

New Design $10^{13} \Omega$ Amplifiers for the Analysis of Noble Gases

Alessandro Santato,¹ Doug Hamilton,¹ Claudia Bouman¹ and Jan Wijbrans²

¹Thermo Fisher Scientific, Bremen, Germany

²VU University Amsterdam, Faculty of Earth and Life Sciences, Amsterdam, The Netherlands

Keywords

Helix MC Plus, Noble Gas Analysis, $10^{13} \Omega$ Amplifier Technology, Ar/Ar, High Resolution

Goal

To test the performance of new high gain amplifiers equipped with $10^{13} \Omega$ feedback resistors on the Thermo Scientific Helix MC Plus Multicollector Noble Gas Mass Spectrometer.

Introduction

On Earth noble gases are present as rare elements and in most of the cases their concentration within samples is extremely low. Therefore, isotope ratio analysis requires a high detection efficiency which implies ultra high vacuum mass spectrometers able to operate in static mode coupled to extremely sensitive detectors. Here we present a comparison between the newly developed $10^{13} \Omega$ amplifiers and the current state-of-the-art $10^{12} \Omega$ amplifier technology for the analysis of $^{40}\text{Ar}/^{36}\text{Ar}$.

Methods

Mass Spectrometry

The Thermo Scientific™ Helix MC™ Plus Multicollector Noble Gas Mass Spectrometer (Figure 1) is the ultimate solution for noble gas analysis. Equipped with a high-resolution magnetic sector analyzer and with a variable multicollector array, which incorporates five Combined Faraday Multiplier (CFM) detectors, enables you to analyze up to five isotopes of neon, argon, krypton and xenon simultaneously, at new levels of resolution.



Figure 1. Thermo Scientific Helix MC Plus Noble Gas MS (right) and NG Prep System (left).

One of the key features of the Helix MC Plus Noble Gas MS is its high resolution capability. The instrument utilizes a large radius geometry and is capable to achieve a valley resolution >1500 and a resolving power >5000 (routinely >7000) when using the high resolution entrance slit. This enables complete resolution of ^{36}Ar from the hydrocarbon interference $^{12}\text{C}_3$ (Figure 2).

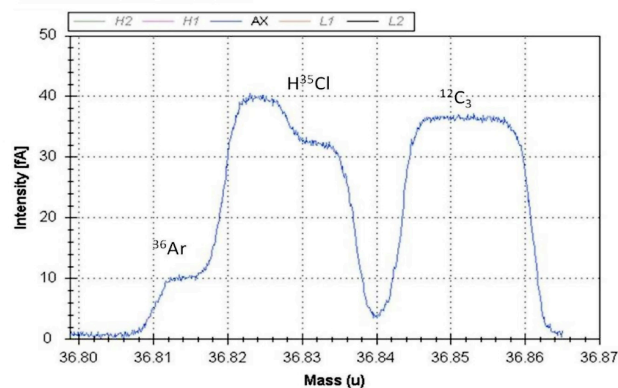


Figure 2. Complete resolution of ^{36}Ar from the hydrocarbon interference $^{12}\text{C}_3$ and partial resolution from the H^{35}Cl .

Sample Preparation

Argon from atmospheric air was prepared with the Thermo Scientific™ NG Prep System™ and used as standard for all the tests.

Circa 2.4×10^{-13} mol of argon were repeatedly analyzed using two different collector configurations.

Collector Configurations

^{40}Ar and ^{36}Ar were analyzed using two different multicollector modes, see Table 1.

Table 1. Scheme showing the two different multicollector settings used in this work.

MC - Set	H2	L2
	^{40}Ar	^{36}Ar
1	Faraday ($10^{11} \Omega$)	Faraday ($10^{12} \Omega$)
2	Faraday ($10^{11} \Omega$)	Faraday ($10^{13} \Omega$)

^{40}Ar was analyzed on a Faraday cup coupled with a $10^{11} \Omega$ amplifier. ^{36}Ar was analyzed on two different detectors: a Faraday cup coupled with a $10^{12} \Omega$ amplifier and a Faraday cup coupled with a $10^{13} \Omega$ amplifier.

Data Analysis

Thermo Scientific Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used for data acquisition and control software.

Results

The decisive improvement in internal precision of the new amplifier is due to the better signal/noise ratio. In fact, the output voltage V of an amplifier depends on the value R of the associated resistor. Therefore, if we pass from a $10^{12} \Omega$ to a $10^{13} \Omega$ resistor we will increase the sensitivity by a factor of 10. Also the electrical Johnson-Nyquist noise of the associated resistor will increase, but only by a factor of $\sqrt{10}$. This allows the new amplifier to have an improvement in the signal/noise ratio of circa 3 times if compared to the $10^{12} \Omega$ amplifiers. To illustrate this we measured the electronic baseline for a period of 9 hours on both $10^{12} \Omega$ and $10^{13} \Omega$ Amplifier (Figure 3).

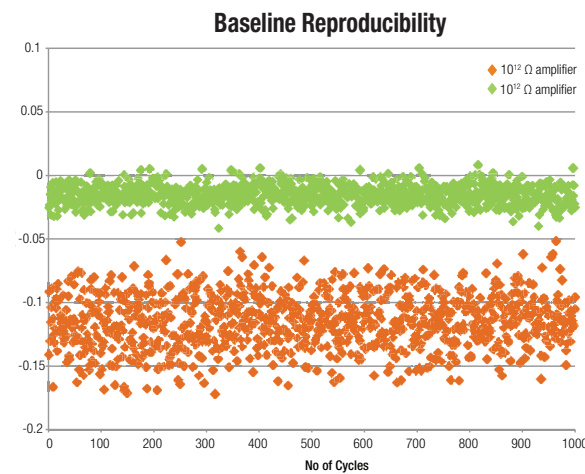


Figure 3. Electronic baseline measured on $10^{12} \Omega$ and $10^{13} \Omega$ amplifiers over 9 hours using an integration time of 33.55 seconds.

Figure 4 shows the reproducibility for $^{40}\text{Ar}/^{36}\text{Ar}$, where ^{36}Ar (beam intensity ~ 3.6 fA, corresponding to 22500 cps) is measured on 10^{12} and 10^{13} ohm Amplifiers. Also internal precision is plotted. The internal precision achieved for $^{40}\text{Ar}/^{36}\text{Ar}$, using the $10^{12} \Omega$ amplifier for the ^{36}Ar , gave values ranged from 0.4-1% (1 RSE) whereas using the new $10^{13} \Omega$ amplifier, used for ^{36}Ar , we were able to achieve internal precision ranging from 0.1-0.4% (1 RSE).

On a 15-sample run the ratio $^{40}\text{Ar}/^{36}\text{Ar}$, using the $10^{12} \Omega$ amplifier for ^{36}Ar , gave a value of 308.9 ± 0.90 (1 SD) whereas with the new $10^{13} \Omega$ amplifier, used for ^{36}Ar , $^{40}\text{Ar}/^{36}\text{Ar}$ was 308.9 ± 0.55 (1 SD).

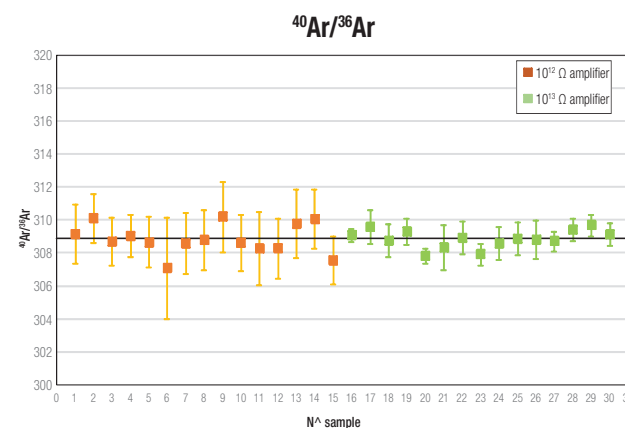


Figure 4. $^{40}\text{Ar}/^{36}\text{Ar}$ AIR. Comparison between Faraday $10^{11} \Omega$ amplifier/ Faraday $10^{12} \Omega$ amplifier and Faraday $10^{11} \Omega$ amplifier/ Faraday $10^{13} \Omega$ amplifier.

The $^{40}\text{Ar}/^{36}\text{Ar}$ ratio was also measured using different aliquots of argon between 10^{-13} and 10^{-14} moles. In Figure 5 is possible to see the improvement in internal precision for the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio measured at different sample size by using the $10^{11} \Omega/10^{13} \Omega$ configuration versus the conventional $10^{11} \Omega/10^{12} \Omega$.

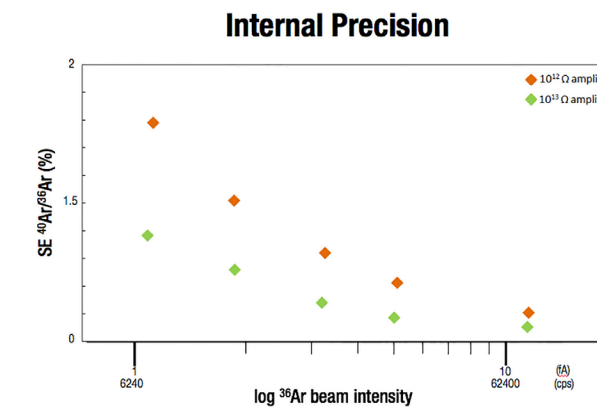


Figure 5. Internal precision (1SE%) as a function of beam intensity on measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratio. Mass 40 was collected on a $10^{11} \Omega$ amplifier while mass 36 was collected both using a $10^{12} \Omega$ and $10^{13} \Omega$ amplifier.

Calibration of the $10^{13} \Omega$ Amplifier

The electronic gains of the $10^{13} \Omega$ amplifier can be calibrated against the other detectors by using the cross-calibration automatic procedure present on the instrument control of the operating software Thermo Scientific Qtegra ISDS Software.

The $10^{13} \Omega$ amplifiers can also be calibrated by measuring the isotopic ratio of a reference gas.

Conclusion

The improved signal/noise of the new amplifiers equipped with a $10^{13} \Omega$ feedback resistor represents a decisive improvement in small sample analysis. Compared with a $10^{12} \Omega$ amplifier, the improvement in the internal precision on the $^{40}\text{Ar}/^{36}\text{Ar}$ reaches a factor of almost 3.

The external precision is also improved. In the $^{40}\text{Ar}/^{36}\text{Ar}$ measurement the new $10^{13} \Omega$ amplifier is capable of achieving a relative standard deviation of 0.18%, which represents a significant progress if compared with $10^{12} \Omega$ amplifier (RSD of 0.29%).

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