value of $20 \pm 2\,°C$. The lower temperature allows slightly better vacuum conditions in the detector and therefore improves sensitivity of the detection. MC-ICPMS operating conditions are presented in Table 1.

The $Nd(NO_3)_3$ solutions were taken up by free aspiration using a Meinhard nebulizer. The solutions uptake rate of the nebulizer was about 100 μL min^{-1}. A gain calibration of the multicollector system was performed before measuring Nd isotope abundance ratios. During measurements 5% HNO_3 solution was used to wash sampling system for 5 min every time. And memory effect was not found because the samples were purified and the concentration of samples is only 100 ng g^{-1}.

Isotope abundance ratios of the neodymium were determined in the following sequence: natural neodymium samples; mixture samples; enriched ^{142}Nd; enriched ^{144}Nd. Between each measurement of different abundance ratios the wash sequence with 5% HNO_3 solution lasted for 5 min.

All measurements were performed under the same conditions, especially the torch assembly position; the solutions uptake rate of the nebulizer; flow rate of nebulizer gas and collision gas; Faraday cup position and a gain calibration of the multicollector system.

2.2. Preparation of standard solutions of two enriched isotopes

Isotopic materials of $^{142}Nd_2O_3$ (sample A) and $^{144}Nd_2O_3$ (sample B) were supplied by the Isotec Inc. (A. Matheson). They were labelled as 98.5 at.% ^{142}Nd and 97.5 at.% ^{144}Nd, respectively.

Isobaric impurities must be removed before measurement because they will interfere with the accuracy of results. Separation process with P507 (mono-2-ethylhexyl-2-ethylhexphosphonate) extraction resin of 200–300 mesh was used to remove rare earth element impurities in neodymium. In order to remove the possible presence of anionic impurities and to decrease cationic impurities, each sample was treated with oxalic acid after separation. The precipitated neodymium oxalate hydrate after filtration, washing and drying was ignited at 850 °C in a muffle furnace, to whose base a current of dry 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, which were analyzed for most impurities using ICPMS.

Table 2
Primary solutions A and B

Sample	A	B
Compound	$^{142}Nd_2O_3$	$^{144}Nd_2O_3$
Purity (%)	99.99	99.99
Weight (g)	0.11777	0.12149
Net weight (g)	0.11776	0.12148
Weight of solution (g)	20.03786	20.52082

Results showed that total content of rare earth element impurities was less than 20 μg g^{-1}, and other impurities were found below the detection limit. Those below 2 μg g^{-1} were: Zn, Th, U, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Rb, Sr, Zr, Nb, In, Sn, Ba, Al, Ca, Mg, K and Na. After an allowance of 100 μg g^{-1} Nd was made for undetected impurities, the chemical purity of samples A and B were assessed as 99.99(2) and 99.99(2)%, respectively.

About 120 mg each of samples of A and B was accurately weighed and dissolved in 0.5 mol L^{-1} HNO_3. Careful manipulation and weighing technique including double weighing and correction for air buoyancy were carried out. Results are shown in Table 2.

2.3. Preparation of mixed solutions AB and the correction factor

For each loading, 30 ratios were recorded with automatic reduction of the background and blank. Measurement was repeated as three replicates for each sample. In the case of samples A and B, results are shown in Table 3.

From these data, the isotopic composition of samples A and B could be readily obtained as shown in Table 4. The

Table 3
Measured isotopic ratios of samples A and B, each three replicates (1s)

Sample	A	B
^{142}Nd/^{144}Nd	168.698(10)	0.006085(5)
^{143}Nd/^{144}Nd	1.2381(2)	0.005669(3)
^{145}Nd/^{144}Nd	0.2072(1)	0.007142(1)
^{146}Nd/^{144}Nd	0.4091(2)	0.006777(3)
^{148}Nd/^{144}Nd	0.00816(1)	0.000948(1)
^{150}Nd/^{144}Nd	0.00699(2)	0.000598(1)

Table 4
Isotopic composition of samples A and B (at.%)

Isotope	A	B
^{142}Nd	0.98246	0.00584
^{143}Nd	0.00716	0.00547
^{144}Nd	0.00582	0.97334
^{145}Nd	0.00122	0.00705
^{146}Nd	0.00241	0.00673
^{148}Nd	0.00050	0.00096
^{150}Nd	0.00042	0.00062

Table 5
Isotopic composition of primary solutions A and B

Sample	A	B
Atomic weight	141.946244	143.921012
$NdO_{1.5}$, molecular weight	165.945344	167.920112
Total micromole Nd	709.6283	723.4419
Micromole ($^{142}Nd + {}^{144}Nd$)	701.3175	708.3799
Micromole ($^{142}Nd + {}^{144}Nd$)/g solution	34.9996 (C_A)	34.5201 (C_B)

^{142}Nd/^{144}Nd ratios in samples A and B are as follows:

$$R_{A(142/144)} = 168.698, \qquad R_{B(142/144)} = 0.005998$$

Then, the isotopic composition of ^{142}Nd and ^{142}Nd in primary solutions A and B can be calculated as shown in Table 5, where the data of the atomic mass of neodymium nuclides were used to calculate the mean atomic weight.

2.4. *Mixed solutions AB and the correction factor $K_{142/144}$*

Portions of the primary solutions A and B were accurately weighed and thoroughly mixed to form a series of seven mixed solutions AB. The respective weights W_A and W_B are shown in columns 2 and 3 of Table 6.

Then, the isotopic ratio $R_{142/144}$ of each mix was measured. Results are shown in column 4 of Table 6.

By applying the following formula (1):

$$K = \frac{W_A C_A (R_{AB} - R_A) - W_B C_B (R_B - R_{AB})}{W_B C_B R_A (R_B - R_{AB}) - W_A C_A R_B (R_{AB} - R_A)} \qquad (1)$$

where W_A, W_B and R_{AB} are given in Table 6 for each mix, R_{AB} is the isotopic ratio $R_{142/144}$ of each mixture, whereas R_A and R_B being calculated from Table 3 as shown above, and C_A and C_B given in Table 5 are all constants for each mix, we could calculate a series of nine values of $K_{142/144}$ with the mean 1.01192(58, 1s).

Since the values of C_A and C_B were calculated from R_A and R_B, the latter, if replaced by KR_A and KR_B, would cause C_A and C_B to have new values. So, a new iterative $K_{142/144}$ was obtained as 1.01225. The other K's could be calculated from $K_{142/144}$ by mass fractionation factor per unit β shown in formula (2). All the K's are shown in Table 7.

$$\beta = \frac{\ln K}{\ln(M_2/M_1)} \qquad (2)$$

Table 7
Final results of β and K's after iterative calculation

β	−0.86865
$K_{142/144}$	1.01225
$K_{143/144}$	1.00608
$K_{145/144}$	0.99399
$K_{146/144}$	0.98806
$K_{148/144}$	0.97643
$K_{150/144}$	0.96508

2.5. *Terrestrial samples of neodymium*

Seven samples of neodymium were collected from China, USA and UK, respectively. They are: (1) 99.99% Nd_2O_3, Aldrich, USA; (2) 99.99% Nd_2O_3 prepared by Changchun Institute of Applied Chemistry, Chinese Academy of Sciences; (3) rare earth adsorption kaolinite, Jiangxi, China; (4) 99.99% Nd_2O_3 prepared by General Research Institute for Nonferrous Metals, China; (5) 99.99% Nd_2O_3, Shanghai Chemical Reagents Corp., China; (6) Bastnaesite, 99.99% Nd_2O_3, prepared by Baotou Rare Earth Research Institute, China; (7) 99.99% Nd_2O_3, Shin-Etsu Chemical Co., Japan. Each sample was dissolved in 0.5 mol L^{-1} HNO_3 to form the loading solution. The measured isotopic ratios for each sample are shown in Table 8.

3. Results and discussion

3.1. *Absolute isotope abundances and atomic weight for neodymium*

The absolute isotopic abundances were calculated from the observed values of isotopic abundances ratios, which are listed in Table 10. According to formula (1), the relative atomic weights of neodymium isotopes, as well as the atomic weight of the neodymium were calculated. The mean absolute isotopic composition of neodymium (2s) is as follows:

27.147(20) at.% ^{142}Nd;
12.182(21) at.% ^{143}Nd;

Table 6
Measured $R_{142/144}$ of mixed solutions (three replicates) and the correction factor $K_{142/144}$ (1s)

Mixed solution number	Weight of solution A, W_A (mg)	Weight of solution B, W_B (mg)	$R_{142/144}$	$K_{142/144}$
1	1.11934	0.87989	1.27242(3)	1.01099
2	1.08570	0.90520	1.19993(2)	1.01150
3	1.07245	0.92978	1.15462(1)	1.01139
4	1.05767	0.93337	1.13341(2)	1.01245
5	1.04933	0.93732	1.11992(3)	1.01243
6	1.03564	0.96667	1.07266(3)	1.01208
7	1.00275	1.00346	1.00084(2)	1.01261
Mean				1.01192(58)

Table 8
Measured isotopic ratios of neodymium in natural samples (three replicates, 1s)

	Sample					
	^{142}Nd/^{144}Nd	^{143}Nd/^{144}Nd	^{145}Nd/^{144}Nd	^{146}Nd/^{144}Nd	^{148}Nd/^{144}Nd	^{150}Nd/^{144}Nd
1	1.12626(22)	0.50829(8)	0.35079(2)	0.73117(11)	0.24782(6)	0.24516(9)
2	1.12657(13)	0.50833(3)	0.35069(4)	0.73103(5)	0.24765(6)	0.24503(7)
3	1.12685(23)	0.50909(6)	0.35064(3)	0.73077(15)	0.24755(10)	0.24482(16)
4	1.12694(26)	0.50896(6)	0.35062(5)	0.73073(18)	0.24743(11)	0.24469(18)
5	1.12642(57)	0.50888(11)	0.35071(8)	0.73105(36)	0.24769(24)	0.24504(36)
6	1.12668(52)	0.50817(11)	0.35068(7)	0.73091(35)	0.24759(21)	0.24492(33)
7	1.12712(36)	0.50901(7)	0.35060(5)	0.73066(24)	0.24741(16)	0.24465(21)
Mean	1.12669(30)	0.50868(39)	0.35068(6)	0.73090(19)	0.24759(15)	0.24490(19)
Corrected	1.14049	0.51177	0.34857	0.72218	0.24176	0.23635

Table 9
Measured isotopic ratios of neodymium in natural samples by TIMS (three replicates, 1s)

	Sample					
	^{142}Nd/^{144}Nd	^{143}Nd/^{144}Nd	^{145}Nd/^{144}Nd	^{146}Nd/^{144}Nd	^{148}Nd/^{144}Nd	^{150}Nd/^{144}Nd
1	1.14562(22)	0.51244(18)	0.34783(8)	0.71950(21)	0.23996(13)	0.23410(19)
2	1.14517(24)	0.51238(17)	0.34791(9)	0.71984(15)	0.24018(10)	0.23443(14)
3	1.14550(34)	0.51307(22)	0.34781(16)	0.71947(32)	0.23997(15)	0.23417(21)
4	1.14562(25)	0.51244(20)	0.34783(12)	0.71950(22)	0.23996(11)	0.23410(15)
5	1.14548(32)	0.51239(16)	0.34785(12)	0.71961(25)	0.24004(10)	0.23420(16)
6	1.14502(28)	0.51195(18)	0.34757(15)	0.71899(35)	0.23982(12)	0.23405(19)
7	1.14502(36)	0.51291(24)	0.34793(18)	0.71993(42)	0.24025(16)	0.23452(22)
Mean	1.14535(27)	0.51251(37)	0.34782(12)	0.71955(31)	0.24003(15)	0.23422(18)
K	0.99621	0.99811	1.00190	1.00380	1.00762	1.01146
Corrected	1.14101	0.51154	0.34848	0.72228	0.24186	0.23691

23.803(14) at.% ^{144}Nd;
8.297(6) at.% ^{145}Nd;
17.190(13) at.% ^{146}Nd;
5.755(8) at.% ^{148}Nd;
5.626(10) at.% ^{150}Nd.

The mean atomic weight can be calculated by formula (3).

$$A_{\mathrm{E}} = \frac{M_{142}K_{142/144}R_{142/144} + M_{143}K_{143/144}R_{143/144} + \cdots + M_{150}K_{150/144}R_{150/144} + M_{144}}{K_{142/144}R_{142/144} + K_{143/144}R_{143/144} + \cdots + K_{150/144}R_{150/144} + 1} \tag{3}$$

where M are the atomic masses of seven neodymium isotopes, K the correction factors and R are the isotopic ratios, respectively.

We also measured the relative atomic weight of neodymium by traditional absolute TIMS method. The measured isotopic ratios for each sample and correction factors are shown in Table 9.

A comparison of the results of the two methods, listed in Table 10, showed that they agreed in absolute isotopic abundances and atomic weight of neodymium within experimental uncertainties. This agreement shows that MC-ICPMS is available to complete the determination of atomic weight.

Table 10
The atomic mass, absolute isotope abundances and atomic weight of the neodymium

Isotopes	Atomic mass [6]	Isotopic abundances (at.%)		Relative atomic weight	
		MS-ICPMS	TIMS	MS-ICPMS	TIMS
^{142}Nd	141.907719	27.147(20)	27.153(19)	38.524	38.533
^{143}Nd	142.90981	12.182(21)	12.173(18)	17.409	17.397
^{144}Nd	143.910083	23.803(14)	23.798(12)	34.255	34.247
^{145}Nd	144.912569	8.297(6)	8.293(7)	12.023	12.018
^{146}Nd	145.913113	17.190(13)	17.189(17)	25.083	25.081
^{148}Nd	147.916889	5.755(8)	5.756(8)	8.512	8.514
^{150}Nd	149.920887	5.626(10)	5.638(9)	8.434	8.452
Relative atomic weight of the neodymium				144.2409	144.2415

Table 11
Results of uncertainty of correction factor $K_{142/144}$ (mixed solution 1)

Mixed solution 1	Propagation factors	Error value
W_A	0.9142	0.00001
W_B	1.1629	0.00001
C_A	0.0292	0.003
C_B	0.0296	0.003
R_A	0.00009	0.01
R_B	0.2301	0.000005
R_{AB}	0.8144	0.0003
$U(K_{142/144})$	0.00025	

Table 12
Uncertainties of correction factor K and absolute isotopic composition

$U(K_{142/144})$	0.00063	U_{142}	0.00010
$U(K_{143/144})$	0.00031	U_{143}	0.00010
$U(K_{145/144})$	0.00031	U_{144}	0.00006
$U(K_{146/144})$	0.00060	U_{145}	0.00003
$U(K_{148/144})$	0.0012	U_{146}	0.00007
$U(K_{150/144})$	0.0018	U_{148}	0.00004
		U_{150}	0.00005

It has advantages of simple pre-treatment, small sampling and rapid measurement. The research work provides a new optional method for value of isotope certified reference materials.

3.2. Discussion of uncertainty

The final uncertainty analysis for the absolute isotopic composition and atomic weight of neodymium was carried out by calculating uncertainty of correction factor K. Through differential of W_A, W_B, R_{AB}, R_A, R_B, C_A and C_B from formula (1) to gain their propagation factors, the uncertainty of nine correction factors $K_{142/144}$ could be calculated. The results are shown in Table 11, where only the data of mixed solution 1 were listed for convenience. According similar method and formula (2), other correction factors $K_{143/144}$, $K_{145/144}$, $K_{146/144}$, $K_{148/144}$ and $K_{150/144}$ were calculated. Then, the uncertainties of absolute isotopic composition of neodymium could be gained, which are shown in Table 12.

Because the uncertainties of atomic masses of neodymium isotopes are all less than 10^{-7}, they can be ignored in the estimation of atomic weight uncertainty. According to formula (3), we calculated the uncertainty of relative atomic weight of neodymium by similar method as uncertainty of correction factor $K_{142/144}$. The final expanded uncertainty of neodymium atomic weight is 0.0017 (coverage factor = 2).

Through comparison of the known values of the atomic weight of neodymium, the value of this work is superior to earlier work. The atomic weight of Nd determined in this study is 144.2409(17) as compared to the presently accepted value of 144.24(3) [6].

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