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Gas evolution regression in high-precision noble gas mass spectrometry

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The precision of noble gas mass spectrometry measurements has improved steadily in recent decades. There have been incremental improvements in electronics, software, and measurement techniques that enable better precision and reproducibility, and there have been fundamental hardware changes that lead to similar improvements but may also demand a reconsideration of common practices. In some cases, improvements can be a double-edged sword, as they reveal geological variation that now exceeds measurement uncertainty in age populations or as higher-precision Ar isotope ratios make it more difficult to obtain statistical plateaus in step-heating experiments. Ongoing developments such as high-resolution quadrupole mass spectrometers and double-focusing sector noble gas mass spectrometers will introduce more variables and increase the need for a community discussion of these issues. As an example, the high-brightness cathode source recently introduced by Isotopx favors measurement at higher trap currents than previously used by most labs measuring Ar isotopes because of its low backgrounds and better efficiency at high currents. This means larger ion beams that decay more rapidly during static vacuum measurements, and the high precision long-integration signal measurements enabled by the ATONA amplifiers mean that these signals exhibit unambiguous exponential decay much more frequently. Despite past calls to either fit isotope ratios [1] or to use exponential regressions for fitting static vacuum noble gas mass spectrometry measurements to both the mechanistic understanding of the gas evolutions and the observable exponential nature of high-precision measurements [2] , these practices remain difficult to implement with some common data reduction software packages and, seemingly, uncommon. In addition to challenges with software and the more complicated math of calculating exponential regressions and their uncertainties, there may also be a preference for a simpler linear regression (or average, in the case of very small samples) to avoid overfitting. I explore different fitting techniques for signals ranging from a few cps to greater than 10 volts, with different detectors and integration times, and compare them to synthetic data to demonstrate the implications for measurement accuracy and uncertainty.

[1] Mark et al. (2010), Geochem. Geophys. Geosyst. 10.

[2] Ni et al. (2023), Anal. Chem. 95.