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Multidynamic Mass Spectrometer Measurements Revisited

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Multicollector mass spectrometers underpin some of the most precise and accurate isotope ratio measurements in geochemistry. Achieving this precision requires large, stable ion beams for long time periods, as well as accounting for relative biases among the collectors. Collector bias is a combination of Faraday Cup efficiencies (FCEs) and electronic amplifier gains measured relative to a reference collector. Although amplifier gains can be measured directly, FCEs are more difficult to determine. Accounting for this is frequently accomplished using a "multidynamic" approach, measuring the isotopes of an element across an array of Faraday collectors, shifting the positions of the isotopic masses up and down the array.

Multidynamic methods can account for relative FCEs and perform a mass bias correction to a known/assumed normalizing isotope ratio. We revisit these methods to determine under what circumstances multidynamic methods work, and what additional information can be gleaned from the measurements. We show that, contrary to many published analyses, this system cannot be solved for unique relative FCEs, at least when using ratios of synchronously measured ion beams. This fact holds even if the full isotopic composition of the element is known. However, unknown isotope ratios are still uniquely determined relative to the normalizing ratio. Gain cancellation is arithmetically perfect for the unknown ratios using a power law with integer masses and is near-perfect using other laws and masses.

One way to track FCE change is to assume two cups behave similarly [1]. However, to uniquely determine all relative collector factors, one of two approaches will work. The first is to make a mid-analysis adjustment to the collector spacing [2] and assume negligible change in mass bias or FCE during the switch. The second is to perform beam interpolation [3], solving for the growth/decay of the ion beam as additional unknown parameters. To efficiently use measured intensity data, we present a penalized spline approach for a weighted least-squares solution solve for unknown isotope ratios and FCEs without overfitting.

[1] Di et al. (2021), JAAS 36, 1489-1502
[2] Makashima and Nakamura (1991), Chem. Geo. 94, 105-110
[3] Wendt and Haase (1998), Chem. Geo. 146, 99-110