

Accurate and Precise Isotope Determination of Trace Level Neodymium

- Excellent mass fractionation stability
- Low and consistent oxide formation
- Accurate and precise isotope determination of trace level Nd

The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of rocks and meteorites provides important information on crustal formation and isotopic evolution of the solar system. Precise and accurate isotope determination of trace level Nd samples is of increasing interest, and is commonly done using TIMS with Nd oxides (NdO^+). However, this technique is facing two analytical challenges: First, is the uncertainties in oxide corrections resulting from different oxygen isotope fractionation due to different loading techniques. Second, is the need for an efficient chromatographic separation of Nd from Pr, aside from Ce and Sm [1]. The MC-ICP-MS has avoided these two potential analytical difficulties, providing an alternative means for precise and accurate isotope analysis of trace level Nd.

A series of Nd JNDi-1 (Japanese Geological Survey Reference Material) standard solutions of different concentrations were measured in this study. Solution was introduced into the mass spectrometer in 2% HNO_3 under 'dry plasma' conditions, using a DSN-100 Desolvating Nebuliser system with a 100 $\mu\text{L}/\text{min}$ glass concentric nebuliser and the Enhanced Sensitivity (ES) interface (see Nu Instruments Application Note AN27).

Data was collected in static mode, with all isotopes measured in Faraday cups connected to pre-amplifiers each fitted with a 10^{11} ohm resistor. A batch analysis consisting of the sequential measurements of JNDi-1 solutions of the following concentrations: 2 ppb, 4 ppb, 6 ppb, 10 ppb, 15 ppb, was repeated 12 times. Each batch started with a 5 min 'on peak' blank measurement of a 2% HNO_3 solution. Each measurement consisted of one block of 60 cycles of 5 sec integration. The measurement duration was 5 minutes, equating to a sample consumption of 1 ng, 2 ng, 3 ng, 5 ng and 7.5 ng, respectively. A 3 min wash was performed after each measurement. No tuning of the instrument or nebuliser was made once the measurements had started.

The ^{140}Ce and ^{147}Sm beams were simultaneously monitored to correct for the unresolvable isobaric interferences of ^{142}Ce on ^{142}Nd , ^{144}Sm on ^{144}Nd , ^{148}Sm on ^{148}Nd and ^{150}Sm on ^{150}Nd (Table 1), using $^{142}\text{Ce}/^{140}\text{Ce} = 0.12565$, $^{144}\text{Sm}/^{147}\text{Sm} = 0.20498$, $^{148}\text{Sm}/^{147}\text{Sm} = 0.74970$ and $^{150}\text{Sm}/^{147}\text{Sm} = 0.49219$ (IUPAC database), respectively.

The Nu Plasma II zoom optics maintain good peak shapes (Figure 1) for all Nd isotopes, allowing accurate and precise isotope measurement.

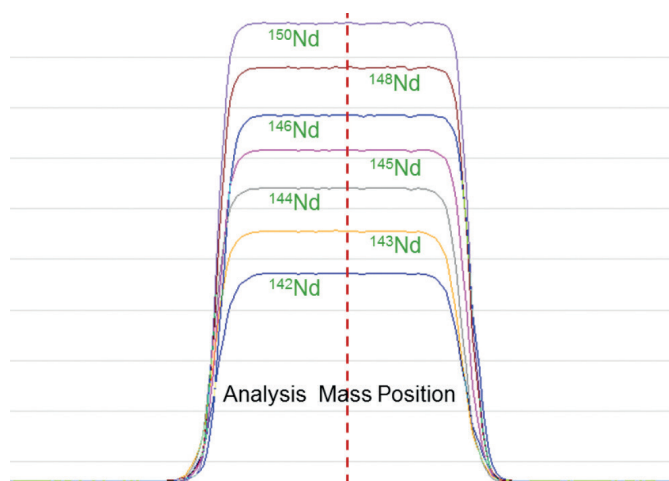


Figure 1: Neodymium isotopes ^{142}Nd , ^{143}Nd , ^{144}Nd , ^{145}Nd , ^{146}Nd , ^{148}Nd and ^{150}Nd in coincidence. The individual traces for different isotopes are not to scale.

The total Nd sensitivity achieved was approx. 700 volts/ppm. The signal intensity remained relatively stable over the course of the sequence. The Nd blank was less than 1 ppt after 3 min wash.

To correct for the mass fractionation, all measured Nd ratios were normalised to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ using the Exponential Law.

High level of Nd oxide formation is often found on the ICP instruments and accompanied by significant non-linear contribution to the instrumental mass-fractionation [2]. In this study, the $^{144}\text{Nd}^{16}\text{O}/^{144}\text{Nd}$ ratio was monitored during the course of the measurement sequence and found consistently below 0.07%.

The corrected $^{143}\text{Nd}/^{144}\text{Nd}$ of the JNDi-1 standard solution was consistent between various sample sizes, and was in agreement with the TIMS reference value (Figure 2).

Table 2 compares the external precision of the corrected $^{143}\text{Nd}/^{144}\text{Nd}$ ratio obtained in this study for each sample size with the theoretical uncertainty calculated based on the shot noise and Johnson noise. The difference between the two values may mainly be attributed to the uncertainty caused by mass fractionation corrections and interference corrections. It is noticed that the measurement precisions were approaching the statistical limit for the given beam intensity and measurement duration in this study.

Collector	H7	X	H6	H5	H4	H3	H2	H1	AX	L1	L2
Isotope	^{150}Sm ^{150}Nd		^{148}Sm ^{148}Nd	^{147}Sm	^{146}Nd	^{145}Nd	^{144}Sm ^{144}Nd	^{143}Nd	^{142}Ce ^{142}Nd		^{140}Ce

Table 1: Nu Plasma II cup configuration used in this study. Grey represents Faraday cups, yellow dummy cup. Interfering isotopes are in blue, monitored isotopes are in green. The collector array also includes 6 full size discrete dynode multipliers and 6 additional Faraday cups.

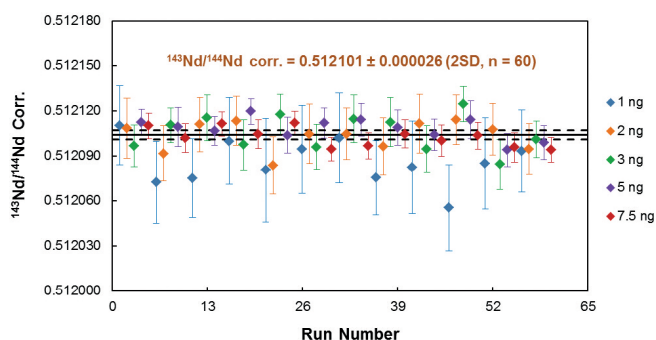


Figure 2: Corrected $^{143}\text{Nd}/^{144}\text{Nd}$ of the 1 ng, 2 ng, 3 ng, 5 ng and 7.5 ng JNDi-1 standard solutions measured over the course of 12 hours. Error bars are 2 SE. The TIMS reference value 0.512104 ± 0.000003 (2σ)^[3] is plotted in black lines.

The excellent external reproducibility of the isotope measurements of trace level Nd on the Nu Plasma II MC-ICP-MS, the consistency of the corrected ratio between samples of various sizes, and the agreement with the TIMS reference value, have demonstrated the low noise of the pre-amplifiers, in addition to the excellent mass fractionation stability with low and consistent Nd oxide formation on the ES interface.

References

- [1] Chu et al., 2009. J. Anal. At. Spectrom. 24, 1534-1544.
- [2] Newman et al., 2009. J. Anal. At. Spectrom. 24, 742-751.
- [3] Gannoun et al., 2011. PNAS. 108, 7693-7697.

Sample Size (ng)	^{144}Nd beam intensity (V)	Zero Duration (s)	Analysis Duration (s)	External Precision (2 RSD, ppm)	Theoretical Uncertainty (2 RSD, ppm)
7.5	2.9	300	300	26 (n=12)	16
5	1.9	300	300	28 (n=12)	20
3	1.2	300	300	46 (n=12)	27
2	0.8	300	300	38 (n=12)	34
1	0.3	300	300	60 (n=12)	60

Table 2: Comparison of the external precisions of the corrected $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the 1 ng, 2 ng, 3 ng, 5 ng and 7.5 ng JNDi-1 standard measured in this study with the theoretical uncertainties based on noise calculations.