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High-throughput high-precision Nd isotope ratios from small samples using syringe based flow injection for MC-ICP-MS

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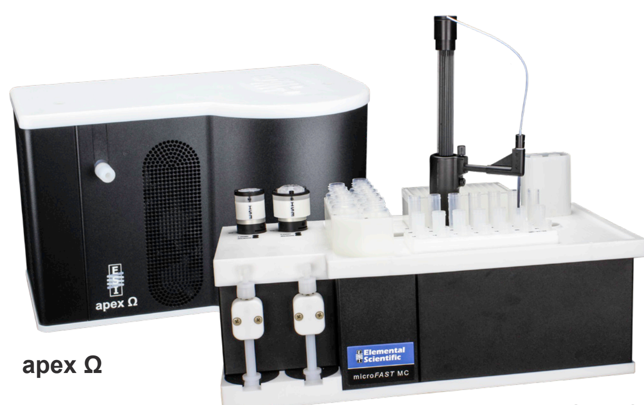
Abstract

Large database of high-precision isotope ratio measurements (Sr, Nd, Pb, U, etc) are required in a wide variety of disciplines (geology, archaeology, anthropology, hydrology, forensics, etc) for both source tracing and understanding geochemical cycles. As a result, high throughput analysis is becoming increasingly important for many applications of radiogenic and non-traditional metal isotopes.

Here we evaluate the combination of the micro*FAST* MC and apex desolvating nebulizer (ESI, Omaha, USA), high-throughput sample introduction system on a NEPTUNE Plus MC-ICP-MS, with Jet Interface option and 10^{13} Ω amplifier for highest sensitivity. The dual loop injection system, syringe loads sample into one loop while syringe injecting sample from the other loop to the nebulizer. Alternating loop injections avoids overhead associated with sample uptake and washout during conventional self-aspiration. This provides very efficient sample handling for a wide range of sample volumes (10s to 100s of µl) increasing both sample utilization and sample throughput. The NEPTUNE Plus sensitivity has been improved through the combination of high-efficiency inlet systems and sampling interfaces to the point that small (ng) samples can be measured at sub-epsilon unit precision.

One application requiring large datasets is the GEOTRACES programme. High-precision $^{143}Nd/^{144}Nd$ isotope ratio measurements are essential for tracing and understanding global seawater circulation patterns. Two key challenges in generating such a datasets are: 1) the low concentration of Nd in seawater (especially in surface waters) and 2) the large number of sample analyses required. Data are reported for measurements from Nd sample amounts ranging 1 – 10 ng. Throughput of over 10 samples per hour was achieved. The external precision achieved for $^{143}Nd/^{144}Nd$ was better than 0.5 epsilon units (2s) for 2 ng samples amounts.



micro*FAST* MC

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Methods

Standards

La Jolla and JNdi 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 HNO_3 (aq).

Sample introduction

Solutions were sampled using a micro*FAST* 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 micro*FAST* MC include precise loading of small sample volumes and software controlled injection rate.

The nebulised solution was introduced to the NEPTUNE Plus 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).

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 $^{146}Nd/^{144}Nd = 0.7129$. 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.

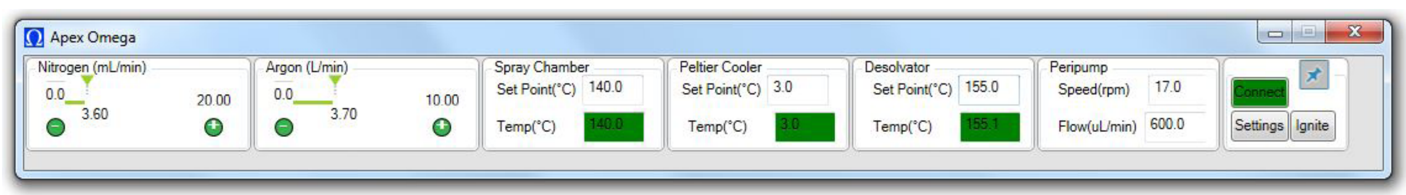


Figure 1. apex Ω screenshot showing software control for precise gas tuning.

Results

Self-aspirating nebulizer with conventional throughput

To establish the basic performance of the Thermo Scientific NEPTUNE Plus with ESI 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).

$^{143}Nd/^{144}Nd$ Repeatability From 16 ng Nd Runs

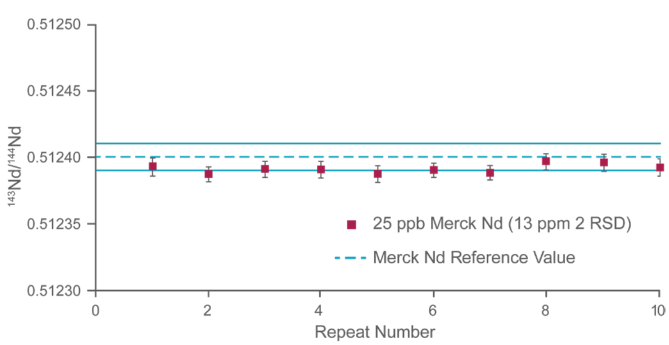


Figure 2. Repeatability of 16 ng Nd runs (25 ng/g solution), using ESI apex Ω with PFA-100 self-aspirating nebulizer and 5-minute acquisition time.

Nd Sensitivity & Oxides Using Thermo Scientific Jet Interface with ESI apex Ω

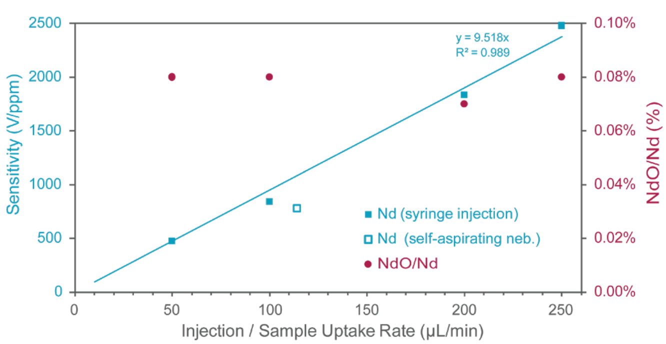


Figure 3. Signal increase is linear with injection rate, and low oxides are maintained up to 250 µl/min.

Sensitivity and oxides

The micro*FAST* 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 µl/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.

Optimising the protocol for measuring small samples

A 10 ng/g Nd solution was injected at different rates (50 – 200 µl/min) and measured for different periods of time (1 – 4 minutes). The data are plotted in Figure 5; precision is comparable for a

$^{143}Nd/^{144}Nd$ Repeatability for Different Acquisition Times and Injection Rates of 10 ng/g Nd Solution

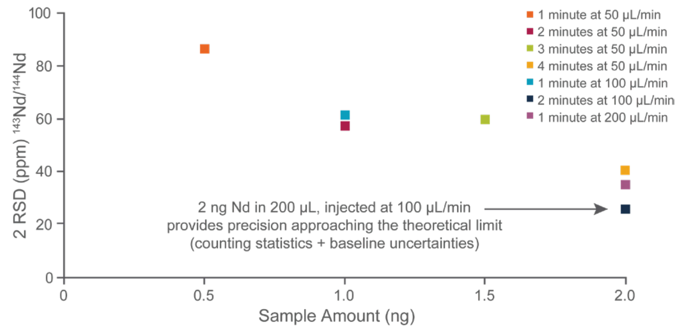


Figure 4. Plot of precision achieved for different injection rates and acquisition times for 0.5 - 2 ng Nd samples.

given sample amount, independent injection rate and acquisition time. A two-minute acquisition time with 100 µl/min injection rate provides the optimal balance of throughput and precision.

Repeatability for 19 analyses / hour

Using the optimal high throughput conditions, 200 µl samples are injected at 100 µl/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.

$^{143}Nd/^{144}Nd$ Repeatability for Different Sample Amounts (2 min Acquisition from 100 µL/min Injection Rate of JNdi)

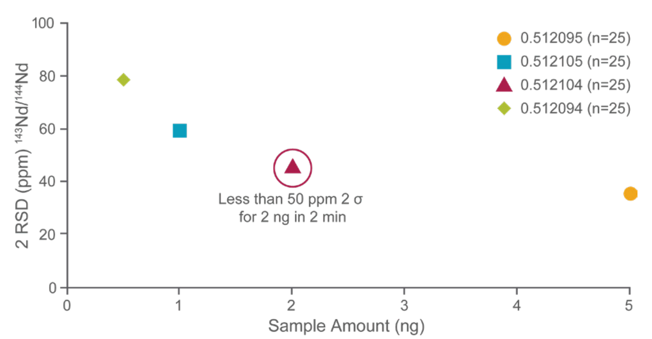


Figure 5. External repeatability of 0.5 - 5 ng JNdi Nd runs, using Thermo Scientific NEPTUNE Plus with ESI apex Ω & micro*FAST* MC.

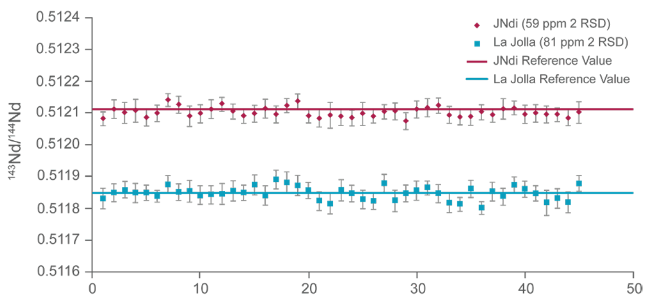
The sample introduction methodology combines complete sample loading and injection with high sample transport efficiency, resulting in near total sample introduction to the ICP. The data in Figure 6 show the external repeatability (2σ) of samples amounts from 0.5 – 5 ng of JNdi Nd. They show that high-precision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

Conclusions

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

- ESI micro*FAST* MC efficiently handles small solution volumes and slashes the overhead time between sample measurements.
- The ESI apex Ω is a new high-efficiency desolvating nebulizer system, offering low-oxides and high sensitivity up to 250 µl/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 $^{143}Nd/^{144}Nd$ isotope ratios can be determined from small Nd samples with a throughput of 16 samples / hour.

$^{143}Nd/^{144}Nd$ Reproducibility for 1 ng Nd Runs



$^{143}Nd/^{144}Nd$ Reproducibility for 2 ng Nd Runs

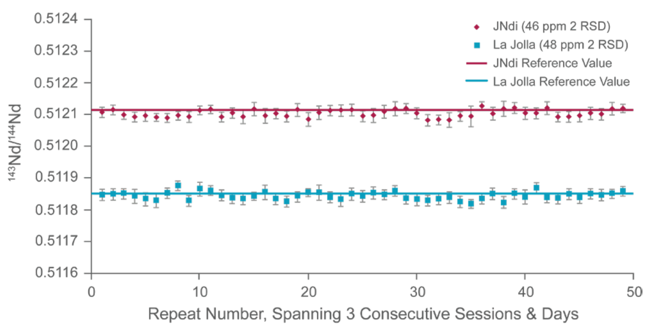


Figure 6. Reproducibility of 1 and 2 ng Nd runs, using Thermo Scientific NEPTUNE Plus with ESI apex Ω & micro*FAST* MC. Data from 3 separate high-throughput sequences, measuring 16 samples / hour, are accurate and precise within 0.5 ε-units (2σ) for the 2 ng runs.

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.

Acknowledgements

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