SMART NOTE SN30439

# SmartNotes

## $10^{13}$ Ω amplifier technology: How low can you go?

### Introduction

Accurate and precise isotope ratio measurements of low intensity ion beams is a prerequisite for applications in isotope geochemistry and nuclear safeguards, in particular investigating minor isotope abundances and/or isotope variations among low sample sizes.

Until recently, small ion beams were measured on ion counters either in single-collector peak jumping or static multi-collection mode using a set of ion counters. Ion counters are characterized by exceptionally low noise levels, but are limited in their dynamic range. Furthermore, ion counters require frequent and precise determination of both their dead time (especially for measurements at high count rates) and element-specific yield. Given the uncertainty on these factors, typical isotope ratio precision levels between 0.2% and 0.4% (2 SD) can be achieved with ion counting measurements. Analytical challenges also arise from low duty cycles as well as signal fluctuations occurring during sequential single collector peak jumping methods, leading to high sample consumption and compromised precision and accuracy of the measured isotope ratios.

Faraday cups connected to Thermo Scientific™ $10^{13}$ Ω amplifier technology overcome the limitations of sequential single collector measurements by enabling low noise 100% duty cycle static multicollector measurements of low intensity ion beams. The proven long-term gain stability of Faraday cup measurements is now extended to the ion counting regime and is overcoming significant limitations like the need of frequent and element-specific detector cross-calibration. The dynamic range of the $10^{13}$ Ω amplifiers exceeds 30 Mcps (about 0.5 V, all signal voltages reported in this smart note refer to a $10^{11}$ Ω scale), i.e. an order of magnitude

higher than any ion counting system while the low noise levels enable static isotope ratio measurements down to precisions and accuracies of <0.1% (2 SD) at beam intensities of 30 kcps.

## How do I calibrate the $10^{13}$ Ω amplifiers?

With the new 3.3 pA current calibration board the gain calibration procedures are fully integrated into the electronic calibration network. Therefore, the gain factors and electronic baselines of all amplifiers available, i.e., $10^{10}$ Ω, $10^{11}$ Ω, $10^{12}$ Ω and $10^{13}$ Ω, can be calibrated conveniently by an automated software routine. This calibration board applies a current of 3.3 pA in positive mode and 1.2 pA in negative mode. The long-term stability of the amplifier gain factors are superior compared to ion counting systems such that calibration procedures are required only on a weekly basis. These gain factors are universally valid for any isotope system.

## How do I select an appropriate baseline integration time?

The uncertainty on the electronic baseline measurement decreases with increasing integration time (Figure 1). For a baseline integration time of 500 s the average uncertainty is ±0.54 µV (2 SD) for 10 individual and consecutively performed electronic baseline measurements. This translates to an uncertainty of 108 ppm (0.1‰; 2 SD) on an isotope signal of 5 mV. For high-precision isotope ratios on small signal beams we recommend an integration time of at least 300 seconds.

## What is the level of long-term precision and stability for gain factors and electronic baselines?

The measured detector noise of the Thermo Scientific $10^{13}$ Ω amplifiers is better than 0.7 µV/24 h (2 SD; Figure 2) resulting in a quantification limit (defined as 5xSD) of 3.5 µV (219 cps). 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; Figure 2).

## How does the signal/noise ratio of $10^{11}$ Ω and $10^{13}$ Ω amplifiers compare?

The average amplifier noise of the $10^{11}$ Ω and $10^{13}$ Ω amplifiers is in the order of 3 µV and 0.4 µV (2 SD, 20 minutes integration time), respectively. The improvement of the baseline noise on the $10^{13}$ Ω amplifiers almost matches the theoretical prediction of factor $\sqrt{100}$ derived from the

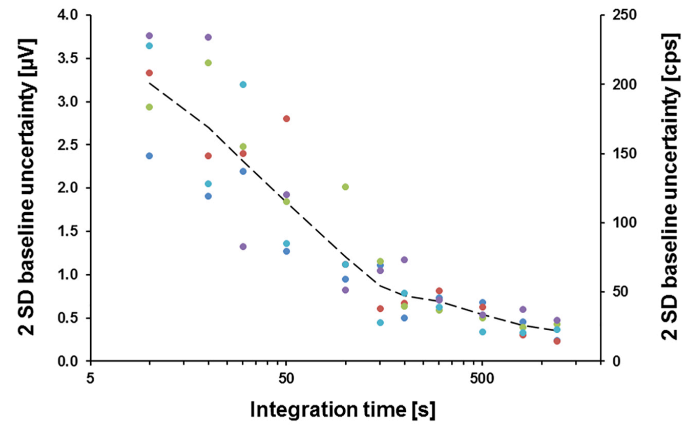


**Figure 1. Uncertainty (2 SD) on 10 individual and consecutively performed electronic baseline measurements of different integration times. Different colors refer to different $10^{13}$ Ω amplifiers installed on the Thermo Scientific™ Triton Plus™ TIMS at the demo facility in Bremen. The average 2 SD baseline uncertainty of all amplifiers is indicated by the dashed line.**

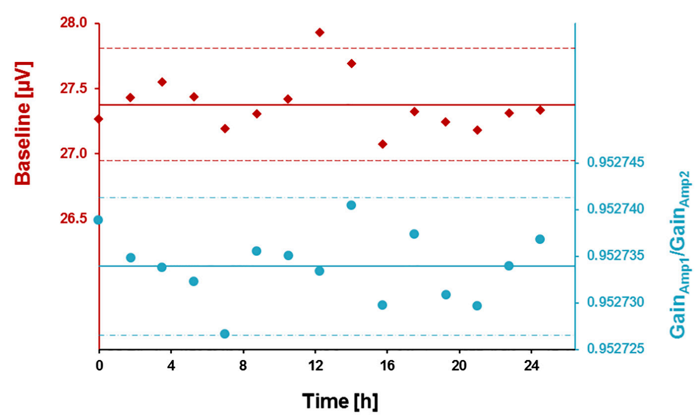


**Figure 2. Electronic baseline and gain factor measurements performed with $10^{13}$ Ω amplifiers within a time interval of 24 h. The 24 h baseline stability is 0.43 µV (red diamonds; 2 SD; Pre baseline wait time is 30 seconds; baseline integration time is 300 seconds). The 24 h inter-channel gain stability is 7.4 ppm (blue dots; 2 SD; Integration time for each gain measurement is 300 seconds; calibration current is 3.3 pA). Thick solid lines represent average baseline and gain factor values; thin dashed lines represent 2 SD of the mean.**

Johnson–Nyquist noise. Assuming an isotope signal of 10 mV the signal/noise ratio for $10^{11}$ Ω and $10^{13}$ Ω amplifiers are about 3500 and 28000, respectively.

## For which instruments is the 3.3 pA current calibration board recommended?

The 3.3 pA current calibration board is recommended for Thermo Scientific™ Triton Plus™ TIMS and an option for Thermo Scientific™ Neptune Plus™ MC-ICP-MS instruments equipped with $10^{13}$ Ω amplifier technology.

The Thermo Scientific virtual amplifier system ensures no compromise for the high precision isotope measurement on high isotope signals (in the range of several V) using the $10^{11}$ Ω amplifiers. Specifically, accurate Sr and Nd isotope ratios with external reproducibilities of < 10 ppm (2 RSD) can be achieved. The use of amplifier rotation during the measurement is implemented in most methods on the Triton Plus TIMS and therefore the 3.3 pA current calibration board is recommended when using $10^{13}$ Ω amplifiers on this instrument. Isotope measurements on the Neptune Plus MC-ICP-MS usually do not use amplifier rotation, because isotope ratios are either corrected by sample standard bracketing or are too short, like for LA-ICP-MS. For customers having their focus on these methods the 3.3 pA current calibration board is not recommended. However, nuclear industry customers working with $10^{13}$ Ω amplifiers on a Neptune Plus MC-ICP-MS benefit from the convenient automated software gain calibration routine without having any compromise in terms of precision and accuracy on isotope ratios of nuclear materials.

**Which level of precision can I expect for my isotope ratios?**

The isotope system of neodymium (Nd) is used to demonstrate the precision and accuracy of $10^{11}$ Ω and $10^{13}$ Ω amplifier set-ups with the new 3.3 pA current calibration board. Results for all signal intensities are accurate and within the estimates of the error propagation from combined counting statistics and baseline noise uncertainties (Figure 3; Table 1). Accordingly, by combining counting statistics and baseline noise uncertainties predictions on the measurement uncertainty on other isotope systems can be made. The level of precision depends on the signal intensity. With this $10^{13}$ Ω amplifier configuration accurate $^{143}Nd/^{144}Nd$ ratio results within a precision level of 0.35‰ (2 RSD) are achieved for $^{143}Nd$ signals of only 1 mV/~63 kcps (Figure 3; Table 1). For $^{143}Nd$ signals higher than 40 mV the $^{143}Nd/^{144}Nd$ precision is better than 34 ppm (2 SD; Table 1).

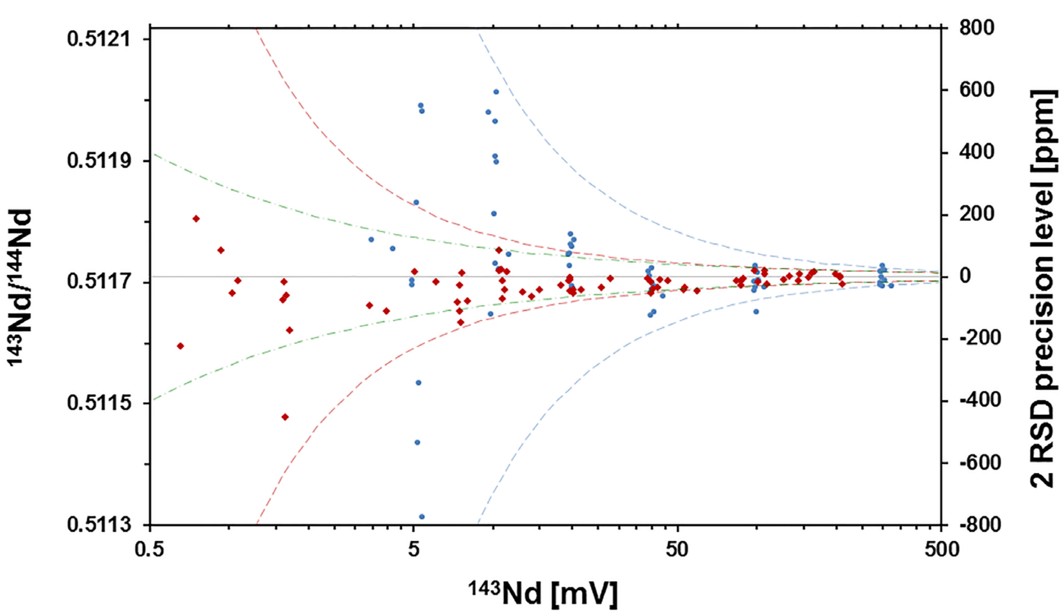


Figure 3. $^{143}Nd/^{144}Nd$ isotope ratios of an Nd single element solution measured at different $^{143}Nd$ signal intensities. All ratios were normalized to $^{146}Nd/^{144}Nd$ of 0.7219 using the exponential mass fractionation law. Each measurement consists of 200 cycles with integration time of 8.389 seconds (blue dots and red diamonds for measurements made with a $10^{11}$ Ω and $10^{13}$ Ω amplifier set-up, respectively). Outliers were rejected using the two sigma criterion. Dashed blue and dashed red lines represent the uncertainty estimate based on amplifier baseline noise and counting statistic uncertainty error propagation (2 SD) respectively. The dashed-dotted green lines represent the counting statistics from shot noise (2 SD).

Table 1. Results from Nd isotope measurements on a single element Nd solution performed on a Triton Plus Multicollector TIMS equipped with the 3.3 pA current calibration board. The uncertainty of 2 SD refers to 10 out of 12 filament measurements at the same signal intensity. Each measurement consists of 200 cycles with 8 second integration time. 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. The average $^{143}Nd/^{144}Nd$ ratios of all series of measurements overlap with the accuracy range of this single element solution of 0.511725 - 0.511745.

| | $10^{13}$ Ω amplifier | | | $10^{11}$ Ω amplifier | | |
|---|---|---|---|---|---|---|
| $^{143}Nd_{start}$ [mV] | $^{143}Nd/^{144}Nd$ | 2 SD | 2 RSD [ppm] | $^{143}Nd/^{144}Nd$ | 2 SD | 2 RSD [ppm] |
| 1 | 0.511692 | 0.000179 | 350 | | | |
| 5 | 0.511700 | 0.000058 | 113 | 0.511724 | 0.000441 | 863 |
| 10 | 0.511726 | 0.000051 | 99 | 0.511865 | 0.000255 | 498 |
| 20 | 0.511718 | 0.000019 | 37 | 0.511759 | 0.000069 | 134 |
| 40 | 0.511717 | 0.000017 | 33 | 0.511712 | 0.000053 | 103 |
| 100 | 0.511730 | 0.000018 | 34 | 0.511723 | 0.000045 | 89 |
| 200 | 0.511733 | 0.000012 | 24 | | | |
| 300 | — | — | — | 0.511731 | 0.000025 | 49 |
| 1000 | — | — | — | 0.511733 | 0.000009 | 17 |
| 3000 | — | — | — | 0.511733 | 0.000004 | 7.5 |

**Which detection system works best for my method?**

The low noise Thermo Scientific $10^{13}$ Ω amplifier technology is bridging the gap between ion counting measurements and $10^{11}$ Ω Faraday cup measurements. The optimum detection system depends on the signal intensity of the measured isotopic system. Specifically, the lowest abundant isotope limits the precision on the isotope ratios. For a three isotope system like Nd, where the masses $^{143}Nd$ (12.2% natural abundance), $^{144}Nd$ (23.8%) and $^{146}Nd$ (17.2%) are commonly used in calculating $^{143}Nd/^{144}Nd$ isotope ratios, a static Faraday detection system connected to $10^{13}$ Ω amplifiers is optimum for $^{143}Nd$ intensities between 0.5 and 200 mV. For lower signals single collector peak jumping or static multi collection may yield higher precision levels, but may require longer analysis time due to lower duty cycles.

**Conclusion**

Low noise static multicollector Faraday measurements with Thermo Scientific $10^{13}$ Ω amplifier technology facilitates enhanced precision and shortened analysis time on small sample loading sizes. They are key to realize the most precise and accurate data, by eliminating the systematic non-linearities seen for ion counters caused by detector biases and dead time effects. With the newly available 3.3 pA current calibration board the gain factors can be calibrated conveniently and simultaneously by an automated software calibration routine. The long-term baseline and inter-channel gain stability is measured to be better than 0.7 µV and 15 ppm (2 SD) respectively. For a three isotope systems such as Nd or Sr, significant improvements in precision and accuracy are achieved for isotope signals between 0.5 and 200 mV. For Nd, precision levels of 34 ppm (2 RSD) are achieved for $^{143}Nd$ signals higher than 40 mV and are still within 0.35‰ (2 RSD) for $^{143}Nd$ signals of only 1 mV.

**Authors and contact information**

Hauke Vollstaedt*, Grant Craig, Nicholas Lloyd, Johannes Schwieters, and Claudia Bouman, Thermo Fisher Scientific, Bremen, Germany.

*Corresponding author: hauke.vollstaedt@thermofisher.com.

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