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Fe Isotopic Analysis by a Nu Plasma 1700 MC-ICP-MS With a 58Fe-57Fe Double-spike

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1) Fe Isotopes on a Nu 1700

Requirements for plasma ionization mass spectrometers:
1. Correction for instrumental fractionation
2. Correction or reduction of Ar-O-N polyatomic interferences

Address instrumental fractionation with the use of double spike method
Address polyatomic interferences by combining:
- Desolvating Nebulizer (DSN) used to reduce Ar-O-N input
- High resolution instrument to fully separate Fe peaks from polyatomic interferences

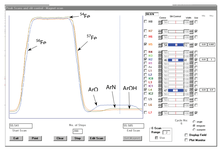
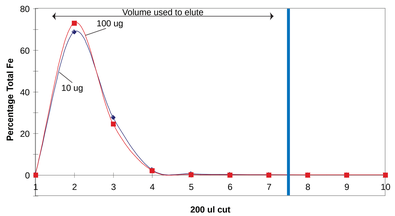


Illustration of resolved Fe masses on the Nu Plasma 1700 (plot by Nu Instruments).

Measurement parameters that improve results:
- HCl-based solutions yield high Fe backgrounds in DSN, so all analyses carried out in HNO3
- Using 15-20V signal intensity on 56Fe to increase intensity for minor isotopes
- Monitoring and correcting 52Cr and 60Ni for potential 54Cr and 58Ni interferences
- Offline on-peak background subtraction
- Frequent peak-centering

2) Fe Separation From Samples



Procedural blank level
Preliminary test using combined column cuts from 4 columns yield <10ng Fe per column, based on measured 56Fe signal intensity, compared to a standard of known concentration

Column chemistry

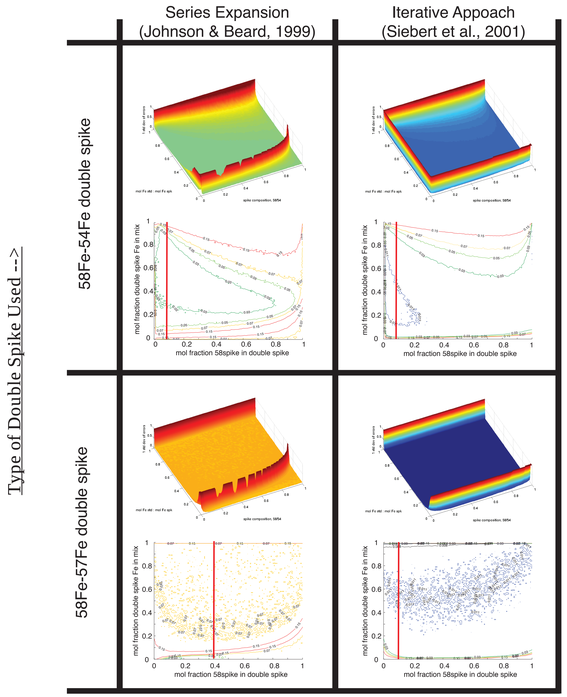
Method:
- AG1X4 100-200 mesh resin in 0.3 ml columns with 6 ml reservoir
- 9M HCl+trace H2O2 to strip sample matrix, while Fe(III) is fixed on the column
- 0.1M HCl to elute Fe
- Running 10-100 ug Fe (<1% of column capacity)

What is plotted:
- Fe elution curve from 200 microliter column cuts, measured by 56Fe signal intensity compared to a standard solution of known concentration

Observations:
- Procedure yields ~100% Fe, while Ni and Cr interferences are reduced to <0.2 mV, corresponding to a factor $>10^5$ difference between 54Fe or 58Fe signal intensity and the intensity of the isobaric interferences in a typical spiked run

3) Double Spike Error Models

Double Spike Data Reduction Algorithm -->

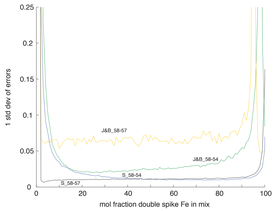


Investigating potential double spikes and data reduction algorithms

What is plotted:
- Predicted error (vertical axis / contoured) for mol fraction of 58Fe in the double spike versus mol fraction of double spike Fe in a sample-spike mixture
- At each composition, all 5xFe/56Fe ratios are perturbed randomly up to 0.01 permil (estimate of best possible measured 1SE) 1000 times, where the plotted error is 1SD (permil) of the differences between the reduced and true values
- A 3-D and contour plot are provided for both 58Fe-54Fe and 58Fe-57Fe double spikes, reducing data with either series expansion of the exponential law (Johnson & Beard, 1999) or an iterative approximation (Siebert et al., 2001)
- Red vertical lines show (near-) optimal double spike compositions for different reduction algorithms.

Observations:
- Predicted error is lower with the series expansion for a 58Fe-54Fe double spike, but for the iterative approach the lowest errors of both spike types and both reduction algorithms are obtained with a 58Fe-57Fe double spike

4) Advantages of Different Double Spikes

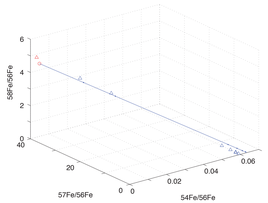


Comparison of optimal spike compositions

What is plotted:
- Error curve for optimal composition of both types of double spike and for both types of data reduction

Observations:
- Series expansion works well for 58Fe-54Fe double spike
- Iterative approach works well for both spikes
- 58Fe-57Fe double spike provides flattest error curve, suggesting it is least susceptible to change in error with different amount of double spike added
- Overall lowest error possible with 58Fe-57Fe double spike, but very close to fast increase in error with added spike

5) 58Fe-57Fe Double Spike Calibration



Data reduction requires knowledge of "true" double spike composition

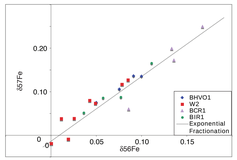
What is plotted:
- In-house standard, with increasing amounts of double spike (blue symbols), were measured (triangles) and used to find the optimal composition of the double spike (red circle) iteratively
- Optimal composition found by iterating fractionation (F) for spike, at each iteration predict true mixtures with that spike, then calculate F for mixtures and spike concentration . "True" double spike composition defined by lowest deviation in predicted spike concentrations, and F values ~1.7

Observations:
- Fractionation-corrected mixtures and "true" double spike should define a mixing line (blue line)

6) Results for Rock Standards:

Rock standard values with respect to IRMM-14:
δ56Fe +/- 2SD (number of analyses):

BHVO-1:	0.079 +/- 0.044 (4)
W-2:	0.039 +/- 0.062 (8)
BCR-1:	0.131 +/- 0.062 (4)
BIR-1:	0.071 +/- 0.064 (4)



What is plotted:
- Individual runs (50 ratios) for rock standards in δ56Fe vs. δ57Fe

Observations:
- Runs plot along exponential fractionation line, suggesting scatter is likely due to limitations of data reduction. Note that modeling predicts higher precision