

Nd and Hf Isotope Measurements Using a Double Focusing Multicollector ICP-MS

Dr. Stefan Weyer, Goethe-Universität, Frankfurt, Germany;
Johannes B. Schwieters, Thermo Fisher Scientific, Bremen, Germany

Key Words

- NEPTUNE
- Hf
- Multicollector ICP-MS
- Nd
- Static Collection

Introduction

The Sm-Nd and Lu-Hf isotope systems are widely used as dating tools and geochemical tracers to provide important information in geo- and cosmochemistry. Because of the recent rapid development of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) it has now gained acceptance in the geoanalytical community. In particular, interest in Hf analysis with MC-ICP-MS has increased as the inductively coupled plasma (ICP) ion source offers improved ionization over traditional thermal ionization (TI). This allows precise Hf isotopic determinations on small sample amounts. Additionally, sample throughput is significantly increased and preparation simplified, compared to what was previously required for TI mass spectrometry (TI-MS).

The Thermo Scientific NEPTUNE is a double focusing high resolution MC-ICP-MS, based on the high precision multicollector technology from the Thermo Scientific TRITON TI-MS and the advanced and proven ICP source and transfer optics from the Thermo Scientific ELEMENT 2 ICP-MS.

This report describes the short- and long-term performance of the NEPTUNE. The short-term reproducibility is demonstrated by the measurement of an Nd standard solution over three and a half hours. The long-term reproducibility of Hf isotope composition measurements is demonstrated for a Hf standard solution that was repeatedly measured over a nine-month period.

Experimental Parameters

As in the ELEMENT 2 ICP-MS, the plasma is capacitively decoupled using a grounded platinum shield. This narrows the energy spread of the ions to ~ 2 eV, improving ion transmission through the mass spectrometer, leading to increased sensitivity. All measurements for these experiments were performed in static multi-collection and low mass resolution mode. Uncertainties of the gain calibration are cancelled out by rotating the amplifiers between the individual cups during the measurement (Virtual Amplifier). The collector configurations for the Nd and Hf measurements are shown in Figures 1a and 1b respectively.

- 50 µl/min self-aspirating PFA concentric nebulizer (MicroFlow PFA-50, ESI NB, USA)
- Quartz dual spray chamber (Stable Introduction System, ESI NB, USA)
- Demountable quartz torch with quartz injector
- Ni sampling and skimmer cones

Table 1: Sample introduction system.

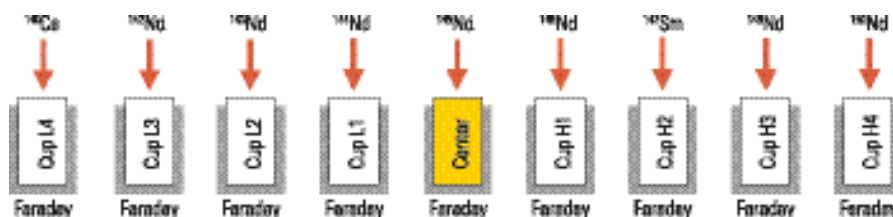


Figure 1a: Collector configuration for Nd measurements in static mode.

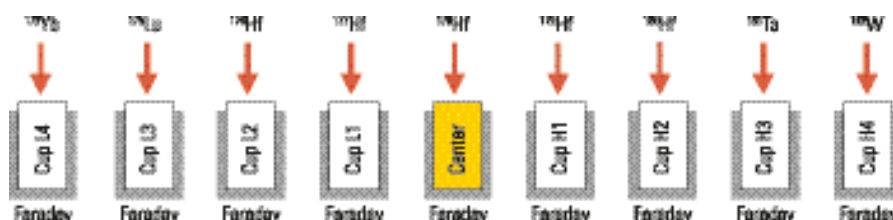


Figure 1b: Collector configuration for Hf measurements in static mode.

Results

Short-Term Reproducibility of Nd Measurements

The short-term precision of Nd determination was assessed by analyzing a 500 ppb Nd standard obtained from Merck in 13 blocks of 16 minutes each. The total analysis time was 3 1/2 hours. With an uptake rate of 60 µl/min this corresponds to a sample consumption of approximately 500 ng per block. For this sample, an ion beam intensity for ^{144}Nd of 1.1×10^{-10} A (11 V) at 10^{11} Ω resistor was recorded:

a sample utilization of 1.4%. The exponential law was applied for mass bias correction using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. The results of this analysis are presented in Table 2 and Figure 2.

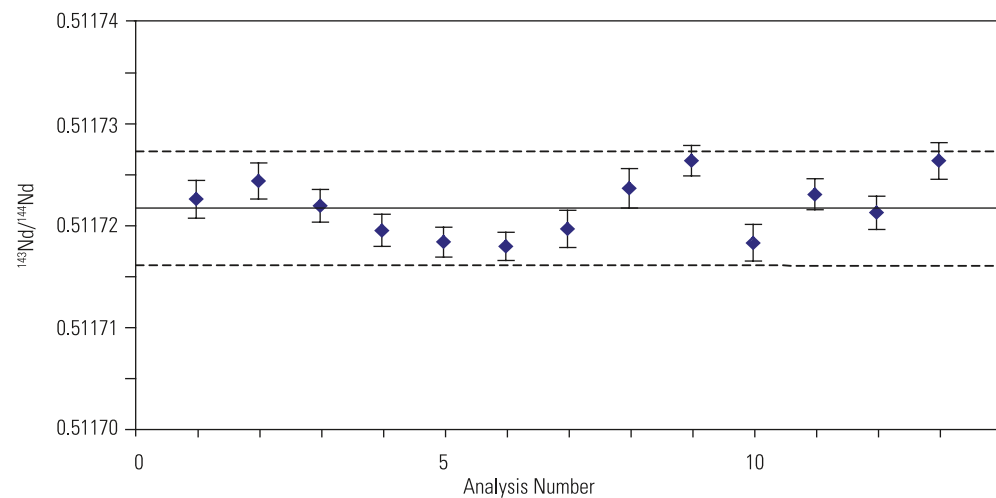


Figure 2: Short-term reproducibility for Nd measurement on a 500 ppb Merck standard solution. Duration: 3 1/2 hours (13 blocks of 16 minutes each).

Isobaric interferences of Sm on masses 144, 148 and 150 were corrected for. Some key observations from these data are summarised below:

- For each 16-minute block, the typical internal precisions for $^{143}\text{Nd}/^{144}\text{Nd}$ were 3-4 ppm (1 RSD).
- This internal precision for $^{143}\text{Nd}/^{144}\text{Nd}$ approaches the counting statistics limit ($1 \text{ RSD} = 1/\sqrt{n}$) and highlights the low noise of the current amplifiers, the stability of the baseline and Faraday collectors, and the excellent peak flatness.
- The average of all 13 blocks (210 minutes) for $^{143}\text{Nd}/^{144}\text{Nd} = 0.511722$ (± 0.000003 , 1 SD).
- The external reproducibility ($n = 13$) for $^{143}\text{Nd}/^{144}\text{Nd}$ is 6 ppm (1 RSD) after correction for mass bias. The uncorrected precision (not shown) of the raw ratios is only 28 ppm (1 RSD), exhibiting the stability of the plasma conditions and mass bias.

	Neptune	1 RSD (ppm)
$^{142}\text{Nd}/^{144}\text{Nd}$	1.141844 (7)	7
$^{143}\text{Nd}/^{144}\text{Nd}$	0.511722 (3)	6
$^{145}\text{Nd}/^{144}\text{Nd}$	0.348423 (1)	3
$^{148}\text{Nd}/^{144}\text{Nd}$	0.241587 (2)	6
$^{150}\text{Nd}/^{144}\text{Nd}$	0.236410 (3)	11

After correction for mass bias and interferences.

Table 2: Isotope composition of the Merck Nd standard.

Long-Term Reproducibility of Hf Measurements

The long-term reproducibility was evaluated from 12 measurements of a 100 ppb JMC* 475 Hf standard (that gave an ^{177}Hf ion beam intensity of 1×10^{-11} (1 V) at 10^{11} Ω resistor over a nine-month period. The analysis time of each measurement was from 15 minutes to several hours, producing time-dependent in-run precisions of between 2 to 18 ppm (1 RSD).

The exponential law was applied for mass bias correction using $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$. Interferences of Yb, Lu, Ta and W were corrected for on masses 176 and 180. The ratios obtained for the JMC 475 Hf standard are shown in Table 3 and Figure 3.

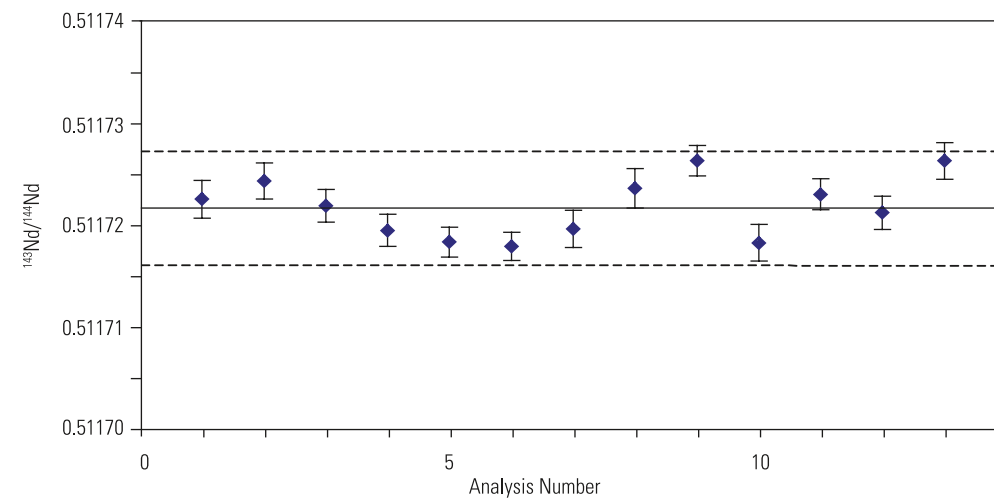


Figure 2: Short-term reproducibility for Nd measurement on a 500 ppb Merck standard solution. Duration: 3 1/2 hours (13 blocks of 16 minutes each).

The mean ratio for $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.282158 (± 0.000003 , 1 SD) agrees with previously obtained values (Blichert-Toft et al., 1997; Nowell et al., 1998). The precision of 11 ppm (1 RSD) over a nine-month period illustrates the excellent long-term stability and external reproducibility of the NEPTUNE MC-ICP-MS.

	Neptune	1 RSD (ppm)	BI-Toft ¹⁾	Nowell ²⁾
$^{176}\text{Hf}/^{177}\text{Hf}$	0.282158	11	0.282160	0.282155
$^{178}\text{Hf}/^{177}\text{Hf}$	1.467236	9	1.467168	
$^{180}\text{Hf}/^{177}\text{Hf}$	1.886705	15	1.886666	

After correction for mass bias and interferences.

¹⁾ Blichert-Toft et al. (1997)

²⁾ Nowell et al. (1998)

Table 3: Isotope composition of the JMC 475 Hf standard.

* www.matthey.com

Conclusion

The NEPTUNE is a high precision MC-ICP-MS that has been shown to exhibit exceptional short- and long-term precisions. Short-term precisions (three and a half hours) for Nd runs are in the range of 6 ppm (1 RSD) and long-term (nine months) precisions for Hf are in the range of 11 ppm (1 RSD).

References

Blichert-Toft J., Chauvel C., and Albarède F. (1997) Separation of Hf and Lu for high precision isotope analysis of rock samples by magnetic sector - multiple collector ICP-MS. *Contributions to Mineralogy and Petrology* 127, 248-260.

Nowell G.M., Kempton P.D., Noble S.R., Fitton J.G., Saunders A.D., Mahoney J.J., and Taylor R.N. (1998) High precision Hf isotope measurements of MORB and OIB by thermal ionisation mass spectrometry: insights into the depleted mantle. *Chemical Geology* 149, 211-233.

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