

Interference Corrections in Isotope Ratio Measurements Using MC-ICP-MS: Examples for Nd-Sm

Key Words

- NEPTUNE
- Interference Correction
- Multicollector ICP-MS
- Neodymium
- Samarium

Introduction

Isobaric interferences are one of the major limitations on the accuracy of isotope ratio measurements made by MC-ICP-MS, and thus, accurate interference corrections are required to achieve precise and accurate isotope ratio measurements. One of the main difficulties in performing interference corrections is how to accurately and precisely assess the mass bias of the interfering isotope(s). We describe and compare the results from three strategies for performing interference corrections, using Nd-Sm data measured on the Thermo Scientific NEPTUNE MC-ICP-MS.

Strategies for Interference Corrections

Neodymium suffers from isobaric interferences from samarium on masses 144, 148 and 150. If the Sm isotope composition of the sample is known, the measurement of the abundance of one interference-free Sm isotope, i.e., ^{147}Sm or ^{149}Sm , allows the calculation of the abundances of the other (interfering) Sm isotopes, i.e., ^{144}Sm , ^{148}Sm and ^{150}Sm . Normally, the IUPAC (International Union of Pure and Applied Chemistry) tabulation of the natural abundances of the isotopes serves as the basis for performing these calculations for interference corrections. If the magnitudes of the interfering isotopes are significant, it becomes necessary to take mass bias into account in order to make an accurate calculation of the abundances of the interfering isotopes. Sm has two isotopes that are interference-free (^{147}Sm and ^{149}Sm). By comparing the measured $^{147}\text{Sm}/^{149}\text{Sm}$ ratio with the true $^{147}\text{Sm}/^{149}\text{Sm}$ ratio, it is possible to assess the mass bias for Sm. This calculated mass bias factor allows to perform an accurate correction for the interferences of Sm isotopes on Nd. For isotopic systems with just one isotope available for the interference correction, mass bias can be estimated from the isotopes being measured (^{85}Rb in case of Sr).

Here, we consider three cases of interference corrections for Sm:

Method 1: Interference correction without considering mass bias for Sm

The abundances of ^{144}Sm , ^{148}Sm and ^{150}Sm are calculated from the measured intensity of ^{147}Sm and the Sm isotopic abundance data from IUPAC.

Method 2: Interference correction including a mass bias factor for Sm which is based on the measurement of $^{147}\text{Sm}/^{149}\text{Sm}$

The change in relative abundances of Sm isotopes due to mass bias is corrected using the mass bias factor for Sm based on the measured $^{147}\text{Sm}/^{149}\text{Sm}$ isotope ratio. The abundances of ^{144}Sm , ^{148}Sm and ^{150}Sm are calculated using the measured intensity of ^{147}Sm and the corrected (mass-bias induced) abundance ratios for Sm.

Method 3: Interference correction considering a mass bias factor for Nd which is based on the measurement of $^{146}\text{Nd}/^{144}\text{Nd}$

The change in relative abundances of Sm isotopes due to mass bias is corrected using the mass bias factor for Sm based on the measured $^{146}\text{Nd}/^{144}\text{Nd}$ isotope ratio. The abundances of ^{144}Sm , ^{148}Sm and ^{150}Sm are calculated using the measured intensity of ^{147}Sm and the corrected (mass-bias induced) abundances for Sm. This must be done iteratively, because the normalizing ratio ($^{146}\text{Nd}/^{144}\text{Nd}$) also suffers from Sm interference. The initial stage of the correction follows the same procedure described in Method 1, thus without considering mass bias. Based on this interference correction a first estimation of the Nd mass bias is calculated (step 1). This initial estimation of the instrumental mass bias is then taken to calculate the abundances of ^{144}Sm , ^{148}Sm and ^{150}Sm . Based on this second interference correction, the Nd mass bias is calculated again (step 2). These steps are repeated several times until the mass bias correction algorithm converges to a constant Nd mass bias value (compare the values for $^{146}\text{Nd}/^{144}\text{Nd}$ in every step in the example given below).

All three types of interference corrections can be performed on-line using the multicollector software that is standard with the NEPTUNE MC-ICP-MS. Here we demonstrate the calculation of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio. This ratio is corrected for the interference of ^{144}Sm according to the three methods described above. The final ratio is then corrected for mass fractionation using $^{146}\text{Nd}/^{144}\text{Nd}$. These measurements were done on a solution of 200 ppb Nd doped with 10 ppb Sm (both from Merck).

Screenshots of the Method Editor program from the multicollector software are included illustrating how these on-line calculations are handled.

Mass bias correction

The normalizations are performed according to the exponential law, where X and R are the isotopic ratios of masses m1/m2 and m3/m4, respectively. M refers to the measured isotope ratio, T refers to the true (unfractionated) isotope ratio, and a = ln[mass3/mass4]/ln[mass1/mass2].

$$\frac{X_M}{X_T} = \left[\frac{R_M}{R_T} \right]^a$$

Method 1: Interference correction without considering mass bias for Sm

Variables	Description	Value
abu144	abundance ¹⁴⁴ Sm in % (IUPAC)	3.1
abu147	abundance ¹⁴⁷ Sm in % (IUPAC)	15
¹⁴⁷ Sm/ ¹⁴⁴ Sm	abu147/abu144	4.83871
m1	mass ¹⁴⁶ Nd	145.91311
m2	mass ¹⁴⁴ Nd	143.91008
m3	mass ¹⁴³ Nd	142.90981
m4	mass ¹⁴⁴ Nd	143.91008
R _T	true ratio ¹⁴⁶ Nd/ ¹⁴⁴ Nd	0.7219
R _M	measured ratio ¹⁴⁶ Nd/ ¹⁴⁴ Nd	
X _T	true ratio ¹⁴³ Nd/ ¹⁴⁴ Nd	
X _M	measured ratio ¹⁴³ Nd/ ¹⁴⁴ Nd	
a	ln[m3/m4]/ln[m1/m2]	-0.504603
Measured Data		
¹⁴³ Nd _M	measured intensity ¹⁴³ Nd (V)	0.9592
¹⁴⁴ (Nd+Sm) _M	measured intensity ¹⁴⁴ (Nd+Sm) (V)	1.919
¹⁴⁶ Nd _M	measured intensity ¹⁴⁶ Nd (V)	1.412
¹⁴⁷ Sm _M	measured intensity ¹⁴⁷ Sm (V)	0.09056
Calculation of ¹⁴⁴ Nd corrected for interference of ¹⁴⁴ Sm		
¹⁴⁴ Sm	¹⁴⁷ Sm _M /(¹⁴⁷ Sm/ ¹⁴⁴ Sm)	0.01872
¹⁴⁴ Nd	¹⁴⁴ (Nd + Sm) _M - ¹⁴⁴ Sm	1.900
Calculation of ¹⁴³ Nd/ ¹⁴⁴ Nd corrected for mass fractionation		
R _M	¹⁴⁶ Nd _M / ¹⁴⁴ Nd	0.742807
X _T	X _M /[(R _M /R _T) ^a]	0.512046

Table 1: Step-by-step calculation of the true ¹⁴³Nd/¹⁴⁴Nd ratio for method 1

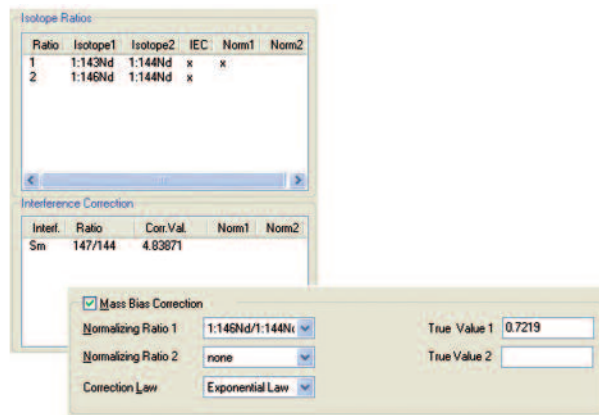


Figure 1: Screenshot of the Method Editor (evaluation pane) for method 1. ¹⁴³Nd/¹⁴⁴Nd is interference corrected (IEC) using the ¹⁴⁷Sm/¹⁴⁴Sm ratio from IUPAC without considering mass bias for Sm. The ¹⁴³Nd/¹⁴⁴Nd ratio is then corrected for mass fractionation using Normalizing Ratio 1 (¹⁴⁶Nd/¹⁴⁴Nd = 0.7219).

Method 2: Interference correction including a mass bias factor for Sm based on the measurement of ¹⁴⁷Sm/¹⁴⁹Sm

Variables	Description	Value
m1	mass ¹⁴⁶ Nd	145.91311
m2	mass ¹⁴⁴ Nd	143.91008
m3	mass ¹⁴³ Nd	142.90981
m4	mass ¹⁴⁴ Nd	143.91008
R _T	true ratio ¹⁴⁶ Nd/ ¹⁴⁴ Nd	0.7219
R _M	measured ratio ¹⁴⁶ Nd/ ¹⁴⁴ Nd	
X _T	true ratio ¹⁴³ Nd/ ¹⁴⁴ Nd	
X _M	measured ratio ¹⁴³ Nd/ ¹⁴⁴ Nd	
a2	ln[m3/m4]/ln[m1/m2]	-0.504603
m5	mass ¹⁴⁷ Sm	146.91489
m6	mass ¹⁴⁹ Sm	148.91718
m7	mass ¹⁴⁷ Sm	146.91489
m8	mass ¹⁴⁴ Sm	143.91199
R Sm _T	true ratio ¹⁴⁷ Sm/ ¹⁴⁹ Sm	1.08507
R Sm _M	measured ratio ¹⁴⁷ Sm/ ¹⁴⁹ Sm	
Y _T	true ratio ¹⁴⁷ Sm/ ¹⁴⁴ Sm	4.87710
Y _M	measured ratio ¹⁴⁷ Sm/ ¹⁴⁴ Sm	
a1	ln[m7/m8]/ln[m5/m6]	-1.52558
Measured Data		
¹⁴³ Nd _M	measured intensity ¹⁴³ Nd (V)	0.9592
¹⁴⁴ (Nd+Sm) _M	measured intensity ¹⁴⁴ (Nd+Sm) (V)	1.919
¹⁴⁶ Nd _M	measured intensity ¹⁴⁶ Nd (V)	1.412
¹⁴⁷ Sm _M	measured intensity ¹⁴⁷ Sm (V)	0.09056
¹⁴⁹ Sm _M	measured intensity ¹⁴⁹ Sm (V)	0.08541
Calculation of ¹⁴⁴ Nd corrected for Sm interference including a mass bias factor from Sm		
R Sm _M	¹⁴⁷ Sm _M / ¹⁴⁹ Sm _M	1.06040
Y _M	Y _T *[(R Sm _M /R Sm _T) ^{a1}]	5.05125
¹⁴⁴ Sm	¹⁴⁷ Sm _M /(¹⁴⁷ Sm/ ¹⁴⁴ Sm)	0.01793
¹⁴⁴ Nd	¹⁴⁴ (Nd+Sm) _M - ¹⁴⁴ Sm	1.901
Calculation of ¹⁴³ Nd/ ¹⁴⁴ Nd corrected for mass fractionation		
R _M	¹⁴⁶ Nd _M / ¹⁴⁴ Nd	0.742499
X _T	X _M /[(R _M /R _T) ^{a2}]	0.511727

Table 2: Step-by-step calculation of the true ¹⁴³Nd/¹⁴⁴Nd ratio for method 2

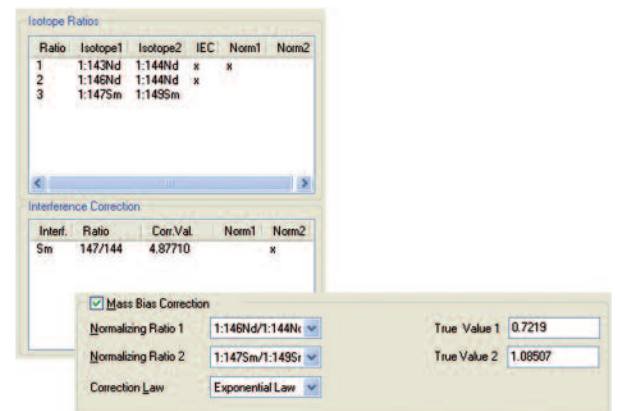


Figure 2: Screenshot of the Method Editor (evaluation pane) for method 2. ¹⁴³Nd/¹⁴⁴Nd is interference corrected (IEC) using the ¹⁴⁷Sm/¹⁴⁴Sm ratio corrected for mass bias using Normalizing Ratio 2 (¹⁴⁷Sm/¹⁴⁹Sm = true ratio). The ¹⁴³Nd/¹⁴⁴Nd ratio is then corrected for mass fractionation using Normalizing Ratio 1 (¹⁴⁶Nd/¹⁴⁴Nd = 0.7219).

Method 3: Interference correction including a mass bias factor for Sm based on the measurement of $^{146}\text{Nd}/^{144}\text{Nd}$

Variables	Description	Value
m1	mass ^{146}Nd	145.91311
m2	mass ^{144}Nd	143.91008
m3	mass ^{143}Nd	142.90981
m4	mass ^{144}Nd	143.91008
R_T	true ratio $^{146}\text{Nd}/^{144}\text{Nd}$	0.7219
R_M	measured ratio $^{146}\text{Nd}/^{144}\text{Nd}$	
X_T	true ratio $^{143}\text{Nd}/^{144}\text{Nd}$	
X_M	measured ratio $^{143}\text{Nd}/^{144}\text{Nd}$	
a2	$\ln(m3/m4)/\ln(m1/m2)$	-0.504603
m5	mass ^{147}Sm	146.91489
m6	mass ^{144}Sm	143.91199
Y_T	true ratio $^{147}\text{Sm}/^{144}\text{Sm}$	4.87710
a1	$\ln(m5/m6)/\ln(m1/m2)$	1.49403

Measured Data		
$^{143}\text{Nd}_M$	measured intensity ^{143}Nd (V)	0.9592
$^{144}(\text{Nd}+\text{Sm})_M$	measured intensity $^{144}(\text{Nd}+\text{Sm})$ (V)	1.919
$^{146}\text{Nd}_M$	measured intensity ^{146}Nd (V)	1.412
$^{147}\text{Sm}_M$	measured intensity ^{147}Sm (V)	0.09056

Calculation of ^{144}Nd corrected for Sm interference including a mass bias factor from Nd

^{144}Sm	$^{147}\text{Sm}_M/Y_T$	0.018569
^{144}Nd	$^{144}(\text{Nd}+\text{Sm})_M - ^{144}\text{Sm}$	1.90059
R_M	$^{146}\text{Nd}_M/^{144}\text{Nd}$	0.742749

STEP 1

$^{147}\text{Sm}/^{144}\text{Sm}_{\text{step1}}$	$Y_T * (R_M/R_T)^{a1}$	5.089032
$^{144}\text{Sm}_1$	$^{147}\text{Sm}_M / (^{147}\text{Sm}/^{144}\text{Sm}_{\text{step1}})$	0.0177959
$^{144}\text{Nd}_1$	$^{144}(\text{Nd}+\text{Sm})_M - ^{144}\text{Sm}_1$	1.901358
$^{146}\text{Nd}/^{144}\text{Nd}_{\text{step1}}$	$^{146}\text{Nd}_M / ^{144}\text{Nd}_1$	0.742447

STEP 2

$^{147}\text{Sm}/^{144}\text{Sm}_{\text{step2}}$	$Y_T * (^{146}\text{Nd}/^{144}\text{Nd}_{\text{step1}}/R_T)^{a1}$	5.085940
$^{144}\text{Sm}_2$	$^{147}\text{Sm}_M / (^{147}\text{Sm}/^{144}\text{Sm}_{\text{step2}})$	0.0178068
$^{144}\text{Nd}_2$	$^{144}(\text{Nd}+\text{Sm})_M - ^{144}\text{Sm}_2$	1.901348
$^{146}\text{Nd}/^{144}\text{Nd}_{\text{step2}}$	$^{146}\text{Nd}_M / ^{144}\text{Nd}_2$	0.742451

STEP 3

$^{147}\text{Sm}/^{144}\text{Sm}_{\text{step3}}$	$Y_T * (^{146}\text{Nd}/^{144}\text{Nd}_{\text{step2}}/R_T)^{a1}$	5.085983
$^{144}\text{Sm}_3$	$^{147}\text{Sm}_M / (^{147}\text{Sm}/^{144}\text{Sm}_{\text{step3}})$	0.0178066
$^{144}\text{Nd}_3$	$^{144}(\text{Nd}+\text{Sm})_M - ^{144}\text{Sm}_3$	1.901348
$^{146}\text{Nd}/^{144}\text{Nd}_{\text{step3}}$	$^{146}\text{Nd}_M / ^{144}\text{Nd}_3$	0.742451

STEP 4

$^{147}\text{Sm}/^{144}\text{Sm}_{\text{step4}}$	$Y_T * (^{146}\text{Nd}/^{144}\text{Nd}_{\text{step3}}/R_T)^{a1}$	5.085982
$^{144}\text{Sm}_4$	$^{147}\text{Sm}_M / (^{147}\text{Sm}/^{144}\text{Sm}_{\text{step4}})$	0.0178066
$^{144}\text{Nd}_4$	$^{144}(\text{Nd}+\text{Sm})_M - ^{144}\text{Sm}_4$	1.901348
$^{146}\text{Nd}/^{144}\text{Nd}_{\text{step4}}$	$^{146}\text{Nd}_M / ^{144}\text{Nd}_4$	0.742451

STEP 5

$^{147}\text{Sm}/^{144}\text{Sm}_{\text{step5}}$	$Y_T * (^{146}\text{Nd}/^{144}\text{Nd}_{\text{step4}}/R_T)^{a1}$	5.085982
$^{144}\text{Sm}_5$	$^{147}\text{Sm}_M / (^{147}\text{Sm}/^{144}\text{Sm}_{\text{step5}})$	0.0178066
$^{144}\text{Nd}_5$	$^{144}(\text{Nd}+\text{Sm})_M - ^{144}\text{Sm}_5$	1.901348
$^{146}\text{Nd}/^{144}\text{Nd}_{\text{step5}}$	$^{146}\text{Nd}_M / ^{144}\text{Nd}_5$	0.742451

Calculation of $^{143}\text{Nd}/^{144}\text{Nd}$ corrected for mass fractionation

X_T	$X_M * [(^{146}\text{Nd}/^{144}\text{Nd}_{\text{step5}}/R_T)^{a2}]$	0.511677
-------	---	----------

Table 3: Step-by-step calculation of the true $^{143}\text{Nd}/^{144}\text{Nd}$ ratio for method 3

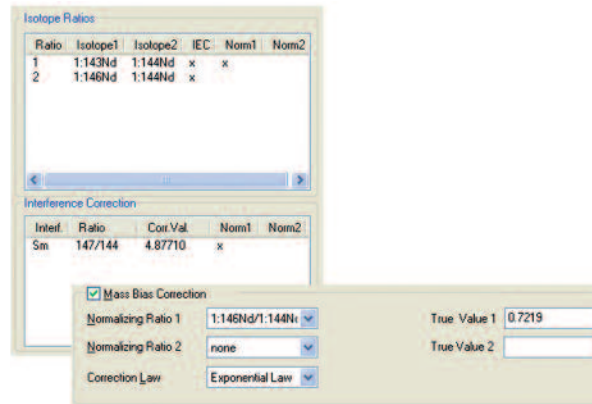


Figure 3: Screenshot of the Method Editor (evaluation pane) for method 3

$^{143}\text{Nd}/^{144}\text{Nd}$ is interference corrected (IEC) using the $^{147}\text{Sm}/^{144}\text{Sm}$ ratio corrected for mass bias using Normalizing Ratio 1 ($^{146}\text{Nd}/^{144}\text{Nd}$). The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is then corrected for mass fractionation using Normalizing Ratio 1 ($^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$).

Results

The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of Merck is 0.511728 ± 20 ppm (1RSD), based on measurements made on more than 50 NEPTUNES in the Bremen factory. Of the three methods discussed here, the most accurate $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is obtained by method 2 ($^{143}\text{Nd}/^{144}\text{Nd} = 0.511727 \pm 11$ ppm), where the mass bias of Sm was determined during the measurement and taken into account for the interference correction. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio obtained by method 1 is off by more than 600 ppm. The ratio is too high due to an overcorrection of the ^{144}Sm on the measured 144 intensity. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio obtained by method 3 is too low by 100 ppm, which results from the fact that the mass bias from Nd is not exactly the same as that of Sm.

	$^{143}\text{Nd}/^{144}\text{Nd}$	1sigma (ppm)
Accepted	0.511728	20
Method 1	0.512046	11
Method 2	0.511727	11
Method 3	0.511677	10

Table 4: The accepted $^{143}\text{Nd}/^{144}\text{Nd}$ compared with the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios obtained by the three different methods (Merck solution)

Summary

Three methods for performing interference corrections using the multicollector software of the Thermo Scientific NEPTUNE MC-ICP-MS have been illustrated. The examples show the importance of performing accurate interference corrections in case where there is a significant amount of the interfering element. These corrections are best done by taking into account a mass bias factor, ideally from the interfering element itself.

Acknowledgements

We thank Dr. Geoff Nowell from the University of Durham for sharing his strategy on performing off-line interference corrections.

References

G.M. Nowell, D.G. Pearson, C.J. Ottey, J. Schwieters & D. Dowall (2003) Long-term performance characteristics of a plasma ionization Multi-Collector Mass Spectrometer (PIMSS): the Thermo Scientific Neptune. In: Plasma Source Mass Spectrometry, Applications and Emerging Technologies, eds. J.G. Holland & S.D. Tanner. Royal Society of Chemistry Special Publication, 307-320.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Africa
+43 1 333 5034 127

Australia
+61 2 8844 9500

Austria
+43 1 333 50340

Belgium
+32 2 482 30 30

Canada
+1 800 530 8447

China
+86 10 8419 3588

Denmark
+45 70 23 62 60

Europe-Other
+43 1 333 5034 127

France
+33 1 60 92 48 00

Germany
+49 6103 408 1014

India
+91 22 6742 9434

Italy
+39 02 950 591

Japan
+81 45 453 9100

Latin America
+1 608 276 5659

Middle East
+43 1 333 5034 127

Netherlands
+31 76 579 55 55

South Africa
+27 11 570 1840

Spain
+34 914 845 965

**Sweden/Norway/
Finland**
+46 8 556 468 00

Switzerland
+41 61 48784 00

UK
+44 1442 233555

USA
+1 800 532 4752

www.thermo.com

Legal Notices

©2006, 2008 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific Inc. products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

Thermo Fisher Scientific
(Bremen) GmbH is certified
DIN EN ISO 9001:2000

AN30111_E 01/08C