

Improvements in TIMS High Precision Isotope Ratio Measurements for Small Sample Sizes

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Key Words

- Thermo Scientific TRITON
- $10^{12} \Omega$ Amplifiers
- Small Sample Sizes
- TI-MS

Introduction

The TIMS analysis of samples as small as a few pico grams is limited by the analytical blank, possible molecular interferences and, last but not least, by the noise of the Faraday detectors. Improvements in sample preparation can help to reduce the blank and interference problems, but a reduction in the detector noise requires instrumental improvements.

Ultimately, Multi-Ion-Counting (MIC) resolves the noise problem. However, the use of this technique is limited by other restrictions: uncertainties in channel cross calibration, possible non-linearity, instability, and the limited dynamic range of the ion counters. There certainly remains a gap in the dynamic range, where ion-counters are not good enough anymore because of their specific limitations, and Faraday cup detectors are limited due to noise.

In this study, we aim to narrow the gap between ion counting and Faraday cup measurements by using a new set of current amplifiers with Tera-Ohm feedback resistors ($10^{12} \Omega$), instead of the standard $10^{11} \Omega$ feedback resistors. The larger resistor results in a 10 times higher gain of the amplifiers, but at the same time the Johnson noise of the resistor only increases by square root of 10.

This promises a 3-fold improvement in signal/noise by using Tera-Ohm amplifiers in Faraday-cup measurements. This assumption was tested and proven in a series of neodymium analyses with signal intensities ranging from 50 mV (3,000,000 cps) down to 0.5 mV (30,000 cps).

The Virtual Amplifier Measurement System: Switchable Amplifiers with Different Gains

The current amplifiers of the Thermo Scientific TRITON TIMS instrument are installed in an evacuated and temperature stabilized housing. Up to 10 current amplifiers with different gains ($10^{10} \Omega$, $10^{11} \Omega$ and $10^{12} \Omega$) can be installed simultaneously. In this study, the amplifier box was loaded with four $10^{12} \Omega$ amplifiers and six standard $10^{11} \Omega$ amplifiers.

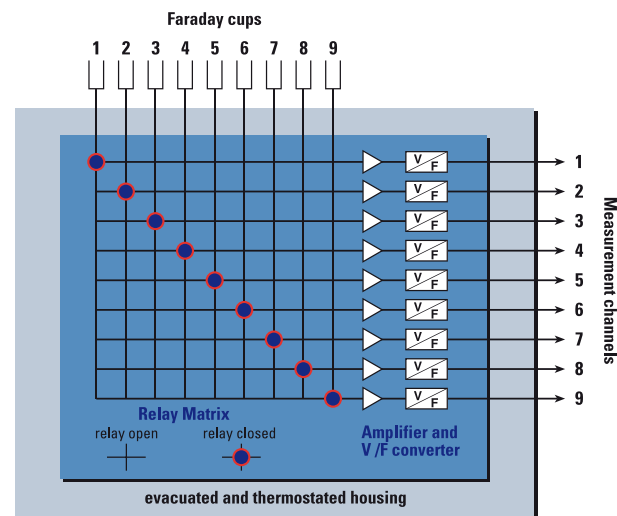
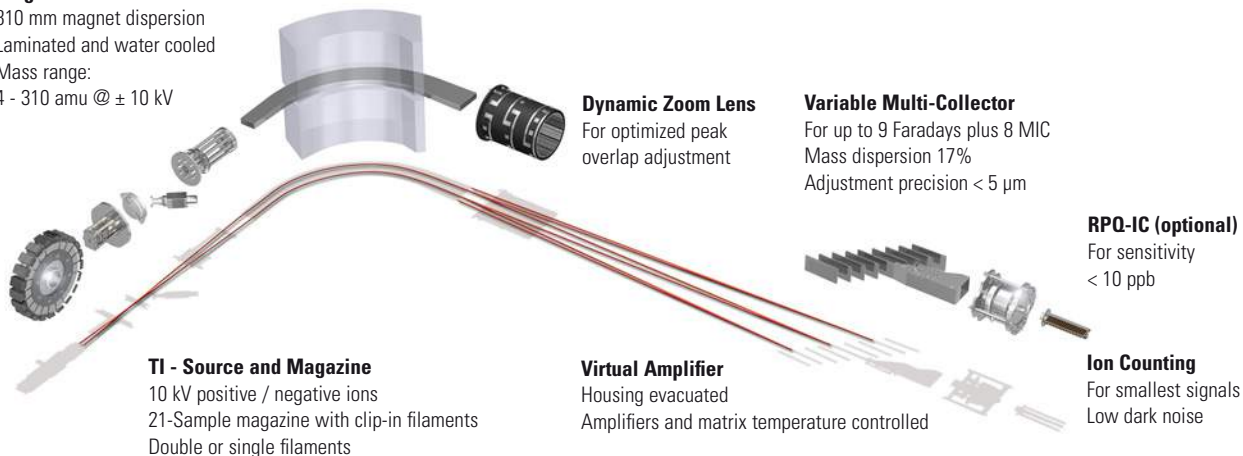


Figure 2: Virtual amplifier system.

Unique to the design of the TRITON a relay matrix connects the amplifier array to the Faraday cup array. The connection scheme between the amplifiers and the Faraday cups is software controlled. This enables the user to tailor the amplifier configuration to the needs of the current analytical task and its required precision.

Magnet

810 mm magnet dispersion
Laminated and water cooled
Mass range:
4 - 310 amu \pm 10 kV



TI - Source and Magazine
10 kV positive / negative ions
21-Sample magazine with clip-in filaments
Double or single filaments

Dynamic Zoom Lens
For optimized peak overlap adjustment

Variable Multi-Collector
For up to 9 Faradays plus 8 MIC
Mass dispersion 17%
Adjustment precision < 5 μ m

RPO-IC (optional)
For sensitivity < 10 ppb

Virtual Amplifier
Housing evacuated
Amplifiers and matrix temperature controlled

Ion Counting
For smallest signals
Low dark noise

Figure 1: Ion optical layout of the TRITON and its main components.

Strategy for the Measurement of Small Signal Intensities on Faraday Cups

The Faraday cup baselines usually are frequently measured during the run, and their reproducibility typically is in the range of 5 - 10 μV , assuming integration times of 30 - 60 seconds. For signal intensities of 1 mV, this would limit the attainable precision and accuracy to about 0.5% to 1%.



Figure 3: Electrical baselines of amplifiers are determined before and after the analysis to get most accurate readings ($< 1 \mu\text{V}$).

Instead of performing the baseline measurement frequently during the run we propose a long baseline measurement before the run and directly after. The full emission profile of the sample is then measured without wasting time and without wasting any sample during baseline integration. The precision of the long baseline measurement is much better since it is based on a longer evaluation time. Ultimately, the baseline measurement should be as long as the sample measurement to minimize the baseline uncertainty.

Stability of Baseline Measurements

The long baseline method proposed here requires a reasonable stability over the total time of measurement. The plot in Figure 4 shows the baseline stability of a standard $10^{11} \Omega$ amplifier over time. For each data point, the baseline has been averaged over an integration time of $\sim 840 \text{ s}$.

The stability appears to be sufficient for this kind of resistor, and there is almost no drift detectable. The reproducibility can be calculated to $\sim 2.5 \mu\text{V}$ (1σ).

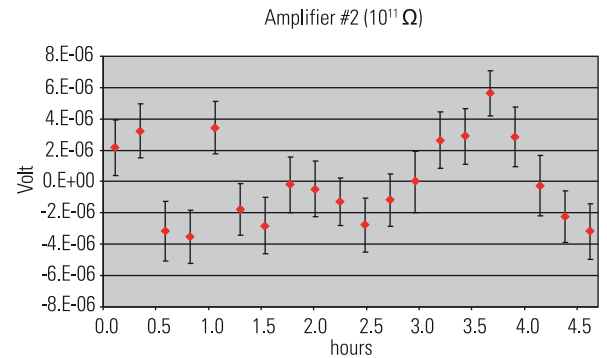


Figure 4: Baseline stability of a standard $10^{11} \Omega$ amplifier.

For comparison, simultaneously recorded baseline data are shown in Figures 5 a-d for $10^{12} \Omega$ amplifiers. The reproducibility is significantly improved by about a factor of four to $\sim 0.6 \mu\text{V}$ (1σ). The improved reproducibility and the excellent stability of the baseline of the $10^{12} \Omega$ amplifiers support the long baseline approach instead of measuring multiple baselines with reduced individual precision during the run.

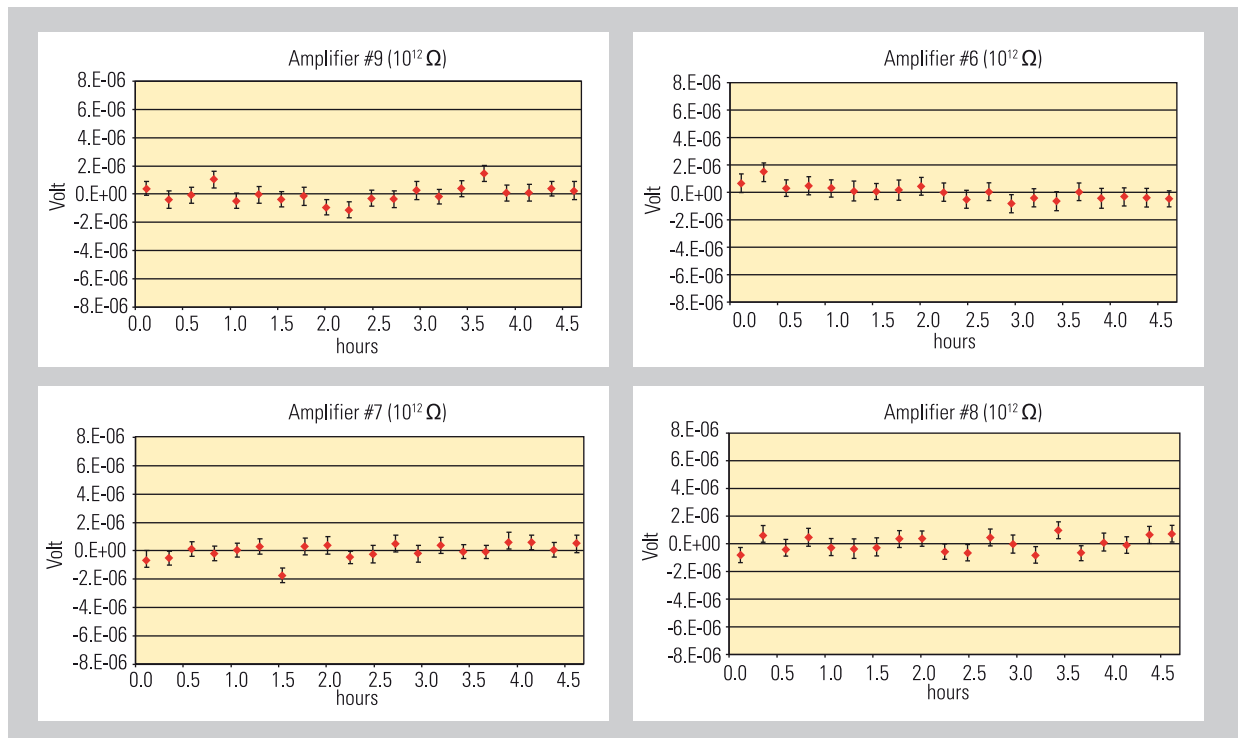


Figure 5a-d: Long term baseline stability of the $10^{12} \Omega$ amplifiers.

Test Measurements and Results: Neodymium at Different Intensities

A “Merck” Neodymium sample was measured at six different ^{144}Nd intensities, ranging from 50 mV down to 1.5 mV. The isotopes ^{142}Nd , ^{143}Nd , ^{144}Nd and ^{146}Nd were detected using $10^{12}\ \Omega$ amplifiers. For comparison, the ^{145}Nd isotope was measured with the standard $10^{11}\ \Omega$ amplifier. Before and after each run, a long baseline measurement was performed. For data evaluation, the mean of both baseline readings was applied. All data are corrected for mass fractionation by normalization to $^{146}\text{Nd}/^{144}\text{Nd}$. Each run lasted about 20 minutes. The signal intensity was rather constant over this period of time.

The data shown in Figures 6a and 6b were collected using only $10^{12}\ \Omega$ amplifiers (^{142}Nd , ^{143}Nd , ^{144}Nd , ^{146}Nd used for normalization). All data points perfectly overlap within the internal precision limits of each run. At 50 mV signal intensity (^{144}Nd), internal precisions of about 35 ppm (1σ , SE) are achieved. The corresponding ^{143}Nd signal intensity is about 25 mV.

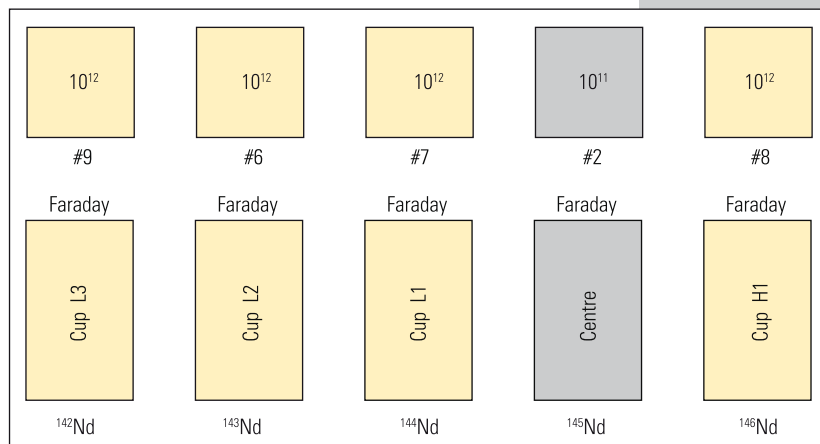


Figure 8: Faraday detectors, cup configuration, and corresponding amplifiers which were used for the Nd-measurements.

Assuming, that the internal precision is determined by the noise of the amplifier, one can estimate the corresponding noise level as follows:

$$25\ \text{mV} \times 35\ \text{ppm} = 0.9\ \mu\text{V}.$$

This is in good agreement with the baseline uncertainty of the $10^{12}\ \Omega$ amplifiers, which has been determined to be $0.6\ \mu\text{V}$ for one amplifier over an integration time period of about 20 minutes. Even for a 10 mV signal (^{144}Nd), i.e. 5 mV on ^{143}Nd , an internal precision of about 120 ppm is achieved. Assuming again that the internal precision is controlled by the noise of the amplifier, one can estimate the corresponding noise level to be:

$$5\ \text{mV} \times 120\ \text{ppm} = 0.6\ \mu\text{V}.$$

This again is in perfect agreement with the typical noise level of the $10^{12}\ \Omega$ amplifiers. At a signal intensity of only 3 mV (^{144}Nd), i.e. 1.5 mV on ^{143}Nd , an internal precision of ~ 380 ppm is achieved. This also corresponds to a noise of just $0.6\ \mu\text{V}$ using 20 minutes integration time.

Finally, at ~ 1.5 mV (^{144}Nd) and 0.75 mV on ^{143}Nd , the internal precision is about 800 ppm, which again corresponds to a noise amplitude of $\sim 0.6\ \mu\text{V}$.

For comparison, data of $^{145}\text{Nd}/^{144}\text{Nd}$ using one $10^{11}\ \Omega$ amplifier are shown in Figure 7. The error bars relative to the mean shown here are about three times larger compared to the measurements using the $10^{12}\ \Omega$ amplifiers.

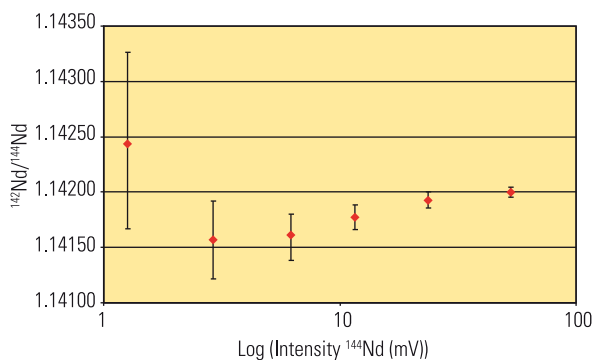


Figure 6a: $^{142}\text{Nd}/^{144}\text{Nd}$ using a $10^{12}\ \Omega$ amplifier.

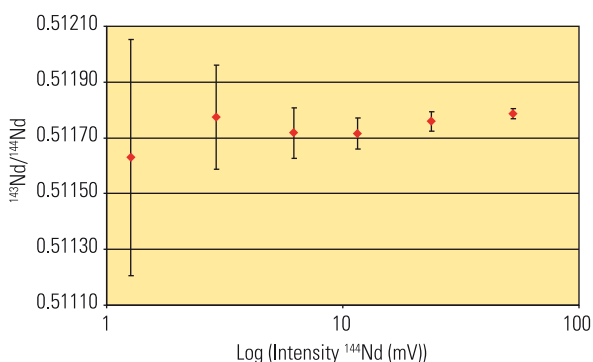


Figure 6b: $^{143}\text{Nd}/^{144}\text{Nd}$ using a $10^{12}\ \Omega$ amplifier.

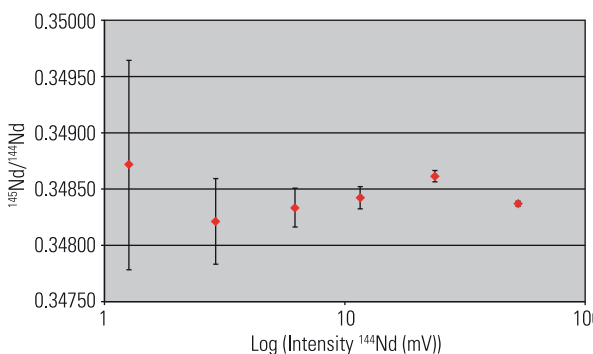


Figure 7: $^{145}\text{Nd}/^{144}\text{Nd}$ using one $10^{11}\ \Omega$ amplifier.

Conclusion and Summary

The noise level of the $10^{12} \Omega$ amplifiers is a factor of three lower when compared to the standard $10^{11} \Omega$ amplifiers. For signal intensities of less than 50 mV, the reduced noise characteristics of the $10^{12} \Omega$ amplifiers show clear advantages.

For a 20 minute integration, the noise level is down to about 0.6 μ V. This allows for the measurement of 1 mV (i.e. 60,000 cps) signal intensities with sub-permil precision (1σ).

Given the limitations of Multi-Ion-Counting (linearity, stability, cross calibration), the $10^{12} \Omega$ amplifiers efficiently reduce the gap between ion counting detectors and Faraday cup measurements.

The only drawback of the $10^{12} \Omega$ amplifier is the slow response time. Compared to the standard $10^{11} \Omega$ amplifiers, the time constant is increased by a factor of 3 to 5. However, for the precise measurement of rather stable ion beam intensities, this is only a minor limitation.



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