

Assessing the boundaries of ion collection in isotope ratio mass spectrometry

Zenon Palacz | Isotopx Ltd, Middlewich, Cheshire, UK.

How small an ion beam can ATONA™ ultra low noise Faraday collectors measure and still get useful data?

When do you need ion counting?

Faraday multicollection positives

- Offers 100% duty cycle, all isotopes measured all the time
- Immune to ion beam instability
- Useful for transient signals
- Simple data collection
- No deadtime correction
- Virtually indestructable

Faraday multicollection negatives

Higher noise than ion counter

Ion counter positives

No noise

Ion counter negatives

- Limited range (<5e6cps)</p>
- Non linearity on some systems
- Deadtime correction
- Peak jumping required minimizes duty cycle.

To compare Faradays and ion counters, we have analysed Osmium using a Phoenix TIMS with an array of ATONA Faraday amplifiers.

We have analysed the Osmium standard DrOss, with an isotopic composition of ¹⁸⁷Os/¹⁸⁸Os 0.16092. An integration time of **30 seconds** was used. Exponential mass fractionation using ¹⁹²Os/¹⁸⁸Os 3.083. All isotopes corrected using Nier oxygen ratios. Oxygen ratios were measured but not applied. Source vacuum was 2e-8mbar before oxygen added and maintained at ~2e-7mbar.

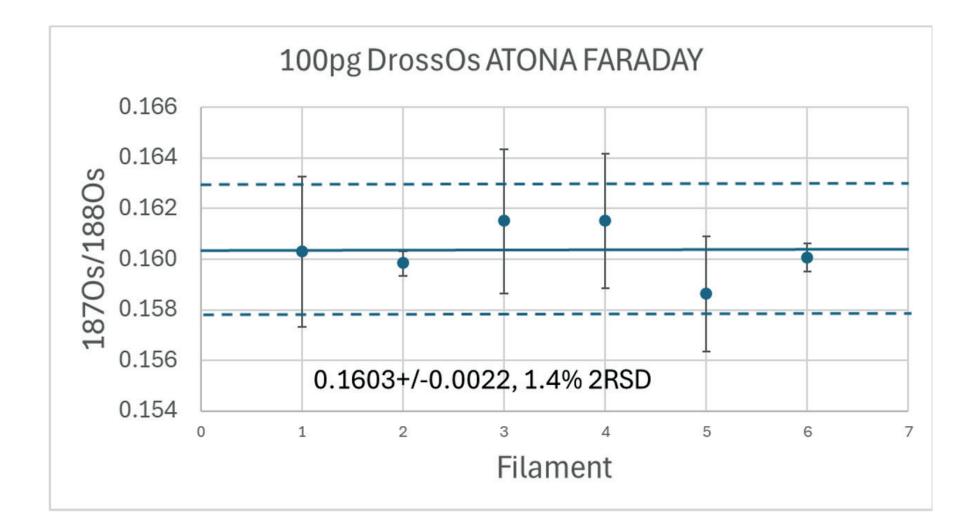
| | | | | | | | 4 | 9 | |
|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------------------|---------------------------------|---------------------------------|---|
| Collector | L5 | L4 | L3 | L2 | Ax | H1 | H2 | Н3 | H4 |
| mass | 232 | 233 | 234 | 235 | 236 | 237 | 238 | 240 | 242 |
| ion | ¹⁸⁴ OsO ₃ | ¹⁸⁵ ReO ₃ | ¹⁸⁶ OsO ₃ | ¹⁸⁷ OsO ₃ | ¹⁸⁸ OsO ₃ | ¹⁸⁹ OsO 3 | ¹⁹⁰ OsO ₃ | ¹⁹² OsO ₃ | ¹⁹² Os ¹⁶ O ¹⁶ O ¹⁸ O |

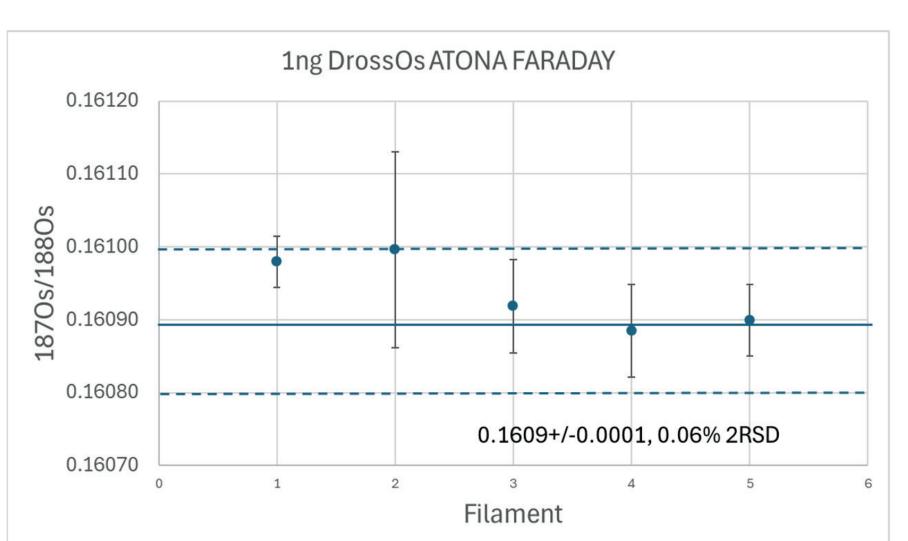


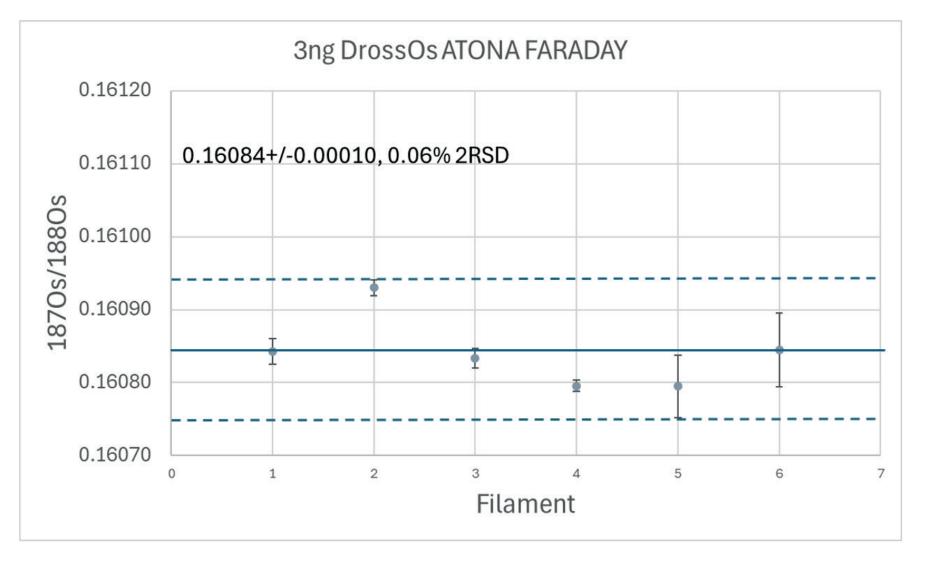
Table 1 shows the expected precision of a STATIC ATONA Faraday measurement using 100, 30 second integrations and compares it to the precision expected for 100 ion counting measurements with a 5 second integration on the 187 Os. At 30 seconds the ATONA noise is $\sim 1e-17$ Amp.

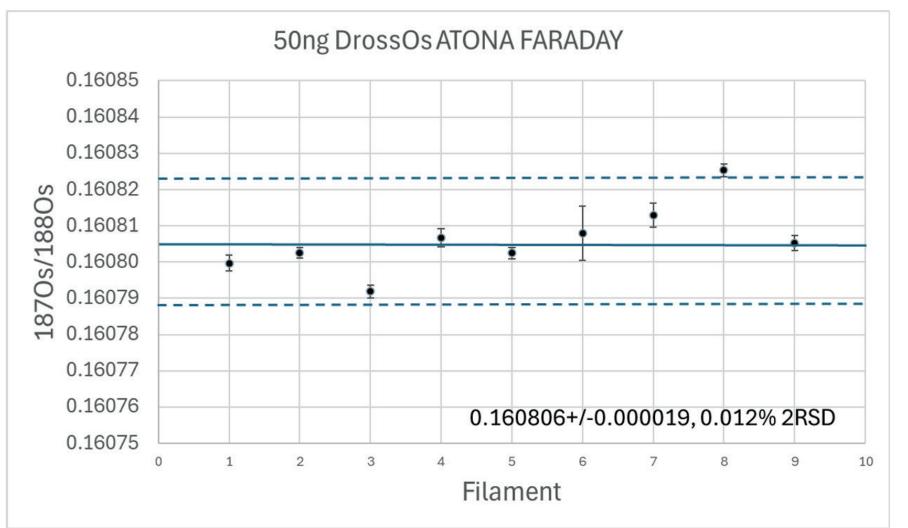
For the largest count rate there is very little difference between the detectors. For larger count rates of ¹⁸⁷Os the major isotopes could not be measured with an ion counter noise reduces with increased integration time.

| | 2RSE[%] | | |
|---------|--------------------------------------|---|--|
| Amp | Faraday | IC | |
| 1.6E-17 | 12.67 | 0.96 | |
| 8E-17 | 2.54 | 0.43 | |
| 1.6E-16 | 1.28 | 0.30 | |
| 8E-16 | 0.27 | 0.14 | |
| 1.6E-15 | 0.14 | 0.10 | |
| | 1.6E-17 8E-17 1.6E-16 8E-16 | AmpFaraday1.6E-1712.678E-172.541.6E-161.288E-160.27 | |

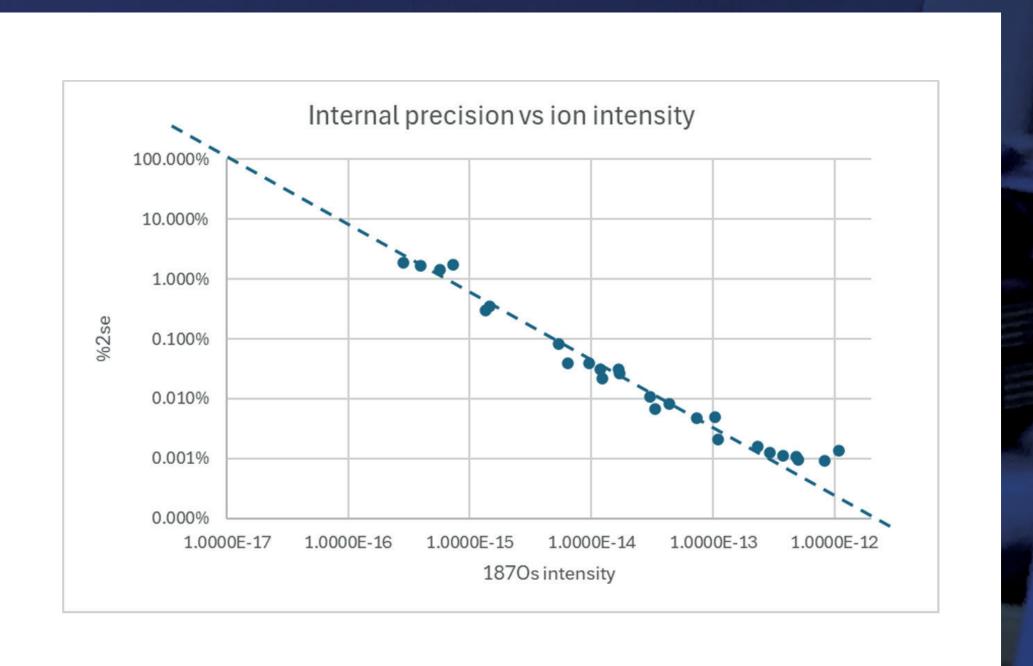








Data from 50ng to 100pg have been obtained. The data are all consistent but slightly lower than the certified value. In the 50ng data there is no correlation between measured oxygen ratio (an error in oxygen correction), or rhenium. It should be noted that small and large ion signals can be measured using the same detector which would not be possible with an ion counter. There is no need for cross calibration or deadtime correction.



Of some note are the variability in the internal precision. This is entirely due to differences in ion beam size resulting from different load quality. However, there is an extremely good relationship between ion intensity and precision. i.e. the number of ions collected controls the precision. 1% 2rse data can be obtained on 2e-16amp (~1000cps) ion signals, which would correspond to much lower sample sizes with better sample loading.

How small an ion beam can ATONA™ ultra low noise Faraday collectors measure and still get useful data?

Answer: ~2e-16amp signal gives 1% 2se data with an integration time of 30secs. ~2e-17amp noise. This is as expected from counting statistics.

When do you need ion counting?

Answer: Ion counting would be needed to improve precision by about a factor of 4 at the 1000cps level and for sample sizes of <100pg.

Excellence in Mass Spectrometry

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