Application Note: 30193

Argon Isotope Ratio Measurements using Different Detector Strategies

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Key Words

- ARGUS VI Collector
- Isotope Ratio Mass Spectrometer
- Ion Counting
- Faraday Cups
- Cross Calibration

Introduction

Argon isotope abundances vary over a large dynamic range which presents a special challenge for the design and configuration of the detector system of any argon isotope ratio mass spectrometer

For large sample sizes, a Faraday cup array employing standard 10^{11} Ω amplifiers is the preferred detector. For medium-sized samples, the Faraday cups used to detect the minor isotopes can be equipped with a higher gain 10^{12} Ω amplifier, which improves the signal to noise ratio and results in excellent precision. For smaller sample, the minor isotopes are measured on an ion counting detector while the major ^{40}Ar beam is still best measured on a Faraday cup detector. For the smallest sample sizes, sequential single collector peak jumping measurements on an ion counting channel is the method of choice. Measuring intensities on the same ion counting collector eliminates all cross calibration and gain drift issues because of the cancellation of the actual gains. The performance of the Thermo Scientific ARGUS VI for different sample sizes is documented, using analysis of air shots.

Experimental Setup

The ARGUS VI is built on a new electronic platform utilizing field-proven hardware from other Thermo Scientific isotope ratio mass spectrometers (DELTA V, MAT 253, TRITON, NEPTUNE) making it an integrated part of the Thermo Scientific isotope ratio MS family. For instance, the Argus VI uses the newly developed CDD (compact discrete dynode) multiplier technology utilized in the TRITON *Plus* and NEPTUNE *Plus* multicollector platforms and the 50 V dynamic range Faraday cup detector technology used in all of the current isotope ratio mass spectrometers. The software is built on a new platform which provides flexible instrument control as well as dedicated data evaluation.

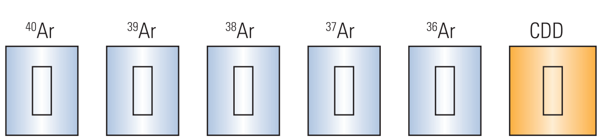

Figure 1: Layout of the ARGUS VI collector: Five Faraday cups plus one new Compact Discrete Dynode (CDD) multiplier.

The ARGUS VI collector array includes 5 Faraday detectors for simultaneously measurement of all argon isotopes, with either 10^{11} Ω or 10^{12} Ω electronically cross-calibrated amplifiers. The dynamic range of the Faraday detection system extends up to 50 V. The number VI collector is a Compact Discrete Dynode (CDD) multiplier providing uncompromised single collector peak jumping measurements of the smallest samples.

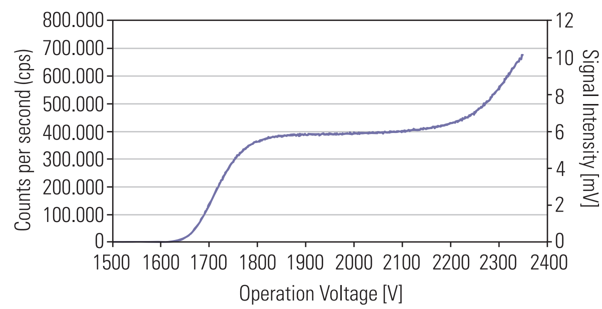

Figure 2: Plateau curve of the new CDD multiplier showing excellent counting characteristics with an extended counting plateau.

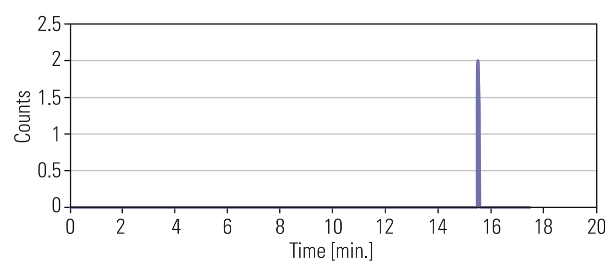

Figure 3: Dark noise counts over time. Total measurement time is about 18 min and in total there are 2 counts detected yielding a dark noise rate of less than 0.2 counts per minute.

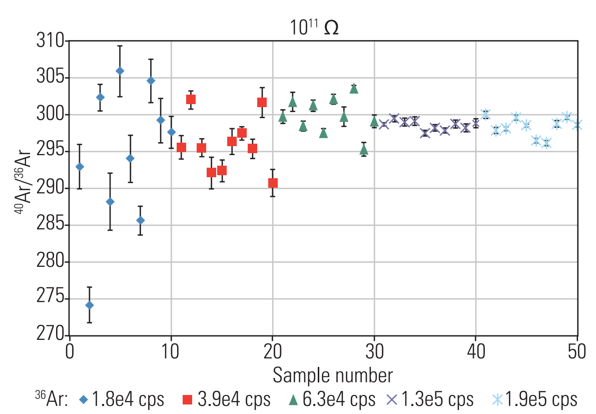

Figure 4: Compilation of measured argon isotope ratios of 5 different air shot gas quantities using 10^{11} Ω amplifiers. ^{36}Ar intensities are in the range of 3 x 10^{-15}A to 3 x 10^{-14}A, i.e. 20 kcps to 200 kcps.

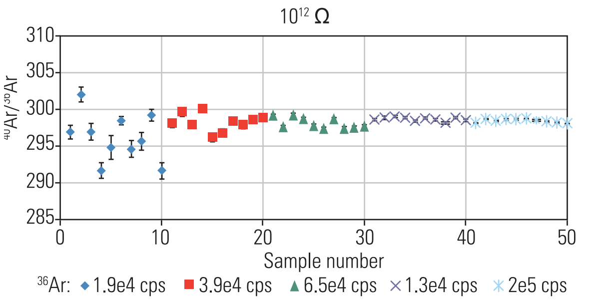

Figure 5: Compilation of measured argon isotope ratios of 5 different air shot gas quantities using 10^{12} Ω amplifiers. ^{36}Ar intensities are in the range of 3 x 10^{-15} A to 3 x 10^{-14} A, i.e. 20 kcps to 200 kcps.

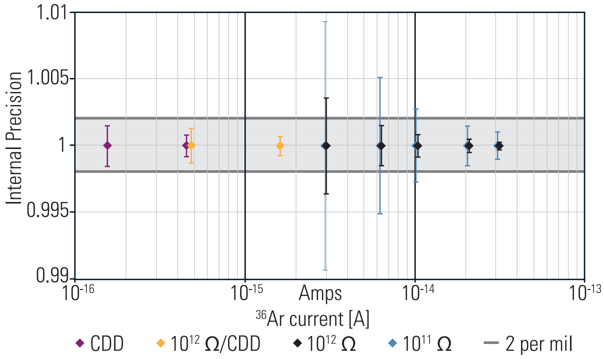

Figure 6: In run standard errors of multicollector Faraday cup measurements and single collector ion counting measurements at different sample sizes.

Results and Discussion

Five different Ar air shot quantities in the range of 3.5 x 10^{-14} mol to 4.2 x 10^{-13} mol prepared in the Thermo Scientific Noble Gas Prep Bench were introduced into the ARGUS VI Noble Gas Mass Spectrometer. For each intensity, a series of 10 runs was measured to acquire data sufficient to calculate the reproducibility for different sample sizes. The detected ^{36}Ar ion current measured in the Faraday cup varied in the range of 2.7 x 10^{-15} A (20 kcps) for the smallest sample size to 3 x 10^{-14} A (200 kcps) for the largest sample size. Each sample was measured for 400 s static data acquisition.

As a comparison, the five different sample batches have been measured with both 10^{11} Ω and 10^{12} Ω amplifiers. The smaller noise level of the high gain 10^{12} Ω amplifier results in smaller (by a factor of 2-3) error bars in comparison to the 10^{11} Ω amplifier (see Figures 4 and 5). In order to explore the performance and the precision achievable with the ion counter, the sample size was further reduced yielding intensities on ^{36}Ar in the range of 1,000 cps to 10,000 cps. The measurement time for each run was 400 s as well.

In Figure 6 the analytical precision of the ion counter measurements is plotted together with the internal precision of the Faraday cup measurements of Figure 4 and 5 for the different ^{36}Ar ion currents.

Figure 6 summarizes the internal precision achieved with the 4 different detector strategies:

1) Multicollector Faraday cup measurements using all 10^{11} Ω amplifier (light blue data points).
2) Multicollector Faraday cup measurements using all 10^{12} Ω amplifier (black data points).
3) Single collector peak jumping measurement with ^{40}Ar measured on a Faraday cup (10^{12} Ω amplifier) and ^{36}Ar measured on the ion counter (orange data points).
4) Single collector peak jumping measurement with ^{40}Ar and ^{36}Ar measured on the ion counter (purple data points).

In the low count rate regime, the signal to noise of the ion counting detector is a major improvement over analog Faraday cup measurements. The error bars in Figure 6 reflect the attainable internal precision of a run limited by signal/noise.

However, considering the external accuracy, the uncertainties due to detector cross calibration, detector linearity and detector stability of the ion counting channel have to be considered. A rough estimate of these uncertainties, a grey bar indicating an uncertainty of 0.2% (1 sigma) is shown in Figure 6. Improved accuracy may be possible but they will require extended cross calibration and precise dead time corrections of the ion counting data. These problems are not present in measurements made on Faraday cup, which are electronically cross-calibrated and which show linearity and robustness over a large dynamic range. For ion counting measurements, uncertainties due to cross calibration, linearity and stability of the ion counter can limit the attainable external precision in the range of 0.2%.

Summary and Conclusion

- The Thermo Scientific ARGUS VI collector array has proven performance for Ar sample sizes ranging from 2 x 10^{-15} to 3 x 10^{-13} mols.
- The Faraday cup array provides the best external and internal precision for sample sizes down to 5 x 10^{-14} mol.
- The new Compact Discrete Dynode (CDD) multiplier extends the dynamic range of the instrument to very low sample sizes.
- For small sample sizes, backgrounds, interferences and fractionation effects have to be considered, which effects can determine the external precision achievable even more than signal/noise considerations.

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