

We greatly appreciate the thoughtful comments from referee Trevor Ireland, an expert in geochemistry and mass spectrometry who has worked with capacitor-based ion detection systems on the SHRIMP ion microprobe. The review is reprinted below in its entirety in italics with author responses shown by indentation where appropriate.

*Referees Comment on ATONA Charge mode system.
Trevor Ireland, RSES ANU.*

This is a timely paper concerning the introduction of the ATONA charge mode collection system to an ISOTOPX NGX.

The challenge of getting the the capacitative feedback system to work has been ongoing for a number of years. Both Cary and Keithley electrometers have had the ability to measure charge accumulation, but getting it to work in a routine analytical setup has been somewhat difficult (see Esat 1995, and Ireland et al. 2014).

We have added a discussion of this background work to our introduction.

The physics behind charge mode and the implications for data collection are interesting, but are not particularly well explained in this paper. Potentially this is because of the patent that is being sought for this system. In any case, the issues concerning the noise floor for a capacitive system effectively relate to a “read” noise in the capacitor system as opposed to the Johnson Noise in a resistive system. Hence, there is a constant noise component in the capacitative read system (see Ireland et al. 2014), and the longer you integrate the better the signal to noise. On the other hand, you continually integrate Johnson Noise and so the signal/noise does not improve as quickly for an increase in integration time. For comparison, we have set up our capacitative system for a 2 s integration and the noise is similar to the 10e-13 ohm resistor, pretty much similar to what is achieved here. The 2s integration is appropriate for an ion microprobe because of the continual change in analytical conditions. A longer integration time is fine for a noble gas instrument because the gas is effectively homogenised in the source and there are only longer term fractionation processes to deal with.

We have attempted to further clarify the operation of the ATONA system in light of these comments, but within the restrictions imposed by Isotopx' trade secrets. The constant noise component highlighted here is one of the advantages of the ATONA compared to the conventional resistor amplifier. In ATONA signal-to-noise ratio increases much faster with an increase in the integration time compared to the resistive amplifier. As suggested here, even longer integration times will be beneficial for more stable systems such as TIMS and stable isotope gas source mass spectrometers.

The work in the Isotope NGX is based around noble gas analysis, and specifically Ar isotopes. On one hand, this is a good system to look at because there is a good dynamic range in the isotope ratios under consideration. It also has the benefit that the ion beam is only changing at a (slow) steady rate allowing a good description of the progression of the counting statistics. The data show that the system performs well at the level commensurate with the measured ratios. On the other hand, Ar isotopes are not typically measured to high precision (e.g. as might be achieved for TIMS or ICP-MS analysis, or even SIMS analysis). This makes it also more difficult to establish the linearity of the system as well.

This is correct, although the measurements of stable zero-beam noise levels we present are an indication of the performance limits of the ATONA in a mass spectrometer with a more stable ion beam such as a TIMS. We expect results from TIMS labs with ATONA amplifiers to be published soon.

It is evident that the noise floor is still an issue for the 36Ar measurements described here. So as the volume of Ar gas is reduced, the error magnification from measuring the $36\text{Ar}/40\text{Ar}$ and resulting corrections to $40\text{Ar}/39\text{Ar}$ are still going to be a limitation and will likely still need to be carried out on an electron multiplier.

We do agree that the noise floor of the ATONA is comparable to an analog electron multiplier, but is not competitive with an ion counting electron multiplier for very small signals.

The benefit of the capacitative system is that measurements can be carried out on more Faraday cups, and potentially without the need for an electron multiplier (ion counter). The noise floor we have achieved is better than 500 c/s which means that for most isotope ratio measurements Charge mode is adequate and very often superior to an electron multiplier. At the upper level of count rates, $250\text{--}1000 \times 10^3$ c/s, the charge mode seamlessly connects with 10^{12} ohm resistor capability. At the lower end, we have measured isotope ratios down to 10,000 c/s, which is well removed from the gain drift and dead time issues of an electron multiplier. As such charge mode does provide that connection between electron multipliers and the traditional resistor feedback amplifiers. But as demonstrated in this paper, it is a complementary aspect of the measurement of isotope ratios in geochemistry.

References

T.M. Esat, Charge collection thermal ionization mass spectrometry of thorium. *International Journal of Mass Spectrometry and Ion Processes* 148 (1995) 159–170.

T.R. Ireland, N. Schram, P. Holden, P. Lanc, J. Ávila, R. Armstrong, Y. Amelin, A. Latimore, D. Corrigan, S. Clement, J.J. Foster, W. Compston, Charge-mode electrometer measurements of Sisotopic compositions on SHRIMP-SI. *International Journal of Mass Spectrometry* 359 (2014) 26–37.