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Tripoli: New Adaptive Monte Carlo Software for Improving the Accuracy of Multicollector Mass Spectrometry

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Motivation

Multicollector mass spectrometers (TIMS and MC-ICPMS) have seen advances in electronics and components. **Statistical interpretation of mass spectrometer data** has not kept pace:

- Baselines uncertainties are often neglected.
- Beam interpolation algorithms underestimate uncertainties.
- Multicollector data is sometimes ignored.
- Detailed data inspection and visualization is often up to the users, with no documentation of the analytical choices made.

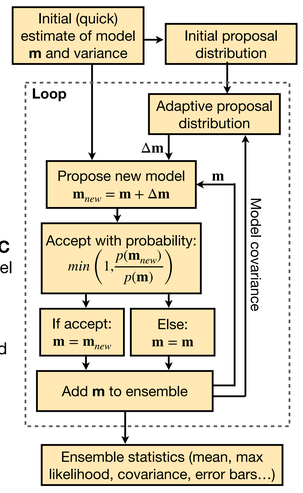
To improve the way users interact with and interpret mass spectrometer data and enhance the quality of the analyses, we have developed new software, **Tripoli**. Tripoli supports:

- Interactive review and archiving of isotopic data,
- **Interactive visualization** at each point in the user's workflow,
- Statistically rigorous calculation of parameters, and
- **Flexible output formats** needed to communicate relevant data and metadata.

Adaptive Monte Carlo Approach

Tripoli works with highly time-resolved raw mass spectrometer data output. Each data point is modeled as the function of log isotope ratio, instrument baseline and gain, mass bias, and time-dependent beam intensity.

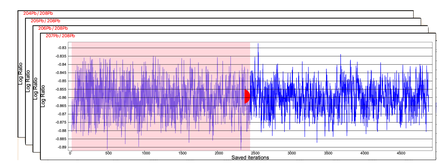
First applying (quick) maximum likelihood, then (slower, Bayesian) Markov Chain Monte Carlo methods, Tripoli creates an ensemble of ratios that fit the data. The most likely model and its uncertainty can then be drawn from the model.

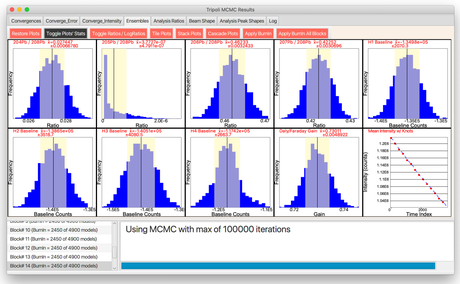


Adaptive MCMC algorithm. Model values (isotope ratios, baseline voltages, gains, etc.) are updated at same time as optimal search parameters.

Benefits of our approach:

- Raw measurements with short integration times constrain beam intensity & estimate data scatter.
- Handles uncertainty in instrument gain/baseline
- Log ratio formulation yields accurate statistics for isotope ratios, uncertainty, and covariance





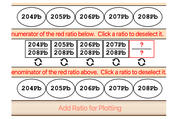
Adaptive MCMC outputs. Top: The MCMC chain for log $^{207}Pb/^{208}Pb$ after ~5000 saved iterations. Red area shows user-specifiable burn-in period to exclude from stats. Bottom: Histograms for the (single block) posterior distributions illustrate mean and (asymmetric) error bars for isotope ratios and other parameters.

Workflows and Screenshots

Session and Analysis. For each analysis, a data file and method file are specified.

spec↓/detector→	PM	H1	H2	H3	H4	cross ref
OP1	204Pb	205Pb	206Pb	207Pb	208Pb	BL1
OP2	205Pb	206Pb	207Pb	208Pb		BL1
OP3	206Pb	207Pb	208Pb			BL1
OP4	207Pb	208Pb				BL1
OP5	208Pb					BL1

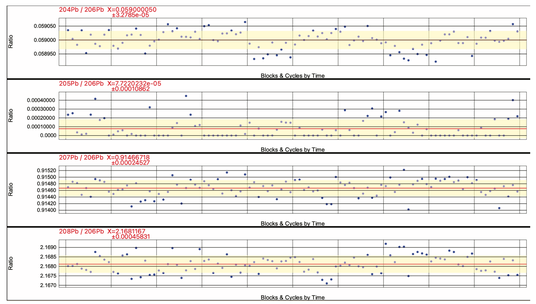
Method files let Tripoli knows which isotope is on each collector at all times, allowing Tripoli to control corrections for baselines and relative gains and propagate relevant uncertainties.



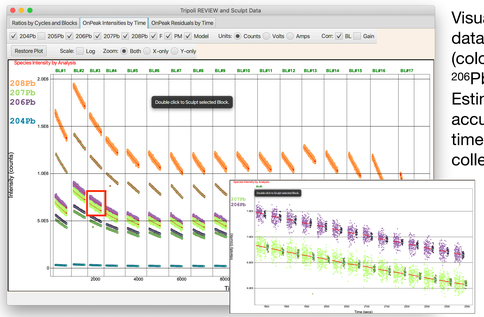
Users can choose which ratios to visualize, plot, and output, even after the analysis is complete.

View Ratios by Cycle/Block

Once an intensity function is fit (by quick least squares or by MCMC), the user can plot the familiar cycle-by-cycle ratios and include/exclude data by block, cycle or data point. Inspection and rejection can happen both before and after the MCMC fit.



View On-Peak Intensities/Residuals by Time

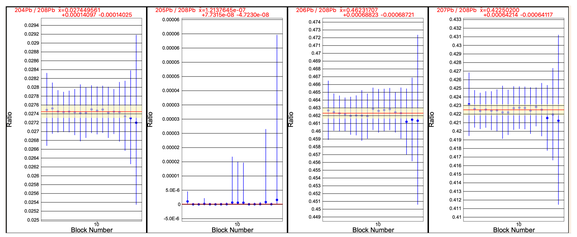


Visualization of full run of NBS982 Pb raw data (scattered points) and best model fit (colored lines). data. Inset: Single block of ^{206}Pb & ^{207}Pb data from same analysis. Estimating beam variations allows Tripoli to accurately calculate isotope ratios through time when beam is measured on different collectors at different times.

Additional On-Peak Residuals plot gives easy way to check success of model fit and measurement scatter for initial and final models.

Analysis Ratios

The final outputs of the MCMC process are block-by-block ratios and their 2σ error bars (blue points/bars) and analysis ratios (red line/ yellow field). Error bars are appropriately asymmetric (esp. low-count $^{207}Pb/^{208}Pb$) due to calc. in log ratio terms.



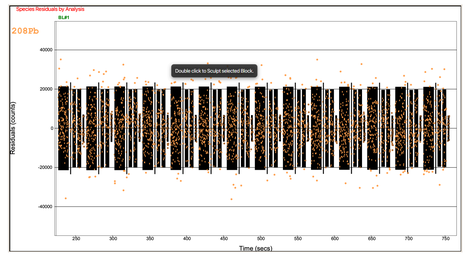
Current Features and Future Developments

Adaptive MCMC Features

- Initial tests show synthetic data results are accurate and precise; real raw example datasets are well-fit by modeling approach.
- MCMC approach is multi-threaded to work on data from multiple blocks at once, reducing the time from data import to inspection.
- Example datasets and visualizations available to test-drive on GitHub (below)!

Still Working On:

- Improved diagnostics for optimal burn-in and MCMC convergence to improve efficiency and reliability of algorithm.
- Flexible parameterization for time-varying elements — use fewer variables when variations are simple (transdimensional approach).
- Empirically estimating uncertainty in the data from scatter about the model (hierarchical method). Current noise model misses some sources of variation.



Residuals + Data Variance

One block of ^{208}Pb data residuals (orange dots) with expected 2σ data noise (black bars). Residuals will ideally be distributed symmetrically around zero with this variance. Current software estimates data noise as combination of baseline noise and shot noise.

Upcoming Tripoli Developments

1. Offer more visualization options (e.g., ratio vs. ratio covariance plots, real-time MCMC convergence visualizations).
2. Add multiple analyses to a session—useful for sample/standard bracketing, tracking long-term behavior of reference materials, or IC/ID pairs.
3. Add time variation for baseline, isobaric interference, relative gains, isotopic fractionation/mass bias, peak tails, etc., to ensure accurate and traceable corrections to isotope ratio measurements.
4. Create interactive applet for designing output file format.

Get Involved!

GitHub Repository

Tripoli Homepage

- We are looking to add mass spectrometer makes/models. Send us your data for any isotope system to Noah at noahmc@ku.edu.
- Try out the beta version on our GitHub page - leave a comment, request, or issue.
- User workshop and video tutorials forthcoming in 2024