An Adaptive Monte Carlo method for analyzing raw multicollector mass spectrometer data

Scott Burdick, Noah McLean, and Jim Bowring

2025 AGU Fall Meeting

The raw data output by a multicollector mass spectrometer is a non-linear function of isotope abundance, mass fractionation, time-dependent beam intensity, instrumental-dependent variables (baseline voltage, instrument gain), and measurement noise. In order to accurately interpret isotopic data in a scientific context, new statistical methods are required to separate the desired isotope ratios from these confounding variables and to provide an improved estimate of their uncertainty. To this end, we have designed an adaptive Monte Carlo (AMC) algorithm for inferring isotope ratios from raw mass spectrometer data for inclusion in the Tripoli data reduction software package.

The AMC algorithm recovers the posterior probability of isotope ratios that fit highly time-resolved peak-hopping data acquired with assistance from instrument manufacturers. We forward model this data as a function of isotope log-ratios, time-dependent beam intensity, and the instrumental parameters, with the option of holding some parameters fixed. Time-varying ion beam intensities are modeled using a cubic spline basis, ensuring flexibility in fitting potentially complicated intensity functions. The algorithm performs a search on these parameters based on the misfit between the forward modeled and raw data weighted by data covariance. The data covariance itself is estimated using a noise model based on beam intensity and electronic noise. After an optimized number of iterations, the algorithm produces an ensemble of possible parameter sets from which the posterior probability, mean isotope log-ratios, and their associated covariances can be drawn. Our framework is additionally capable of generating realistic synthetic datasets given an input set of parameters, mass spectrometer method, and noise model, which can aid the community in method testing and validation.

We present details of the AMC methodology and give applications to multiple isotope systems and TIMS and MC-ICPMS collector setups. We demonstrate its effectiveness for scenarios with varying values of isotope ratio, intensity, data quality, and complexity of the beam intensity function. We furthermore give examples of realistic synthetic data generation and data and analysis visualization provided by the Tripoli software.