

High-throughput High-precision Nd Isotope Ratios from Small Samples Using Syringe Based Flow Injection for MC-ICP-MS

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Overview

Purpose: To evaluate $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio precision from high-throughput small-sample measurements.

Methods: Nd standards were analysed using a Thermo Scientific NEPTUNE *Plus* MC-ICP-MS with Elemental Scientific microFAST MC apex Ω sample introduction system.

Results: Sixteen two-nanogram samples per hour can be measured with 0.5 ϵ -unit external reproducibility (2σ).

Introduction

Large datasets of high-precision $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio measurements are required for tracing and understanding global seawater circulation patterns. Two key challenges in generating such datasets are: 1) the low concentration of Nd in seawater and 2) the large number of sample analyses required.

Here we evaluate the combination of the Thermo Scientific™ NEPTUNE *Plus*™ MC-ICP-MS with Elemental Scientific microFAST MC apex Ω sample introduction system for rapid determination of $^{143}\text{Nd}/^{144}\text{Nd}$ from small Nd sample amounts.

Methods

Standards

La Jolla and JNd_i neodymium isotopic reference materials were treated as unknowns, and were measured against an in-house standard (Certipur® Neodymium ICP Standard lot # HC077146). The solutions were diluted in high-purity HNO₃ (aq).

Sample Introduction

Solutions were sampled using a microFAST MC syringe-driven, dual-loop, valve injection system. For rapid sample changeover the system rinses and loads one loop whilst injecting a sample from the other loop to a PFA nebulizer. Alternating loop injections provides steady state signal and three orders of magnitude washout in 60s. Overhead times from uptake and washout are greatly reduced and sample utilisation is increased. Other advantages of the microFAST MC include precise loading of small sample volumes and software controlled injection rate.

The nebulised solution was introduced to the NEPTUNE *Plus* MC-ICP-MS via an apex Ω desolvating system. The apex Ω integrates heating, condensing, and membrane desolvation with complete software control for high precision remote tuning (Figure 1).



FIGURE 1. Image of Elemental Scientific apex Ω and screenshot showing software control for precise gas tuning.

A two-minute sample injection and one-minute changeover is used to achieve a throughput of 19 analyses per hour.

Mass Spectrometry

A Thermo Scientific NEPTUNE *Plus* MC-ICP-MS with Jet Interface Option was used. The high-sensitivity Jet sample cone with standard H-type skimmer cone provides an intermediate sensitivity with low oxides, this combination is recommended for Nd isotope accuracy. For other isotopic systems the X-type skimmer cone offers further sensitivity enhancement.

Acquisition times from 1 – 4 minutes were tested (4.2 second integration times). Peak centre and baseline calibrations were performed daily prior to each measurement sequence. Blanks were measured, but were not corrected for as they were insignificant.

Data Analysis

The Nd isotope ratio data were corrected with a linear mass bias correction using the conventional $^{146}\text{Nd}/^{144}\text{Nd} = 0.7129$. The linear correction fitted the light masses better than exponential, as with other MC-ICP-MS instruments neither model fits perfectly. A small secondary external correction was applied from the in-house standard, which was run at 10 ng/g concentration and measured every ten ‘sample’ measurements.



FIGURE 2. Thermo Scientific NEPTUNE Plus MC-ICP-MS with Elemental Scientific microFAST MC apex Ω .

Results

Self-aspirating nebulizer with conventional throughput

To establish the basic performance of the Thermo Scientific NEPTUNE Plus MC-ICP-MS with Elemental Scientific apex Ω , a test was made using a self-aspirating nebulizer and conventional acquisition times. A precision of 0.13 ε -unit (2σ) is achieved for six 16 ng samples per hour (Figure 3).

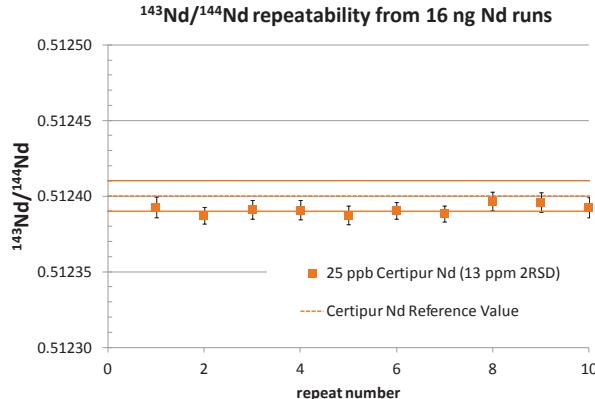


FIGURE 3. Repeatability of 16 ng Nd runs (25 ng/g solution), using Elemental Scientific apex Ω with PFA-100 self-aspirating nebulizer and 5-minute acquisition time.

Sensitivity and Oxides

The microFAST MC allows the user to specify a precise injection rate for their sample. Figure 4 shows that in combination with the apex Ω , sensitivity is linear with injection rate, and oxides remain constant up to at least 250 $\mu\text{l}/\text{min}$. The unique desolvation and injection rate control qualities of this setup allow the user to choose how to run a solution: short and concentrated or long and dilute.

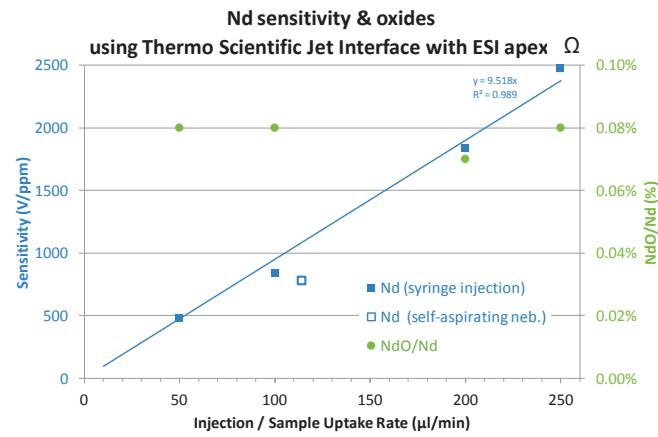


FIGURE 4. Signal increase is linear with injection rate, and low oxides are maintained up to 250 $\mu\text{l}/\text{min}$.

Optimising the protocol for measuring small samples

A 10 ng/g Nd solution was injected at different rates (50 – 200 $\mu\text{l}/\text{min}$) and measured for different periods of time (1 – 4 minutes). The data are plotted in Figure 5; precision is comparable for a given sample amount, independent injection rate and acquisition time. A two-minute acquisition time with 100 $\mu\text{l}/\text{min}$ injection rate provides the optimal balance of throughput and precision.

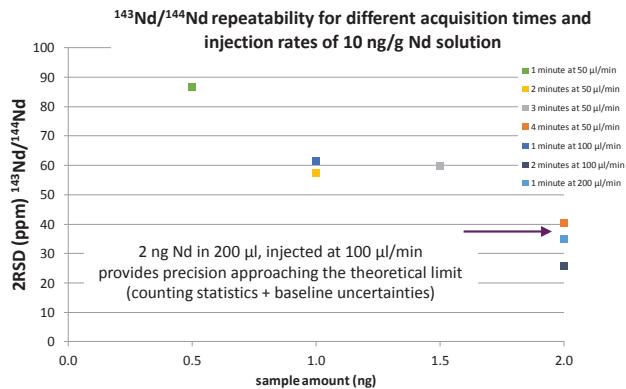


FIGURE 5. Plot of precision achieved for different injection rates and acquisition times for 0.5 - 2 ng Nd samples.

Repeatability for 19 analyses / hour

Using the optimal high throughput conditions, 200 μ l samples are injected at 100 μ l/min. In one-hour 16 samples were measured, with a 10 ng/g bracketing standard and a blank measured every 10 samples. A series of measurement sequences were made, with solution concentrations from 1 - 25 ng/g Nd interspersed through the sequences.

The sample introduction methodology combines complete sample loading and injection with high sample transport efficiency, resulting in near total sample introduction to the ICP. The data in Figure 6 show the external repeatability (2σ) of samples amounts from 0.5 – 5 ng of JNDI Nd. They show that high-precision isotope ratios can be measured with this setup, and with a high sample throughput.

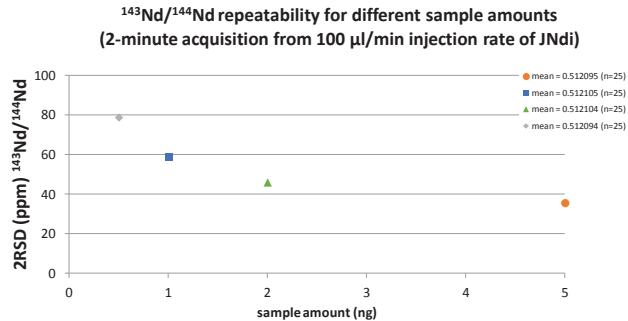
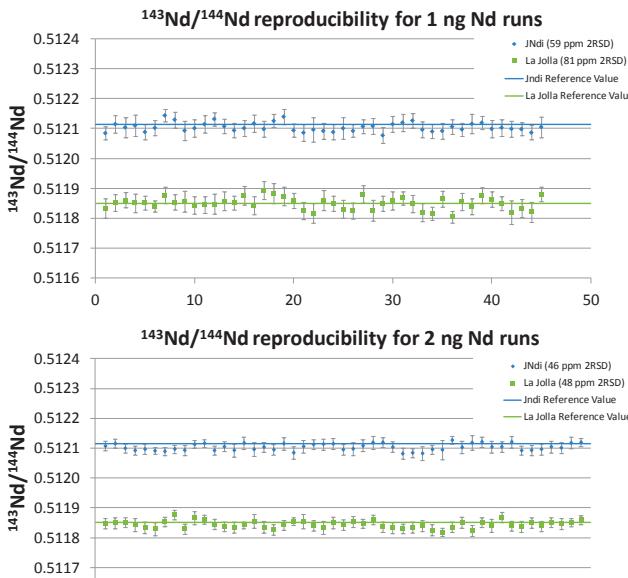


Figure 6. External repeatability of 0.5 - 5 ng JNDI Nd runs, using Thermo Scientific NEPTUNE Plus MC-ICP-MS with Elemental Scientific apex Ω & microFAST MC.

Figure 7 shows the external reproducibility from three separate sequences of high-throughput measurements. For two nanogram runs, measured at a rate of sixteen samples per hour, a precision of 0.5 ϵ -units (2σ) is realised.



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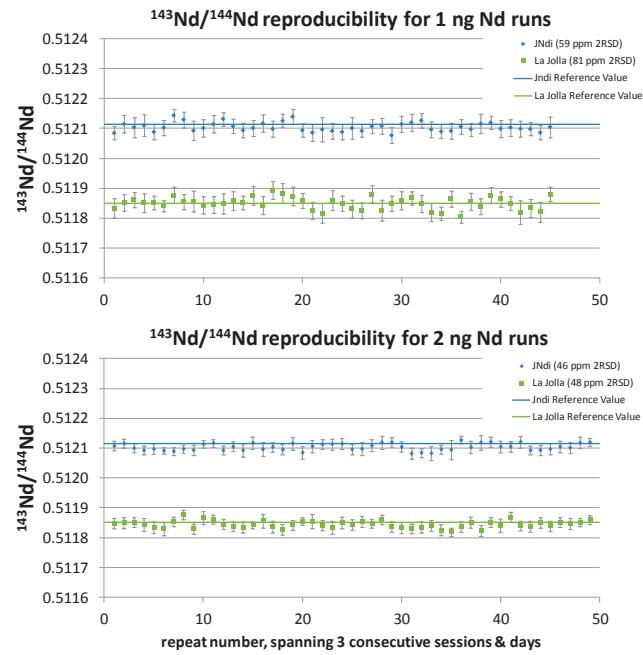


Figure 7. Reproducibility of 1 and 2 ng Nd runs, using Thermo Scientific NEPTUNE Plus with MC-ICP-MS Elemental Scientific apex Ω & microFAST MC. Data from 3 separate high-throughput sequences, measuring 16 samples / hour, are accurate and precise within 0.5 ϵ -units (2σ) for the 2 ng runs.

Conclusions

An experimental setup was optimized for highest sample throughput. Precise and accurate $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios can be determined $< 0.5 \epsilon$ -units (2σ) for 2 ng Nd samples with a throughput of 16 samples per hour.

- Elemental Scientific microFAST MC efficiently handles small solution volumes and slashes the overhead time between sample measurements.
- The Elemental Scientific apex Ω is a new high-efficiency desolvating nebulizer system, offering low-oxides and high sensitivity up to 250 μ l/min introduction rate. Gas flows are tuned via software for optimal stability.
- In combination with Thermo Scientific NEPTUNE Plus MC-ICP-MS, accurate and precise $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios can be determined from small Nd samples with a throughput of 16 samples / hour.

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