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TECHNICAL NOTE 30493

$10^{13}$ AMPLIFIER TECHNOLOGY

# Expanding the analytical range utilizing $10^{13}$ Ω amplifier technology: Measurement of 100 pg Nd samples


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**Keywords**

$10^{13}$ Ω amplifier technology, isotope ratio, neodymium, small samples, Triton Plus TIMS, counting statistics


## Goal

To extract accurate and precise Nd isotope ratios from small samples; 100 pg Nd samples being applicable to a wide range of geochemical applications, including the fields of cosmochemistry and marine biogeochemistry.

## 1. Introduction

The precise and accurate measurement of low intensity ion beams is required by numerous applications in isotope geochemistry, e.g. when sample amount or the element of interest is limited, the abundance of the isotope measured is low, or when interfering isotopes need to be monitored to apply precise interference corrections. For these measurements the accuracy and precision is ultimately limited by the noise of the detection system. Until recently, ion beam intensities of lower than $1 \times 10^{-13}$ A were preferentially measured on ion counters due to their exceptionally low noise levels. However, ion counters are limited in their dynamic range and require frequent and precise determination of both their dead time and element-specific yield. Considering the uncertainty on these calibrations, external reproducibilities and inter-lab comparisons of isotope ratio measurements are limited to 0.2% and 0.4% (2 RSD) although better internal precisions can be achieved. Where a single ion counter is used in sequential peak jumping methods further analytical challenges arise from low duty cycles as well as fluctuations in signal, leading to high sample consumption and compromised precision and accuracy of the measured isotope ratios.

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The radiogenic and stable isotope systems of the rare-earth metal neodymium (Nd) have numerous applications in geochemistry, geochronology, paleoceanography, sedimentology and cosmochemistry (Faure and Mensing, 2005). Due to low Nd concentrations in geochemical reservoirs, e.g. 1.3 µg/g in the Earth's mantle, 0.47 µg/g in CI chondrites or 4 pg/g in deep seawater (Frank, 2002; Palme and O'Neill, 2014), studies are limited by the amount of Nd and/or require processing of large sample amounts.

In this Technical Note it is demonstrated how the analytical range can be expanded by utilizing a Thermo Scientific™ Triton Plus™ Thermal Ionization Mass Spectrometer (TIMS) equipped with $10^{13}$ Ω amplifier technology. The static multicollection of low intensity ion beams by $10^{13}$ Ω amplifiers overcomes the limitations of sequential single collector measurements by enabling low noise, 100% duty cycle measurements, and further benefits from the Faraday cup technology with its proven long-term stability. The dynamic range of the $10^{13}$ Ω amplifiers exceeds 30 Mcps (0.5 V, all signal voltages reported in this Technical Note refer to a $10^{11}$ Ω scale), i.e. significantly higher than any ion counting system. The low noise levels enable isotope ratio measurements down to precisions and accuracies of <1‰ (2 RSD) at beam intensities of only 30 kcps. For Nd, accurate results with precision levels of 34 ppm (2 RSD) on the $^{143}Nd/^{144}Nd$ isotope ratio have been already demonstrated for $^{143}Nd$ signals higher than 40 mV and are still within 0.35‰ (2 RSD) for $^{143}Nd$ ion currents of only 1 mV using Nd loads of 300 ng (Vollstaedt et al., 2017). Finally, filament loading procedures, signal stability, ion yield and blank contributions may have a significant impact on measurement precision and accuracy when measuring sample amounts of less than 1 ng. Here, the performance of the Triton Plus TIMS equipped with $10^{13}$ Ω amplifiers and a 3.3 pA current calibration board is tested on 100 pg Nd loads of the reference material JNdi-1 (distributed by the Geological Survey of Japan).

## 2. Methods

### 2.1. Sample loading

The small sample sizes investigated in this study required a concise and reproducible loading procedure. Here, paraffin film "dams" were used to confine the sample loading area on the filament. Specifically, paraffin film was glued at a filament current of 1.2 A on each side of an outgassed rhenium (RE) zone refined (ZR) double filament, leaving an untouched part about 0.2 cm in the middle of the filament ribbon. The current was then switched to 0 A and 1 µL of a 0.25 M $H_3PO_4$ solution was pipetted onto the filament and slowly evaporated to near dryness at 0.5 A. One microliter of a 100 pg/µL Nd JNdi-1 solution was consecutively loaded on top of the $H_3PO_4$ and dried down at 0.5 A. The filament current was then slowly ramped up to 1.2 A when the paraffin film was starting to burn off the filament. It is important to evaporate the paraffin film slowly to avoid heavy boiling. The paraffin film is completely burned off at about 1.8 A. The sample was glowed at dark red filament color for about 5 seconds (about 2 A filament current) before the current was put to zero. The filament was mounted on a sample turret together with an outgassed Re ZR filament on the ionization side.

### 2.2. Instrumentation

A Triton Plus TIMS equipped with five $10^{13}$ Ω amplifiers and a 3.3 pA current calibration board was used in this study (see Vollstaedt et al. (2017) for details). The measured detector noise of the $10^{13}$ Ω amplifiers is better than 0.7 µV/24 h (2 SD) using a 20 minute baseline integration time. The inter-channel gain stability of the $10^{13}$ Ω amplifiers, i.e. the gain factor of amplifier 1 divided by the gain factor of amplifier 2, was measured to be better than 15 ppm/24 h (2 SD, see also Vollstaedt et al. (2017)).

### 2.3. Filament heat-up procedures

The heating of the ionization and evaporation filaments is the most critical step of the Nd isotope measurement. The following method was found to work best for the filaments used in this study, but different filament batches might require different parameters.

The ionization filament was heated with a rate of 160 mA/min to 1650 °C (corresponding to about 3.5–3.7 A or 10 kcps on $^{187}Re$) while the evaporation filament was heated with a rate of 50 mA/min to 1200 A. A 20 min electronic baseline was measured in between. The analyzer gate valve was then opened and the $^{144}Nd$ signal was focused on the SEM in the center cup position. The evaporation filament current was then increased at 35 mA/min until the $^{143}Nd$ signal reached 5 mV with periodic peak center and focus routines. At $^{144}Nd$ signals higher than 1 Mcps, the $^{145}Nd$ signal was used for signal monitoring, peak center and focus.

## 2.4. Isotope measurement

At a $^{143}$Nd signal of 5 mV the method was started using the cup configuration shown in Table 1. An integration time of 8.389 s per cycle was used.
The total number of cycles per sample with a $^{143}$Nd signal of higher than the cutoff value of 11 mV (see section 2.5) depended on the signal evolution and was between 28 and 71 cycles (corresponding to 4 to 10 minutes measurement time). Between 1-3% of the loaded Nd was collected during the measurement.

**Table 1. Cup configuration for Nd isotope measurements on a Thermo Scientific Triton Plus Multicollector Thermal Ionization Mass Spectrometer.**

| Cup | L3 | L2 | L1 | C | H1 |
|---|---|---|---|---|---|
| Amplifier | $10^{13}$ | $10^{13}$ | $10^{13}$ | $10^{13}$ | $10^{13}$ |
| Isotope | $^{142}$Nd | $^{143}$Nd | $^{144}$Nd | $^{145}$Nd | $^{146}$Nd |

The filament current was constantly increased during the measurement at 35 mA/min until the signal maximum was reached. The heating rate was then manually and continuously increased to maintain the signal intensity until no Nd was left on the filament. A typical signal evolution is shown in Figure 1.

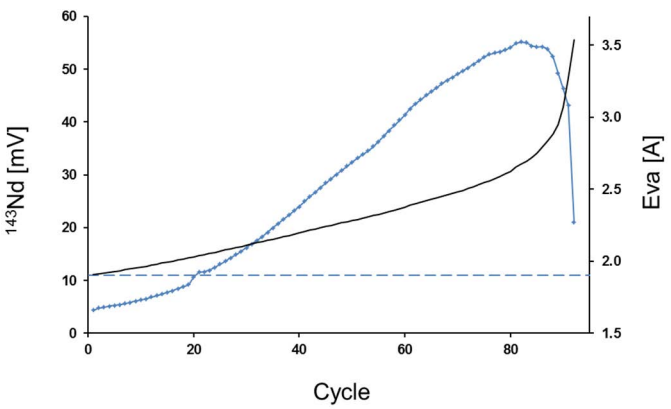


**Figure 1. Typical $^{143}$Nd signal evolution of a 100 pg Nd sample measurement (solid blue line with blue diamonds).** The measurement was started at an $^{143}$Nd signal of 5 mV. After the signal intensity maximum was reached the heating rate of the filament (solid black line represents absolute evaporation filament current) was adjusted to maintain the maximum Nd signal. Dashed blue line refers to the cutoff signal of 11 mV that was used in this study (see section 2.5).

## 2.5. Data reduction

To compensate for the different response and decay times of the $10^{13}$ Ω amplifiers a tau correction integrated into the Triton Plus software was applied, following the principles outlined in Craig et al. (2017). Following tau correction of the signal data, ratios were calculated and normalized to $^{146}$Nd/$^{144}$Nd of 0.7219 using the exponential mass fractionation law, and an outlier test using the two sigma criterion was applied to the measurement cycles. To account for the two most important factors contributing to measurement uncertainty, e.g. signal/noise ratio and total number of ions collected (counting statistics), a minimum $^{143}$Nd signal of about 11 mV was defined for all samples measured in this study. This signal was calculated using the Microsoft™ Excel™ Solver™ add-in and resulted in the lowest external reproducibility of the 13 samples measured in this study. All cycles with a $^{143}$Nd signal lower than this value were discarded from further evaluation.

## 3. Results

Thirteen individual filaments loaded with 100 pg of Nd were measured within this study (Table 2). Three samples were discarded because of bad signal evolutions, e.g. having two distinct maxima in $^{143}$Nd. The inclusion of these samples does, however, not substantially change the overall results in terms of accuracy and precision. The remaining 10 samples yield a $^{143}$Nd/$^{144}$Nd ratio of 0.512110 ± 0.000051 (2 SD; Figure 2) which agrees with the values of 0.512099 ± 0.000005 (2 SD) of Garçon et al. (2018) and 0.512115 ± 0.000007 (2 SD) of Tanaka et al. (2000) determined on 100–1000 ng Nd loadings, i.e. amounts that are 1,000 to 10,000 times larger than used in this study. Accordingly, accurate $^{143}$Nd/$^{144}$Nd ratios with a precision level of 99 ppm (2 RSD) can be achieved on 100 pg Nd loads using the $10^{13}$ Ω amplifier technology. The level of precision is about 20% better compared to a previous study on 100 pg aliquots of a Nd standard solution measured using prototype $10^{13}$ Ω amplifiers (Koornneef et al., 2014).

**Table 2. Results for Nd isotope measurements on 100 pg JNdi-1 aliquots.** The measurement consisted of 28–71 cycles with 8.389 second integration time of a $^{143}Nd$ signal higher than 11 mV. All ratios were normalized to $^{146}Nd/^{144}Nd$ of 0.7219 using the exponential mass fractionation law. Outliers were rejected using the two sigma criterion.

| Run | $^{143}Nd/^{144}Nd$ | 2 SE | 2 RSE [ppm] | 2 $RSD_{cs}$ [ppm] | Cycles |
|---|---|---|---|---|---|
| 1 | 0.512074 | 0.000057 | 112 | 100 | 71 |
| 2 | 0.512163 | 0.000077 | 150 | 124 | 28 |
| 3 | 0.512086 | 0.000041 | 81 | 89 | 68 |
| 4 | 0.512134 | 0.000062 | 121 | 109 | 36 |
| 5 | 0.512103 | 0.000040 | 79 | 74 | 65 |
| 6* | 0.512048 | 0.000065 | 127 | 135 | 36 |
| 7 | 0.512120 | 0.000069 | 135 | 137 | 32 |
| 8 | 0.512096 | 0.000052 | 102 | 68 | 61 |
| 9* | 0.512090 | 0.000086 | 168 | 137 | 36 |
| 10 | 0.512116 | 0.000048 | 94 | 89 | 36 |
| 11* | 0.512024 | 0.000075 | 146 | 141 | 32 |
| 12 | 0.512115 | 0.000039 | 76 | 70 | 67 |
| 13 | 0.512096 | 0.000037 | 71 | 68 | 69 |
| Average (± 2 SD; n = 10) | | | | | |
| | **0.512110** | **0.000051** | | | |

*Bad run, excluded from average and uncertainty calculation (see main text)

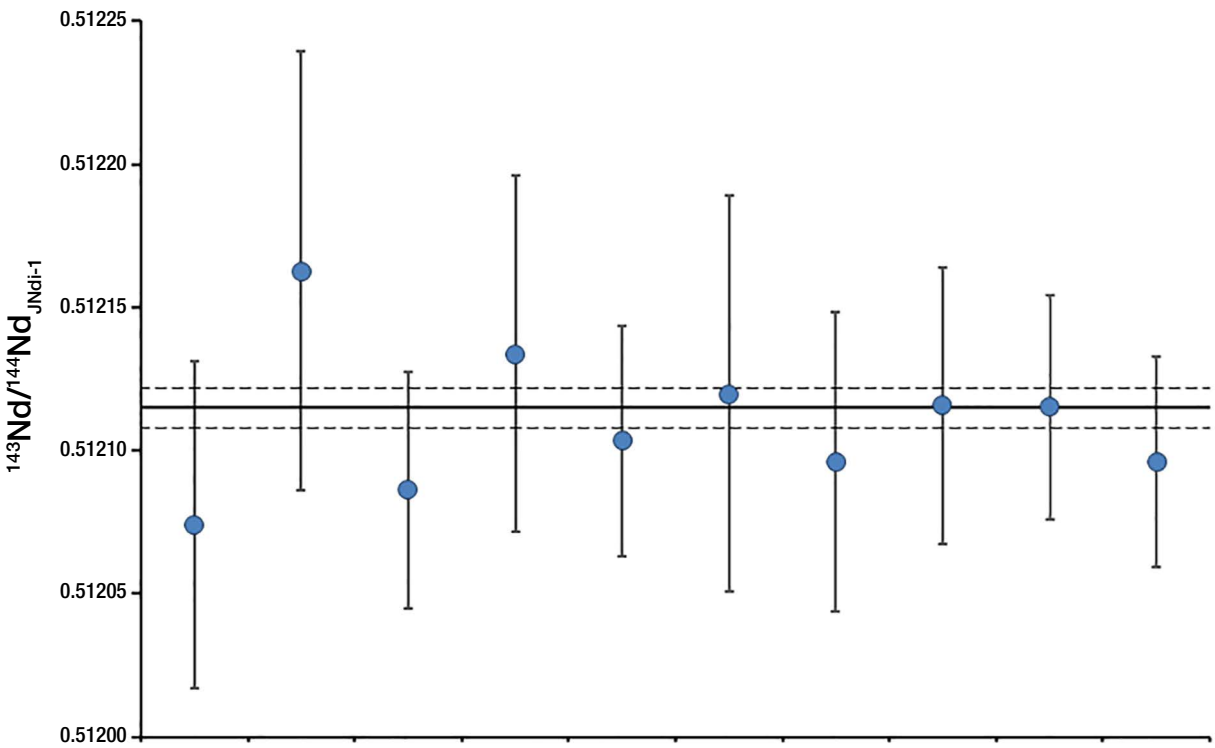


**Figure 2. Results for Nd isotope measurements on 100 pg JNdi-1 aliquots (blue dots with 2 SE error bars; Table 1).** Solid and dashed black lines refer to the average and 2 SD uncertainty values for JNdi-1 by Tanaka et al. (2000).

## 4. Discussion

### 4.1. Counting statistics

The relative uncertainty derived from counting statistics ($RSD_{cs}$) was calculated using the following equation:

$$2 * RSD_{cs}\left(\frac{^{143}Nd}{^{144}Nd}\right) = 2 * \sqrt{\left(RSD_{cs(^{143}Nd)}\right)^2 + \left(RSD_{cs(^{144}Nd)}\right)^2}$$

With $RSD_{cs(^{143}Nd)}$ and $RSD_{cs(^{144}Nd)}$ being defined as:

$$RSD_{cs(^{143}Nd)} = \sqrt{\frac{1}{counts_{(^{143}Nd)}}}$$

$$RSD_{cs(^{144}Nd)} = \sqrt{\frac{1}{counts_{(^{144}Nd)}}}$$

The uncertainty on the $^{146}Nd/^{144}Nd$ is neglected because of the rather small influence of the mass fractionation correction on the TIMS. The internal precisions of the 10 individual runs are between 71 and 150 ppm (2 SE) and strongly depend on the amount of collected ions during the measurement. This is manifested in the accordance of the internal precision, with counting statistic uncertainty of single measurements that coincide within about 30 ppm (Table 2). Additionally, the external reproducibility of the 10 replicate measurements of 99 ppm (2 RSD) is within this precision level. This further proves that the low noise $10^{13}$ Ω amplifier technology connected to the highly stable Faraday cups produces accurate data with a precision level that is ultimately limited by counting statistics. This is in contrast to ion counting measurements, which generally yield worse external reproducibility than internal reproducibility, as a result of uncertainties on the ion counter yield and dead time calibration. It is anticipated that the precision and accuracy of measurements with $10^{13}$ Ω amplifiers on even smaller samples sizes are also not limited by the detection system, but rather by blank contributions, loading and heating techniques and mixing processes of different reservoirs on the filament (see also section 4.2).

### 4.2. Cutoff signal

For these extremely small sample runs it is required to have a reproducible loading and measurement technique to yield the best precision and accuracy. During the measurement the sample is completely consumed, leading to extreme fractionation factors, particularly at the end of the measurement (Figure 3). In this study fractionation factors:

$$\beta = \frac{\left(ln \left.{}^{146}Nd/{}^{144}Nd\right/ 0.7219\right)}{ln\left(\left.m^{146}Nd/m^{144}Nd\right.\right)} = 2.5$$

were observed (>8%/amu) where $m^{14X}$Nd is standing for the mass of the respective isotope. Isotope mass fractionation has been shown to generally follow the exponential fractionation law in TIMS (Hart and Zindler, 1989; Russell et al., 1978). However, for extreme fractionations, e.g. during the very early and late run, deviations from the exponential fractionation law are observed that were previously explained by mixing/unmixing of isotopically heterogeneous sample reservoirs on the filament (Hart and Zindler, 1989). Accordingly, it is required to discard measurements with extreme fractionations from further evaluation. Specifically, it is important to use a similar fraction of the measurement for all samples for evaluation. Furthermore, uncertainties in the baseline measurements will have a negative impact on the accuracy of measured isotope ratios for low ion signals.

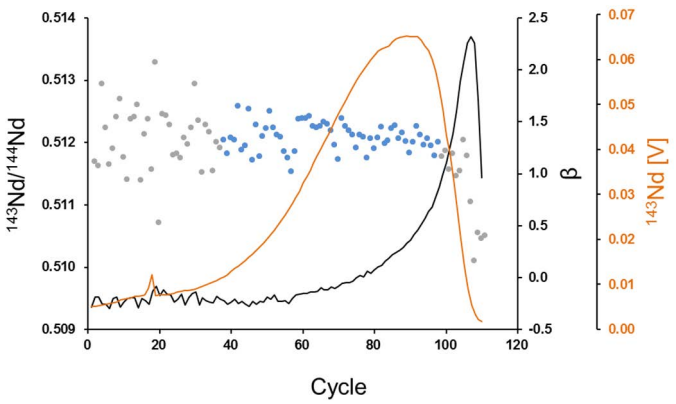


**Figure 3. Mass fractionation corrected $^{143}Nd/^{144}Nd$ ratios (blue and grey dots) and mass fractionation coefficient β (solid black line) of a representative sample.** Blue and grey dots represent ratios that were above or below the cutoff $^{143}Nd$ signal of 11 mV, respectively. The signal evolution (solid orange line) is shown for comparison.

Based on the considerations previously discussed, a minimum isotope signal ("cutoff signal") is defined to discard measurements with low signal/noise ratios and extreme fractionations. This cutoff signal should be the same for every measurement to ensure comparability between sample runs. In this study, a minimum $^{143}Nd$ signal of about 11 mV was defined, because it yielded in the best precision for the 13 samples investigated.

## 5. Conclusion

Within this study, the accuracy, precision and performance of the Thermo Scientific $10^{13}$ Ω amplifier technology was tested on small samples sizes of 100 pg Nd. Ten replicates of JNdi-1 yield a $^{143}Nd/^{144}Nd$ ratio of 0.512110 ± 0.000051 (2 SD), which agrees with previously published values on Nd loadings being 1,000 to 10,000 times higher. This level of precision is at least factor 10 better compared to ion counting measurements, and further benefits from a 100% duty cycle resulting in a greater number of ions being collected. The measurements also take advantage of software-based tau correction and gain calibration procedures. The long-term stability of the gain factors lead to a similar level of internal and external uncertainty, which is at the limit of counting statistics, and proves that the $10^{13}$ Ω amplifiers produce accurate data with a precision level that matches the theoretical limit, even for loading sizes of 100 pg. The Triton Plus TIMS utilizing the $10^{13}$ Ω amplifier technology significantly expands the isotope geochemist toolbox for measurements down to sample size ranges, which previously were inaccessible for high precision measurements.

## 6. Acknowledgments

Janne Koornneef and Matthew Jackson are thanked for fruitful discussions and providing the JNdi-1 standard solution.

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