
The IMPROVE Aerosol Sampling and Generation System and XRF Standards

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Calibration Standards for XRF - Problem in the Scientific Community

- Ideal standards:
 - Same matrix as samples
 - Same substrate as samples
 - All elements of interest
 - Same mass range as samples
 - Micromatter standards used in the XRF community
 - Not made of particulate matter (metals, CuSx)
 - deposited on nuclepore (or mylar)
 - One or two elements per standard
 - Most certified standards are higher mass than IMPROVE
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Objectives of our work

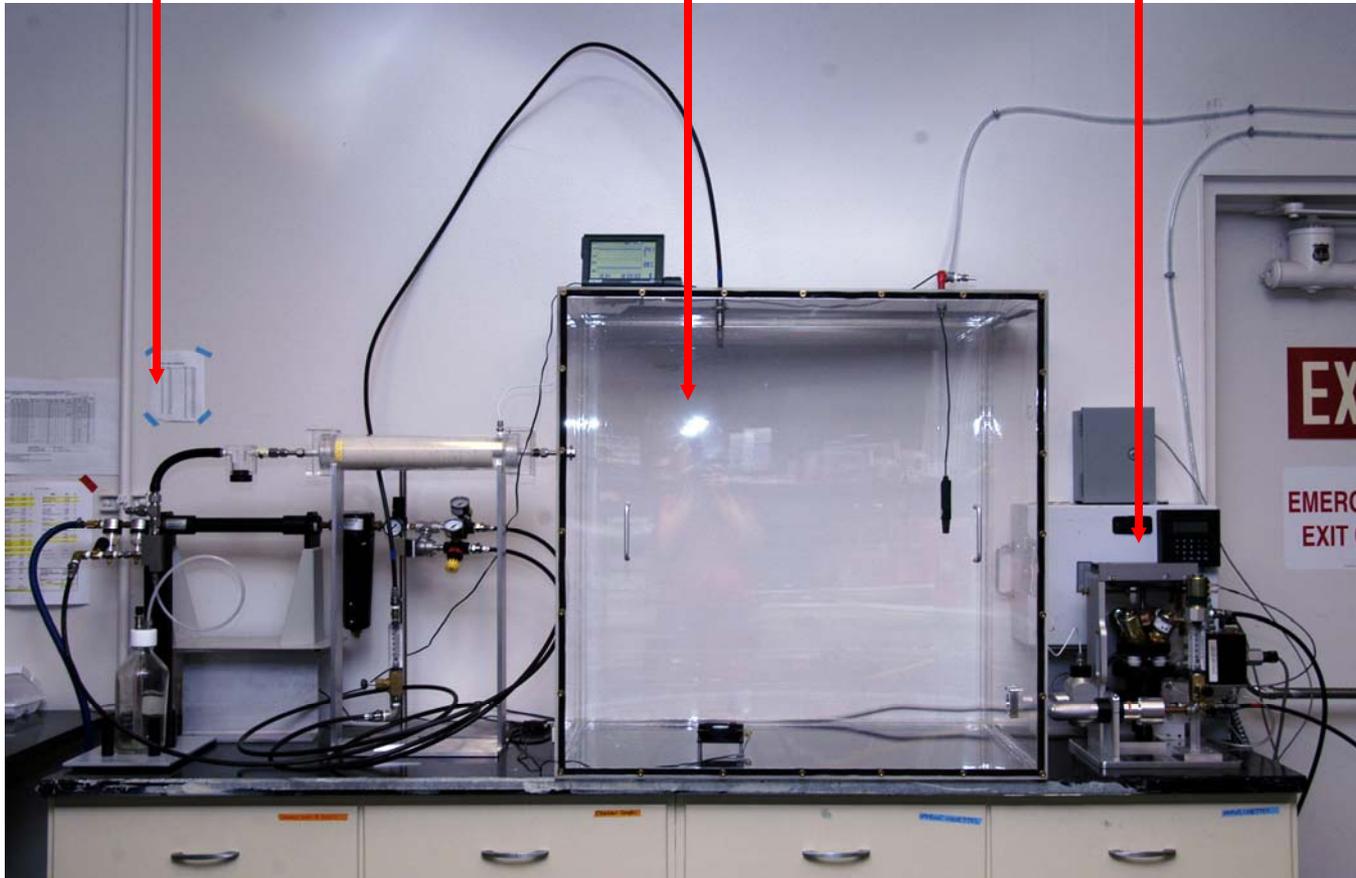
- Create “reference filters” → ideal standards
 - IMPROVE Aerosol Generation and Sampling System
 - Generate pure, stoichiometric particulate matter deposits of known composition
 - IMPROVE network mass range
 - Teflon filters using an IMPROVE sampler
 - **Short term goal:** characterize IMPROVE XRF system
 - **Long term goal:** Produce XRF standards that improve accuracy of elemental measurements
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Aerosol Generation and Sampling System

Generation System

Mixing Chamber

IMPROVE PM_{2.5} Sampler

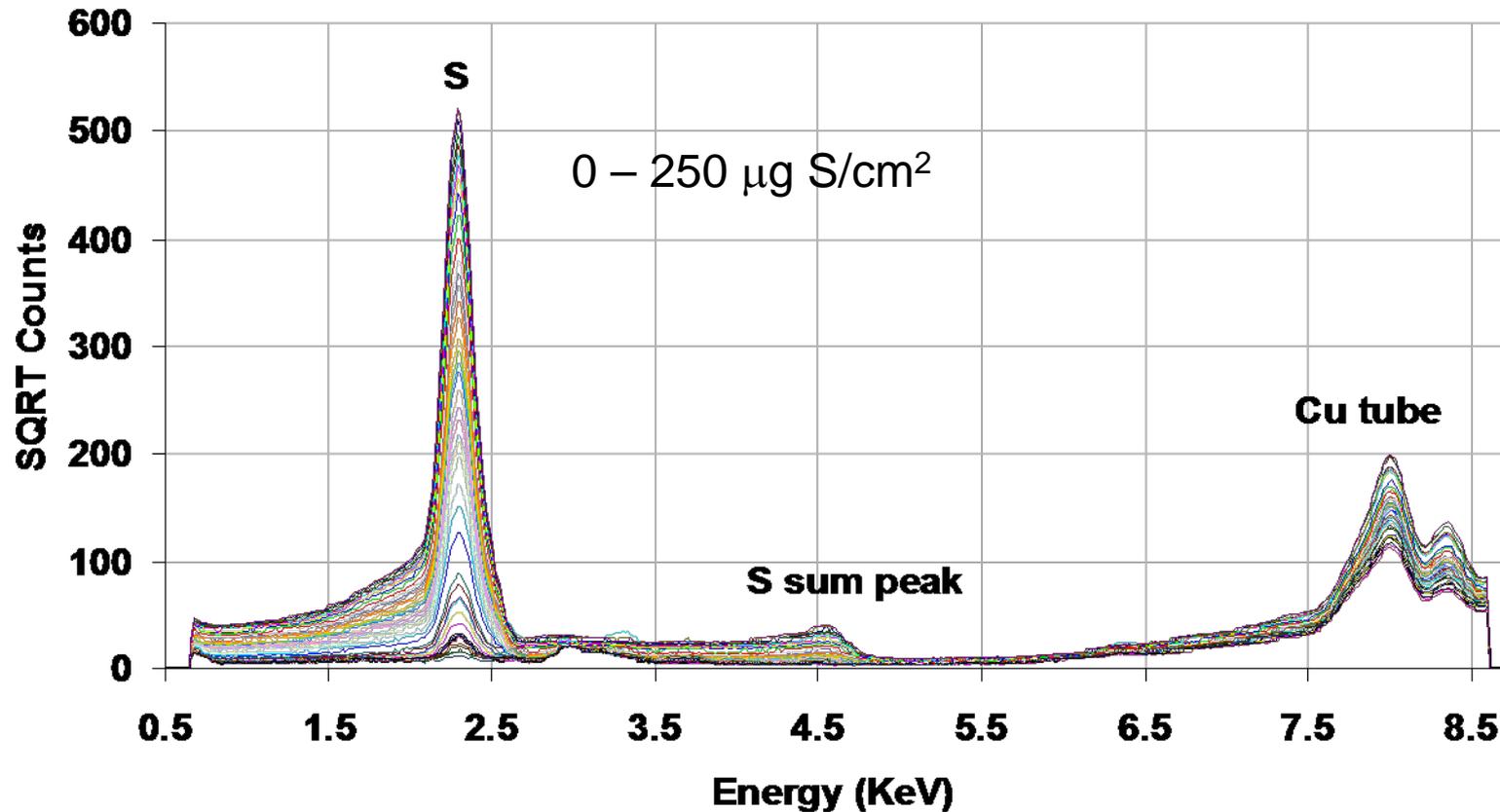


Upgrades this year

- Improved RH monitoring
 - Three locations: Diffusion dryer, chamber and sampler inlet
 - Upgraded sampling line between chamber and sampler
 - Better stability of chamber concentration
 - Parallel sampler
 - TSI 3076 Constant Output Atomizer
 - New sampler program
 - Better control of sampling time
 - New TSI Filtered Air Supply
 - Continuous operation for up to 24 hours
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Two current projects

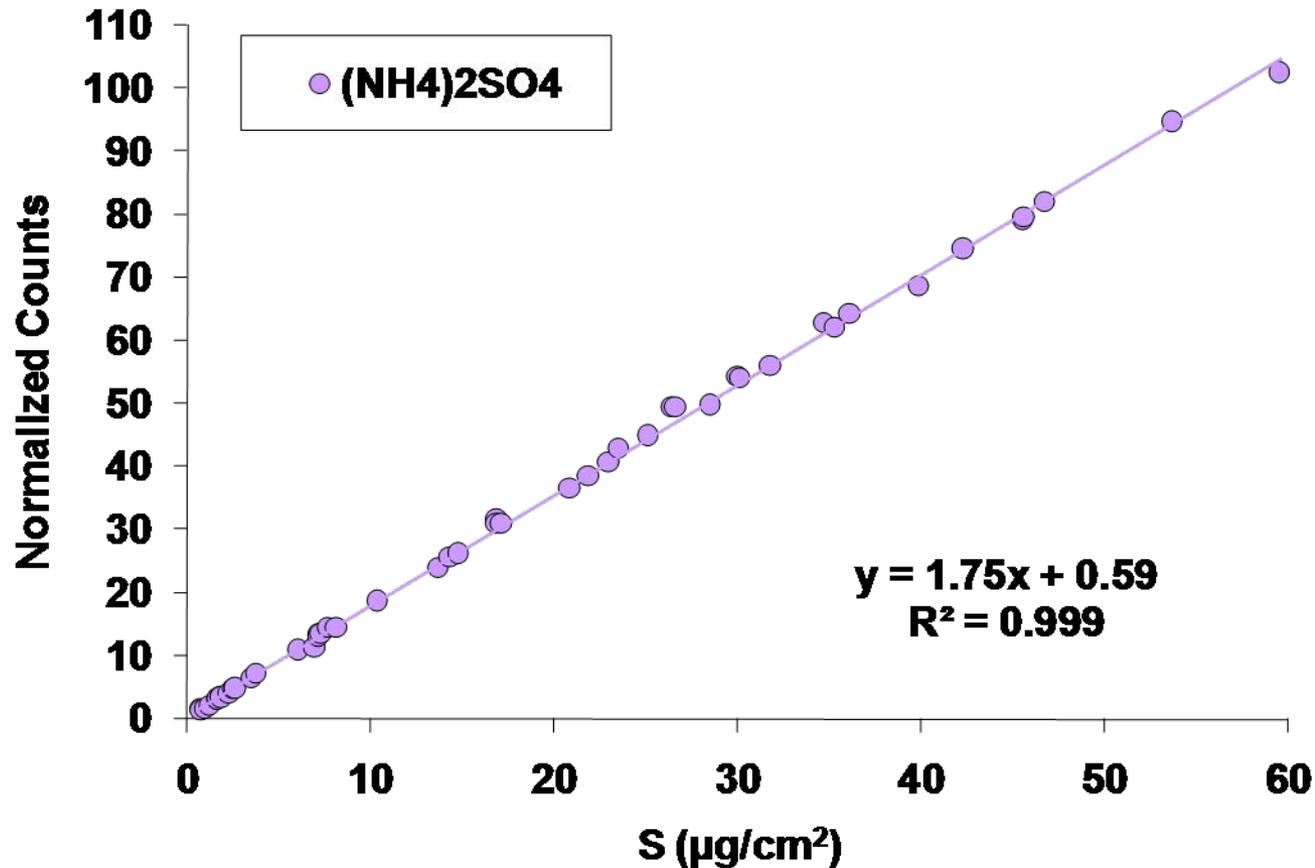
- Characterize XRF response to individual elements
- Interference of Si measurement by S



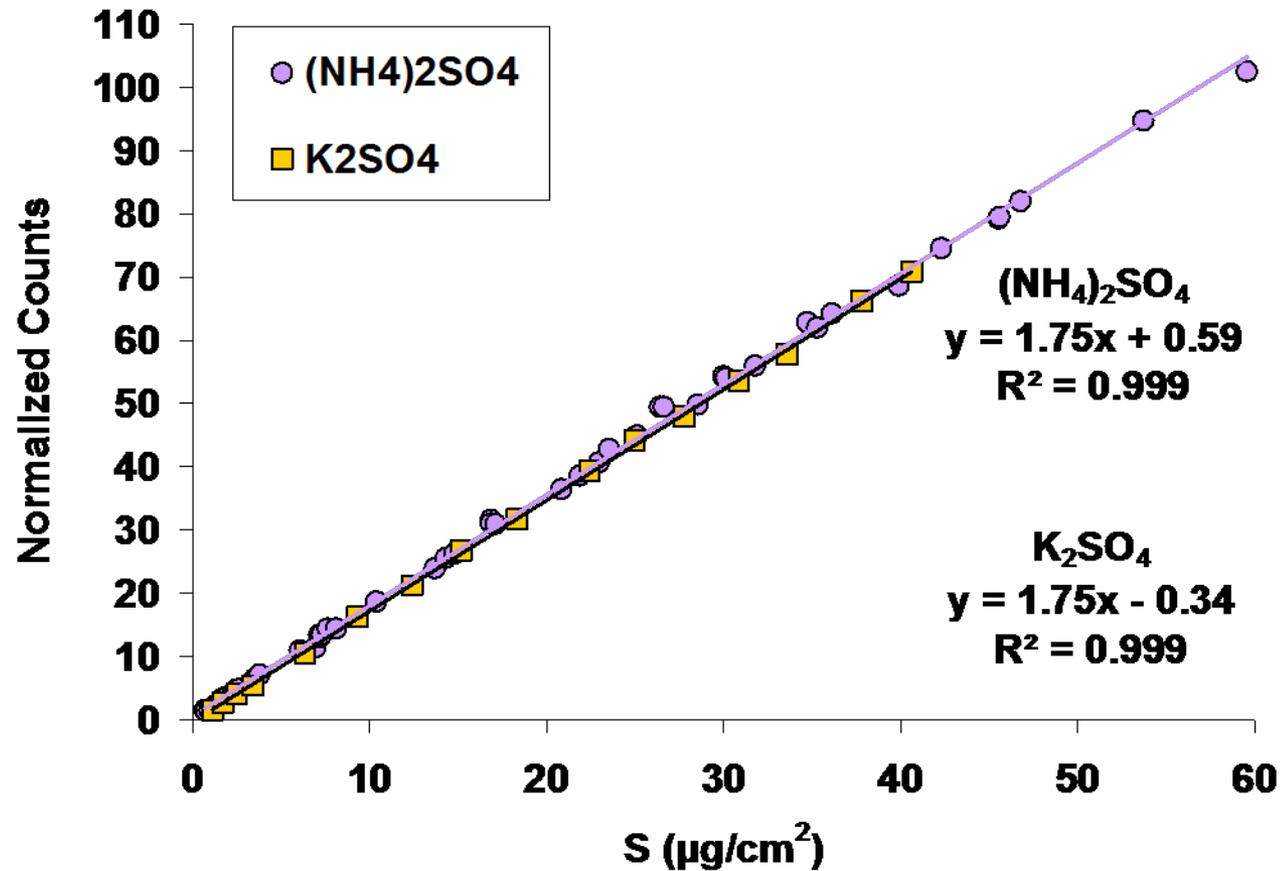
Project 1: Characterize XRF response to individual elements

- Created reference filters
 - $(\text{NH}_4)_2\text{SO}_4$
 - K_2SO_4
 - KCl
 - Measurements
 - XRF
 - Mass
 - IC (not completed)
 - Analysis of contamination
 - XRF
 - IC (not completed)
 - FTIR (preliminary results)
 - Filters to be analyzed by DRI
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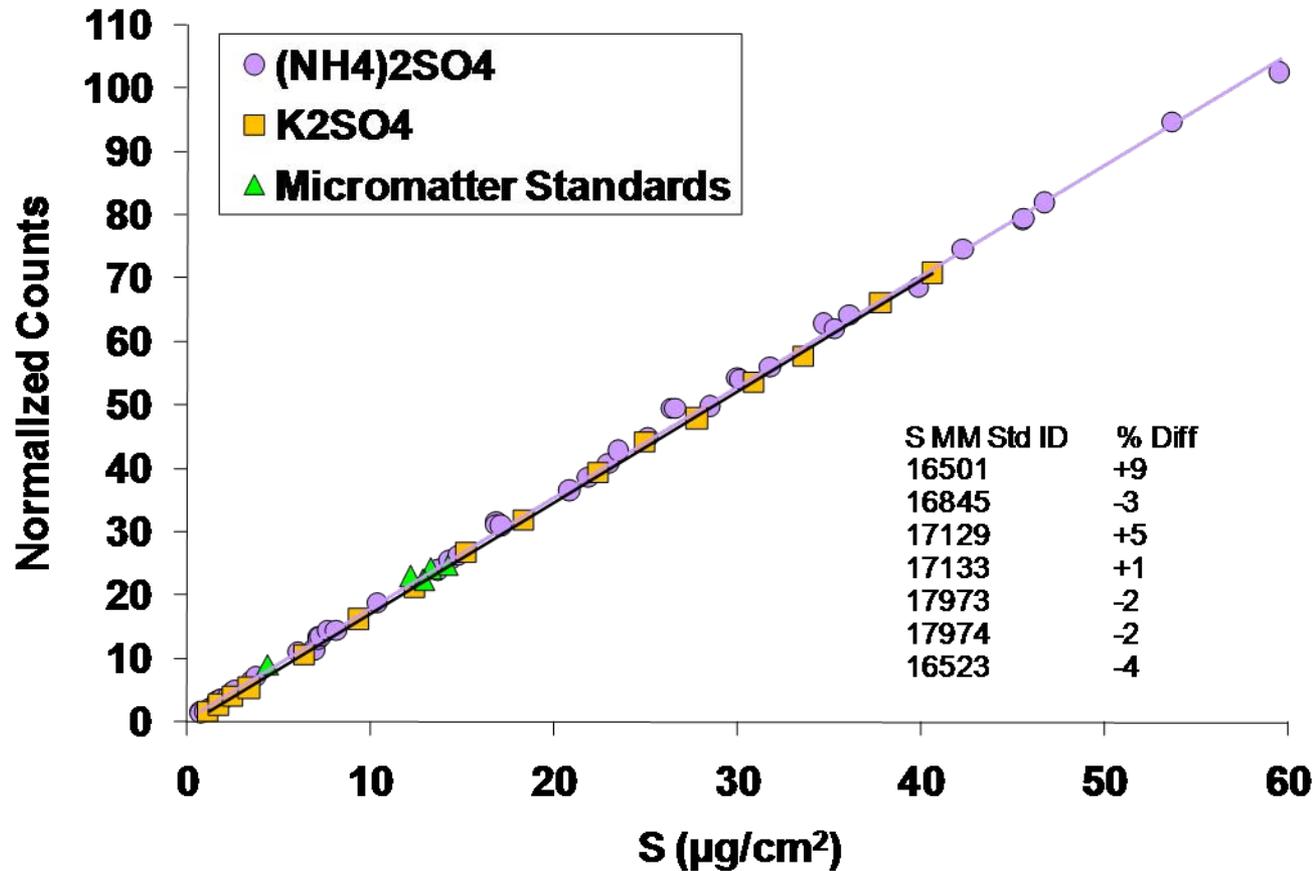
S-XRF compared to S-gravimetry



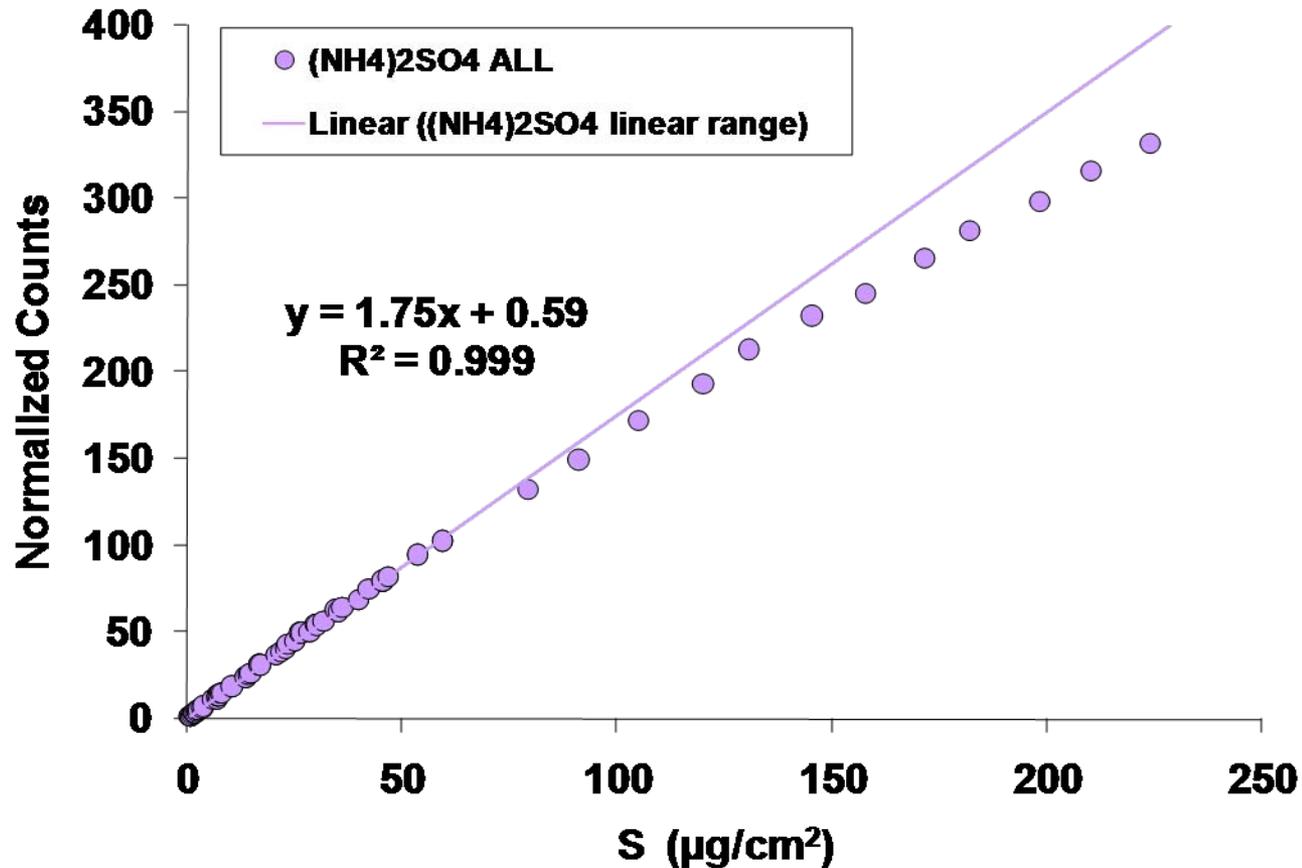
S from K_2SO_4



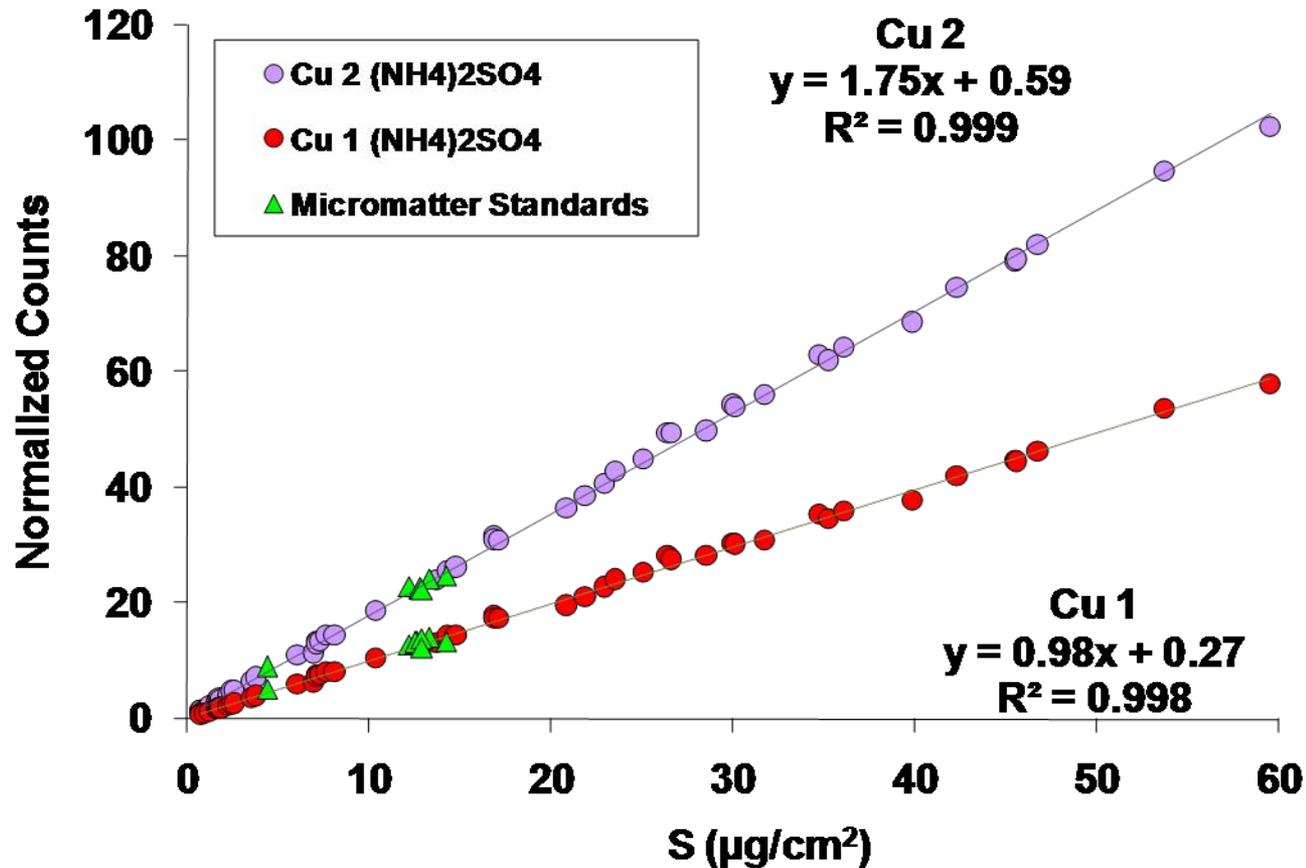
Micromatter Standards



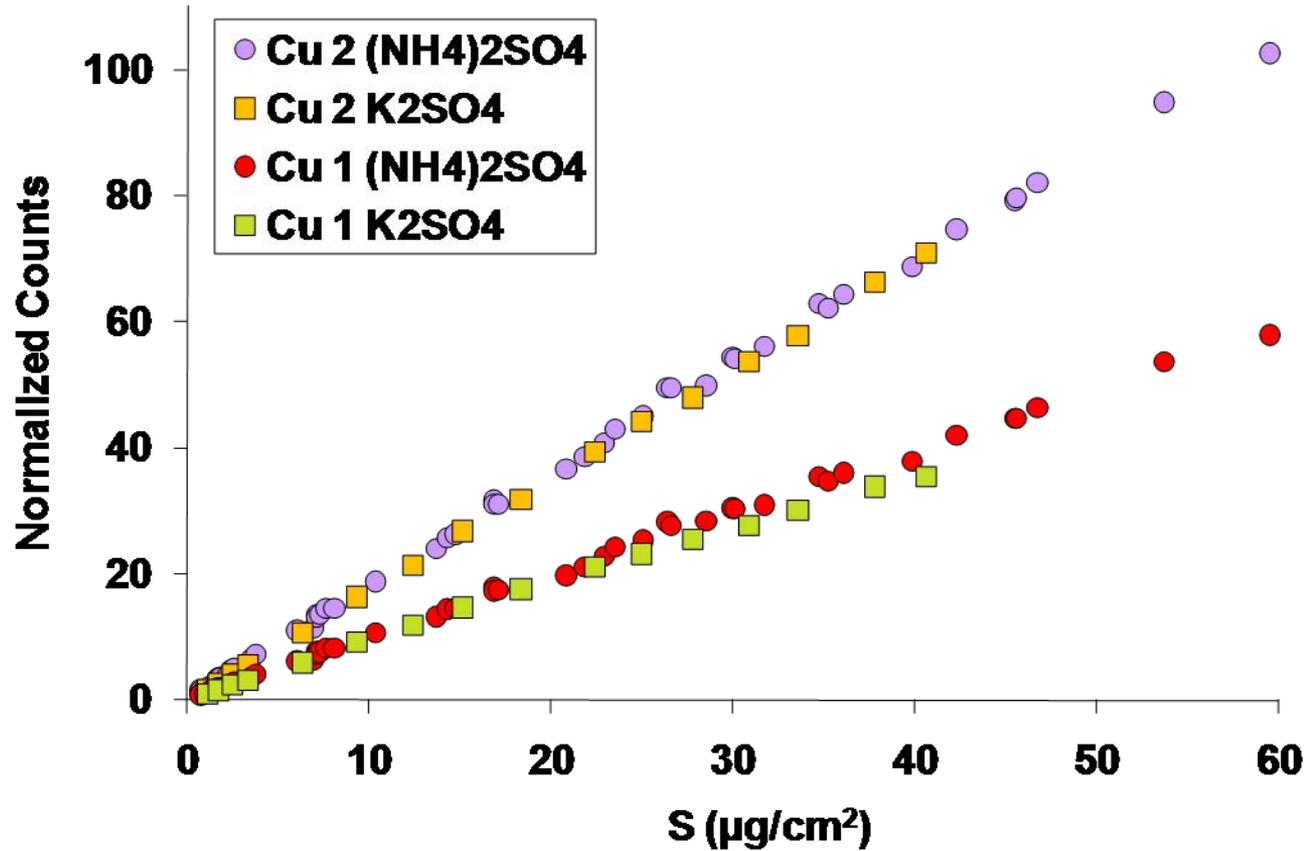
Response at high S loadings



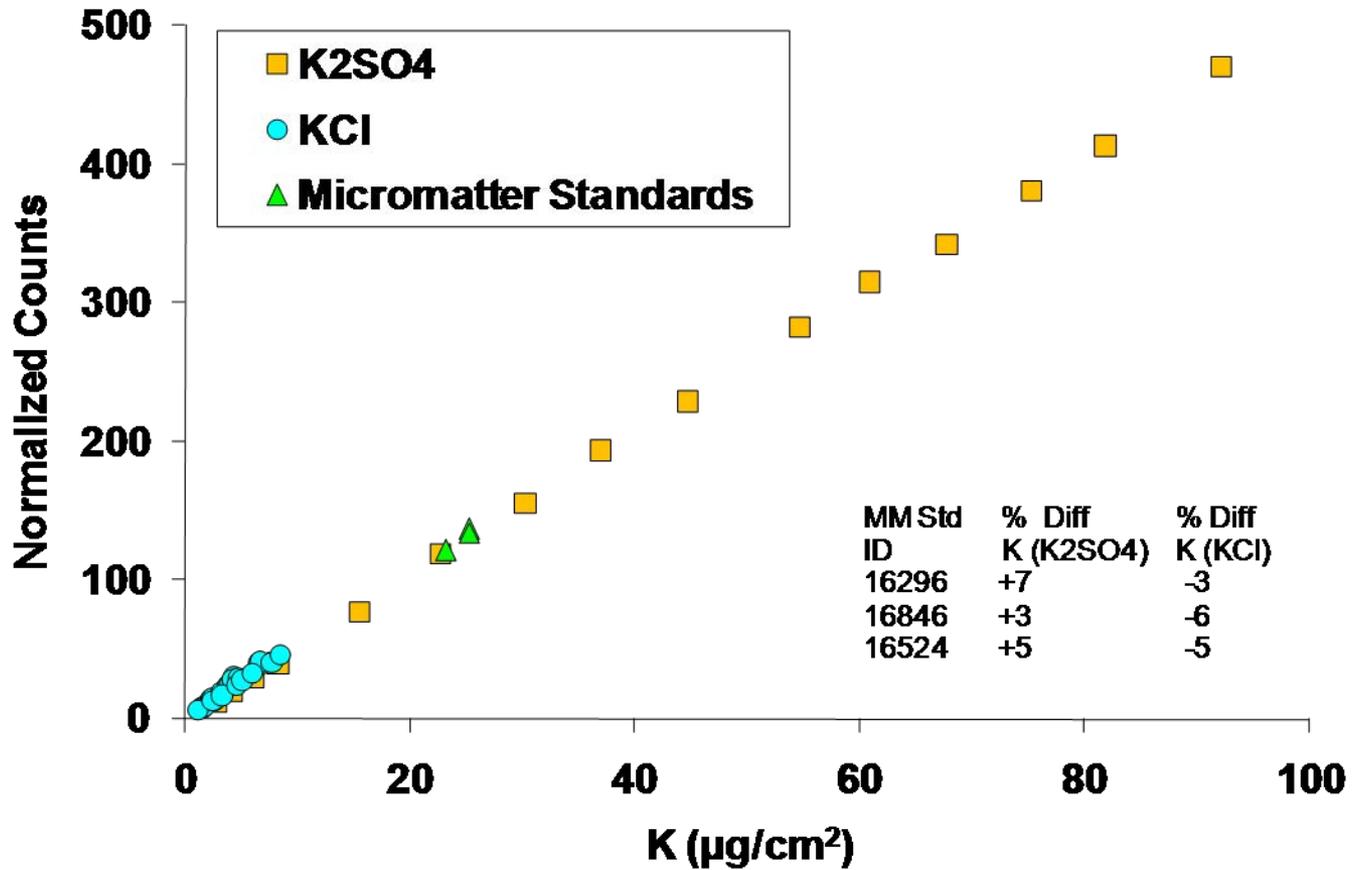
Different response by two Cu-XRF systems



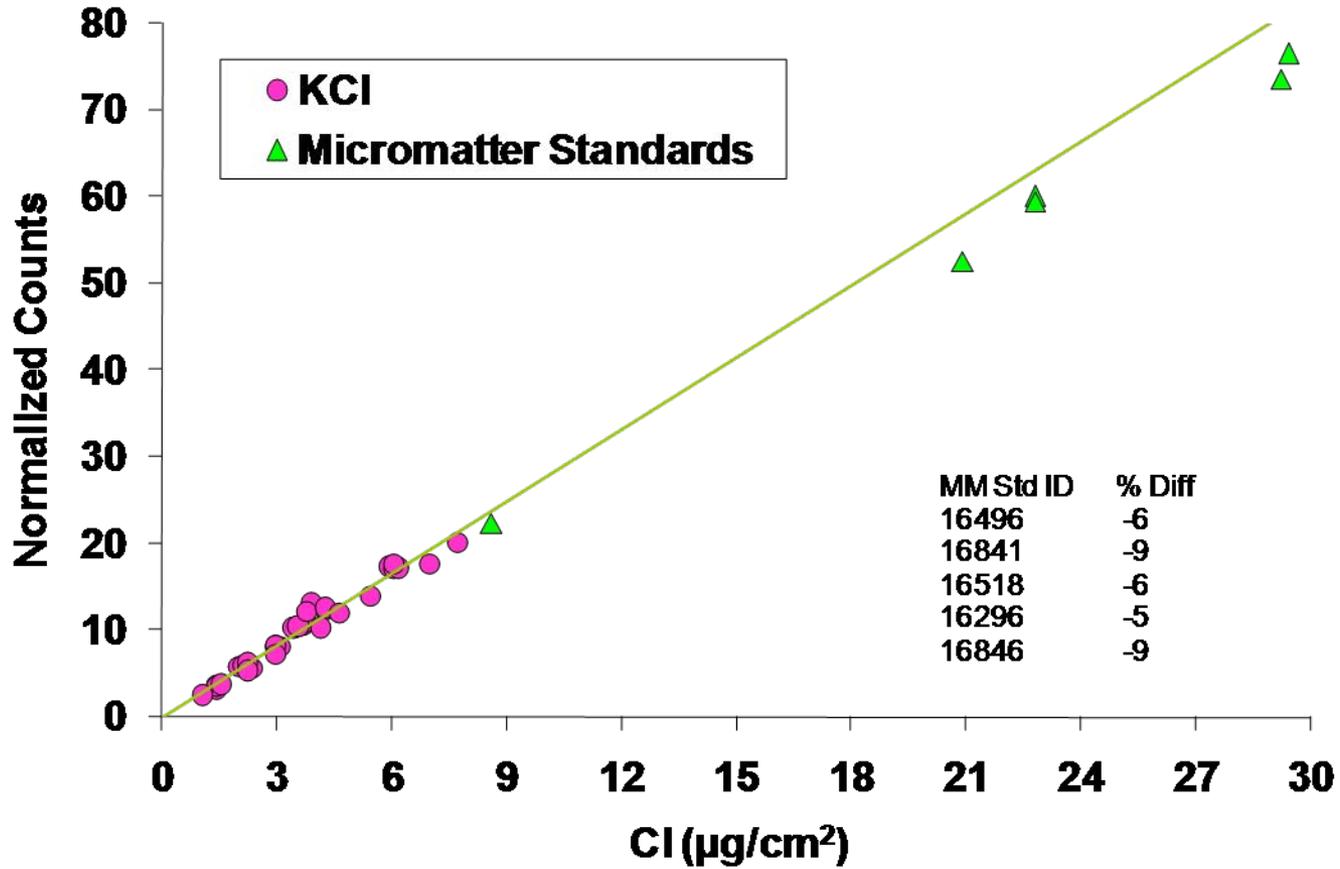
K_2SO_4 response on Cu1



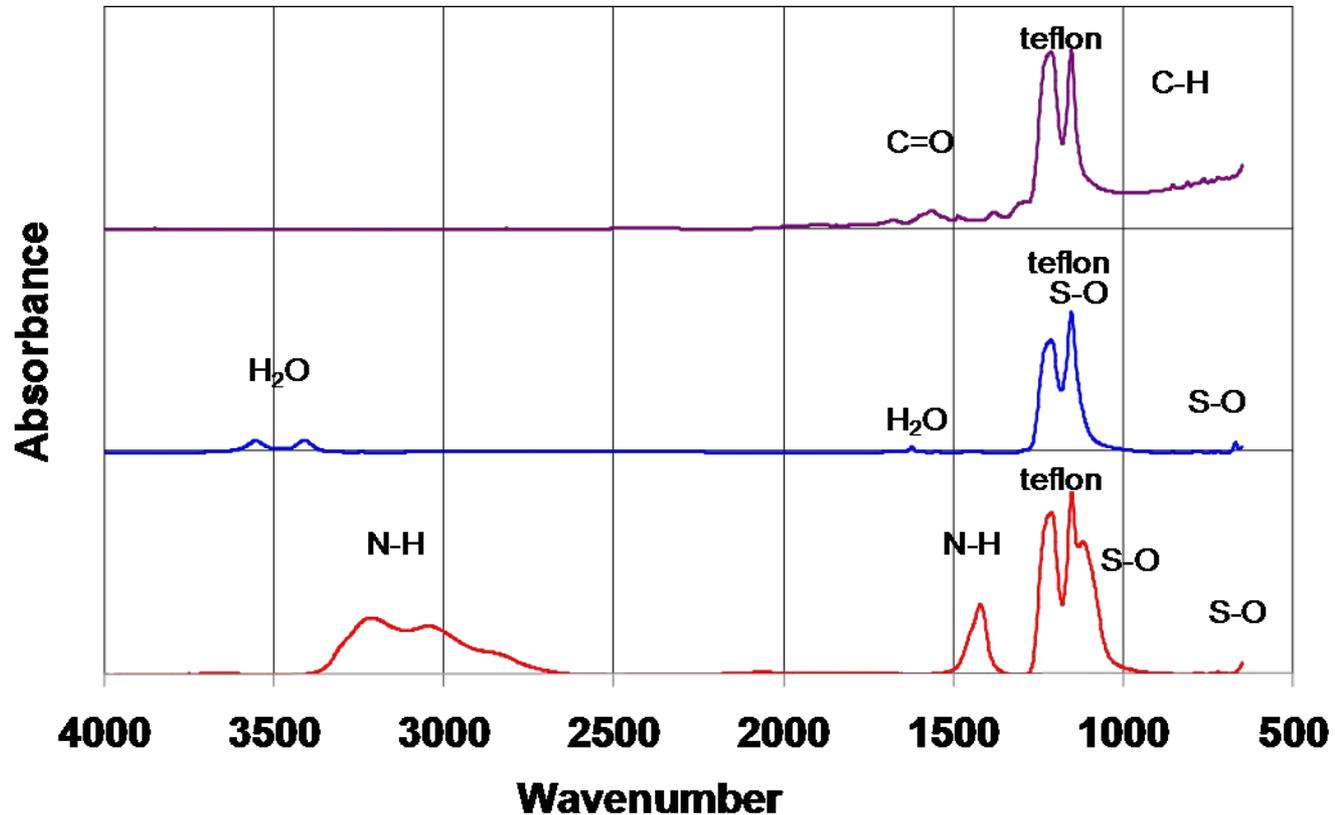
K



Cl



Analysis of Contamination – by FTIR water and organics

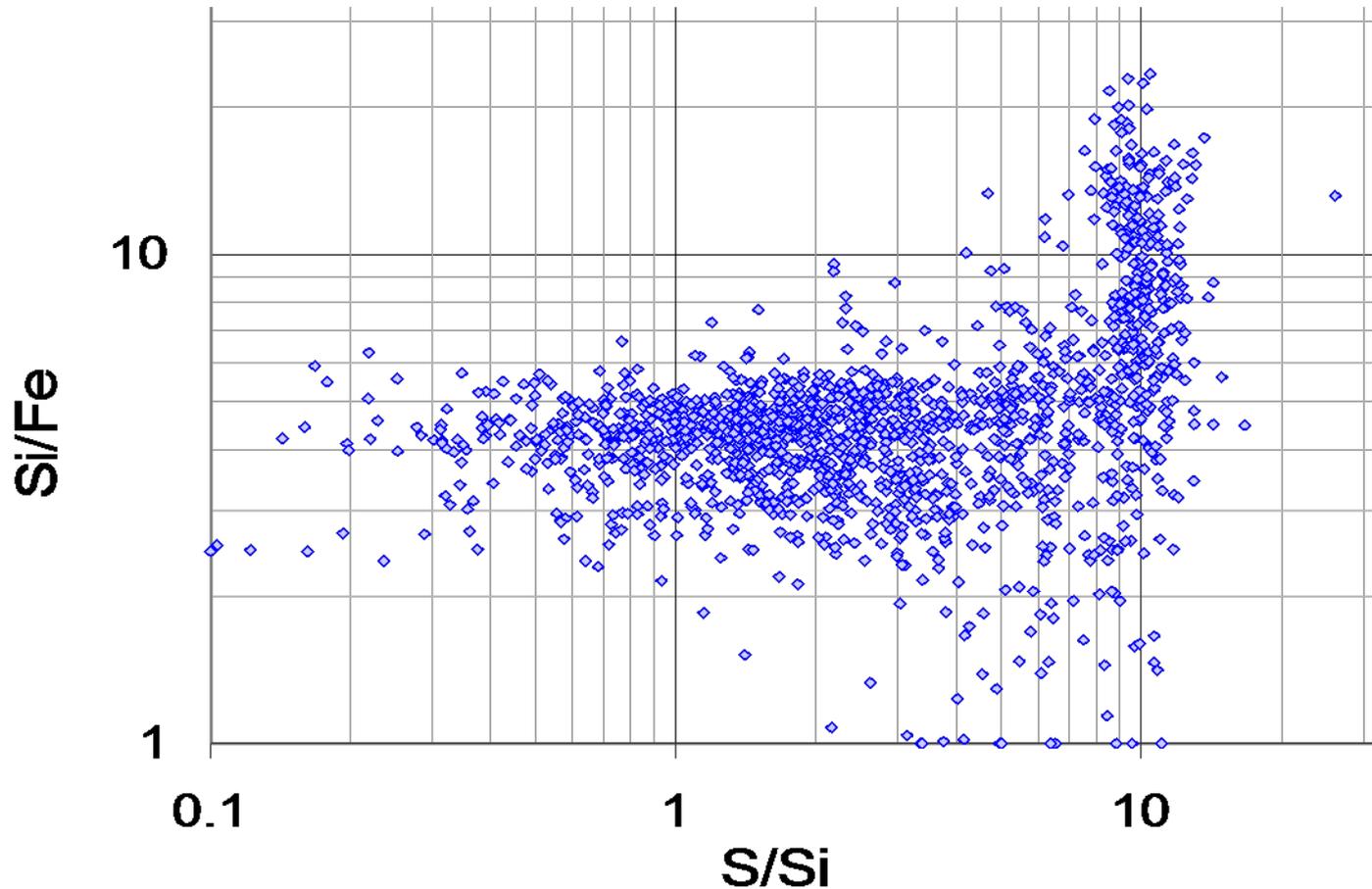


— 155 ug Amm. Sulfate — 219 ug CaSO₄-2H₂O — 187 ug KHP

Summary of Reference Filters

- Created PM reference filters
 - Characteristics of our systems
 - S (IMPROVE range), K, Cl are linear
 - Two Cu systems have different responses
 - S from K_2SO_4 on Cu1 not linear
 - Stoichiometry & contamination (in progress)
 - Compare to commercial XRF (in progress)
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Project 2: Interference in Si by S – Data Advisory, Warren White



July 2004 IMPROVE samples. Si >10 MDL.

Values outside the plotting range are plotted at the appropriate boundary.

Experimental Determination of Si interference by S

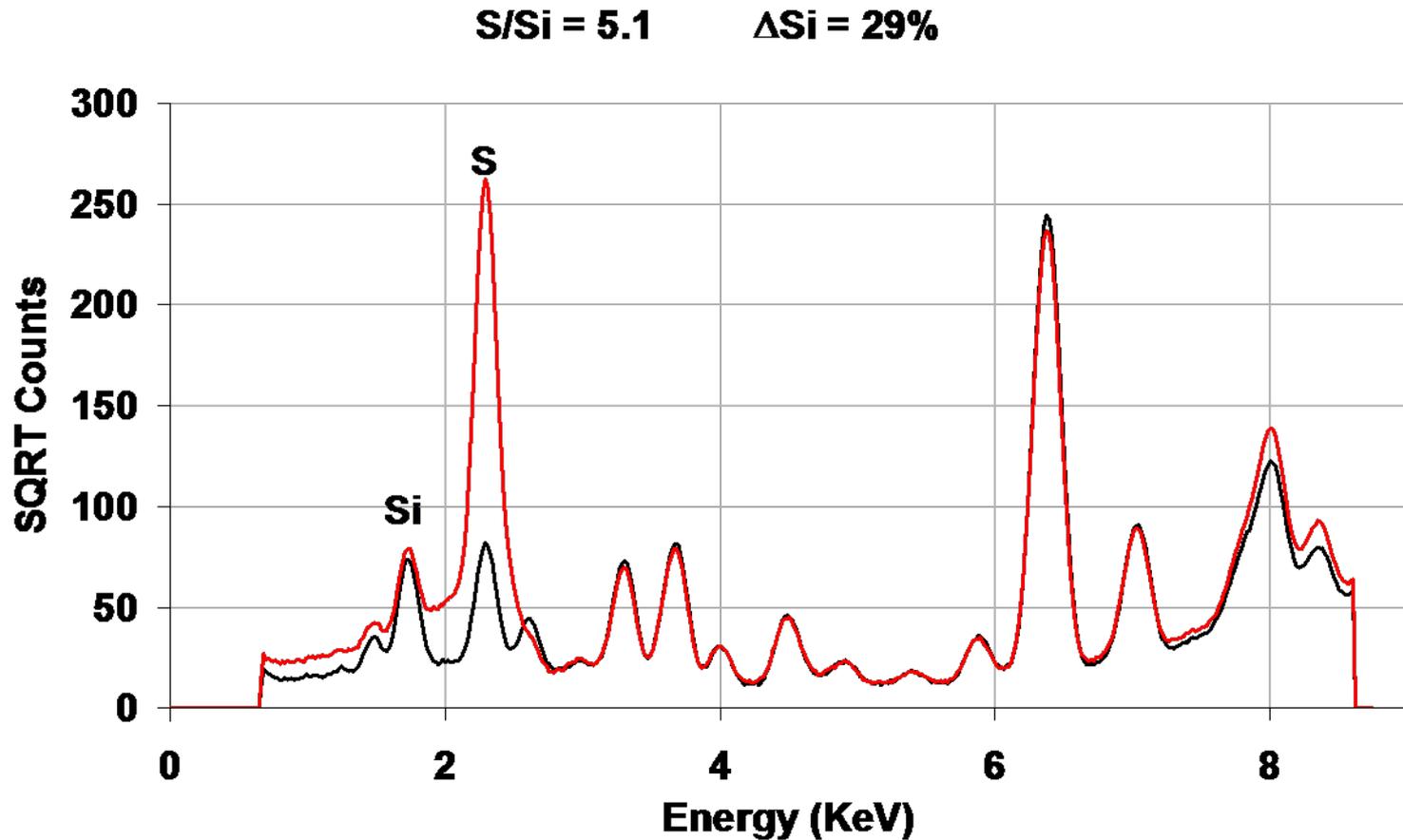
- $PM_{2.5}$ IMPROVE samples
- Dusty site
- S and Si by XRF
- Add S to obtain range of S/Si
 - Use aerosol chamber/sampler
- S and Si by XRF



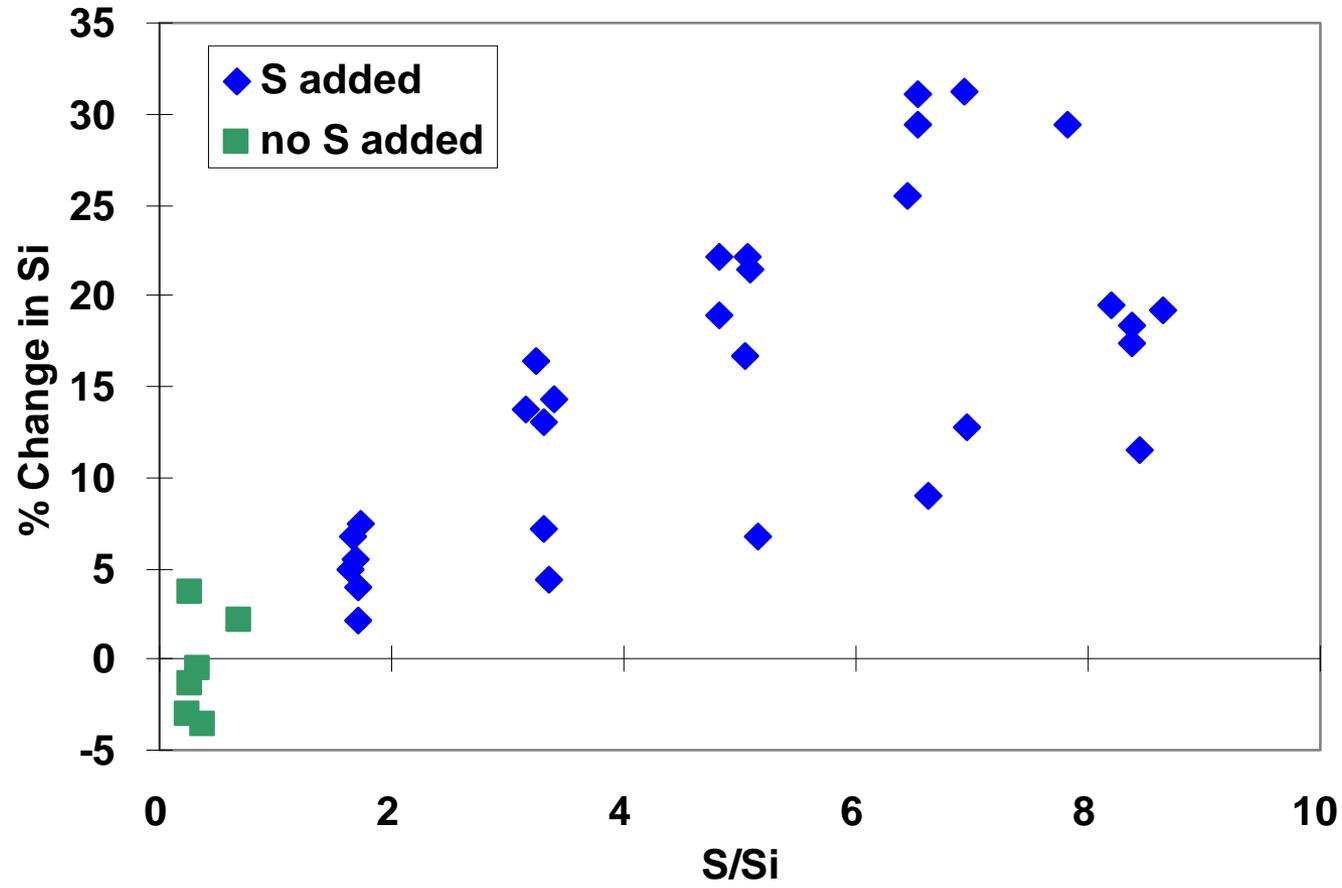
Sampling site near UC Davis



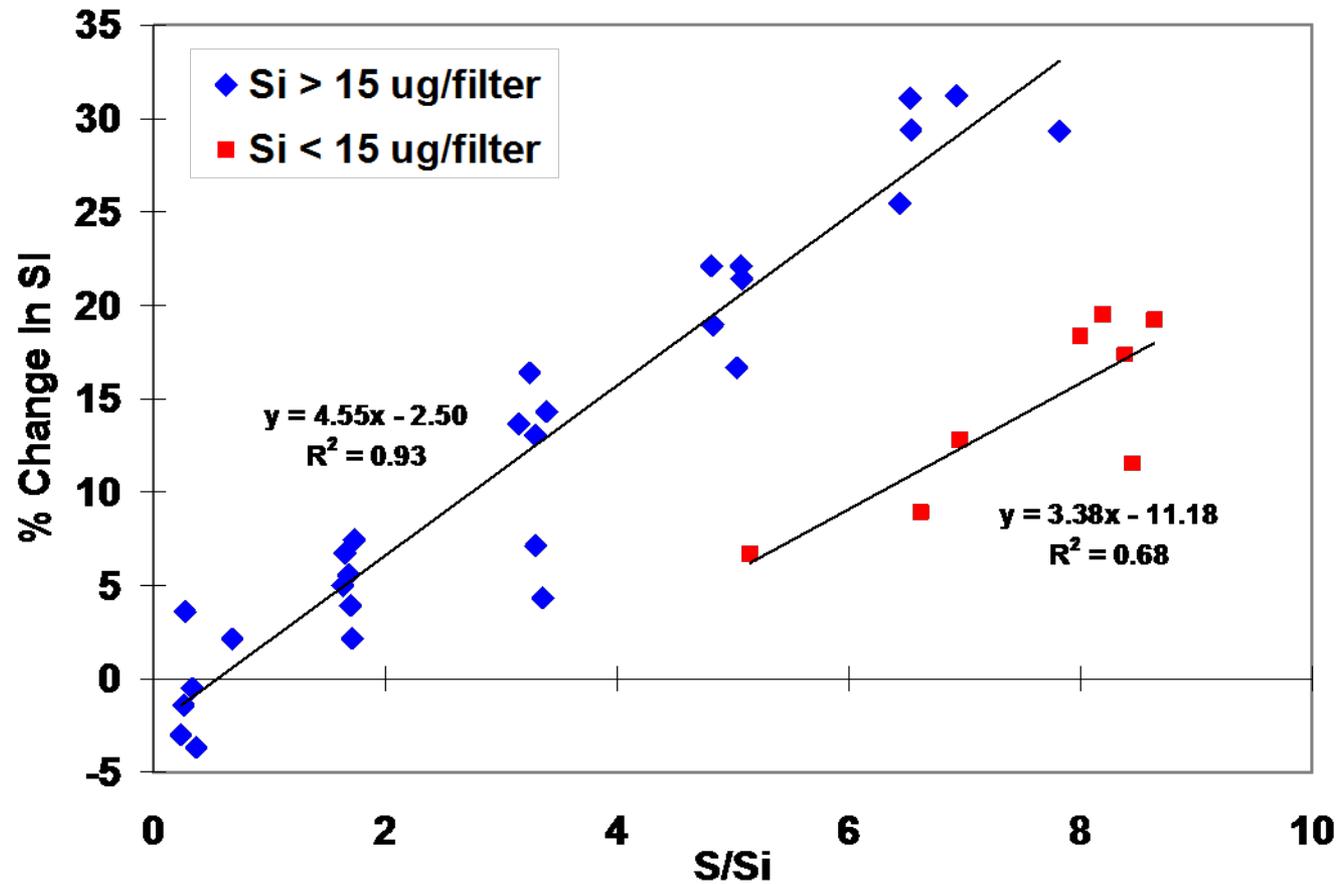
Spectral Change due to Added Sulfur



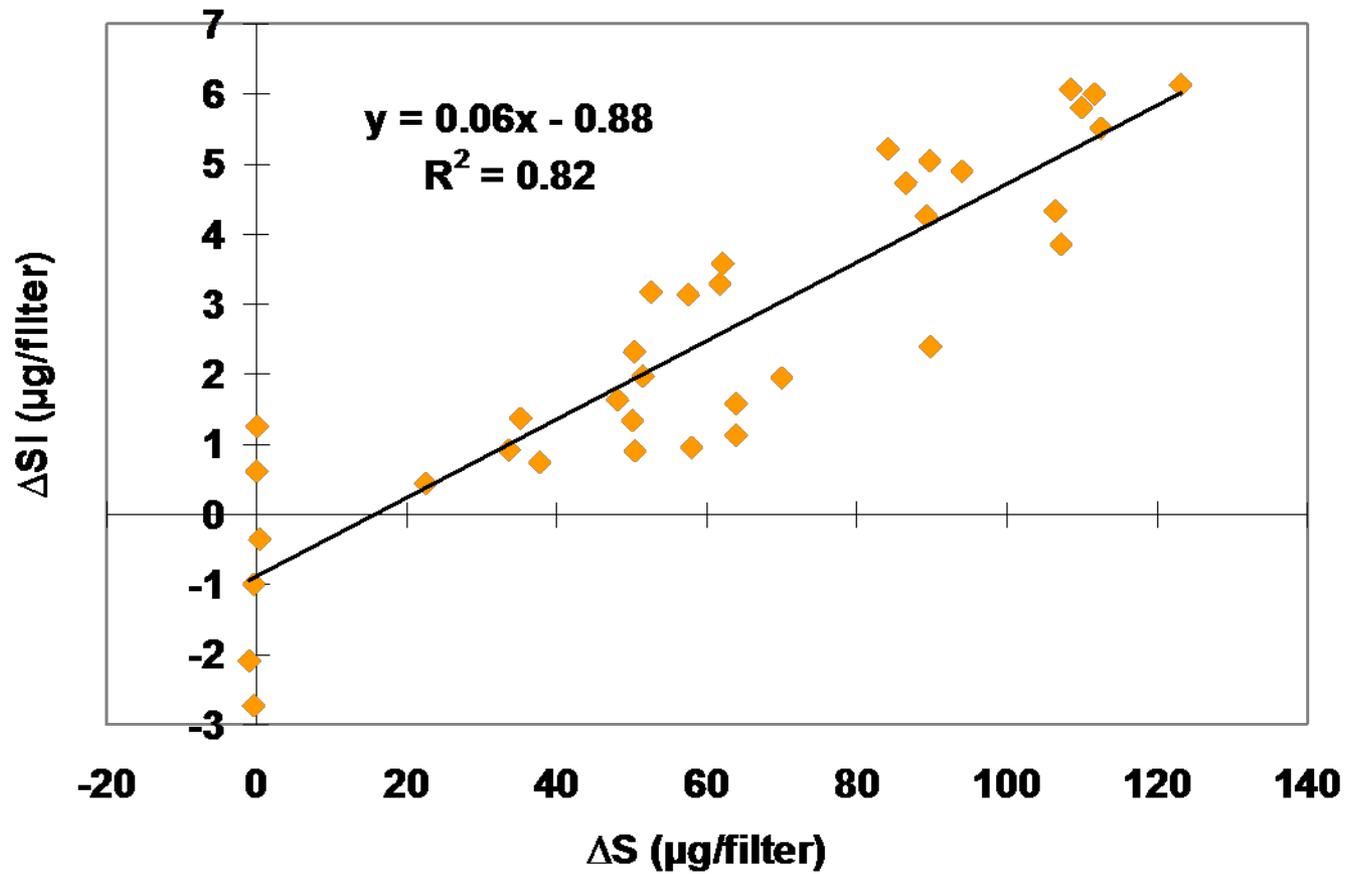
% Change in Si



% Change as Function of Mass



ΔSi vs. ΔS

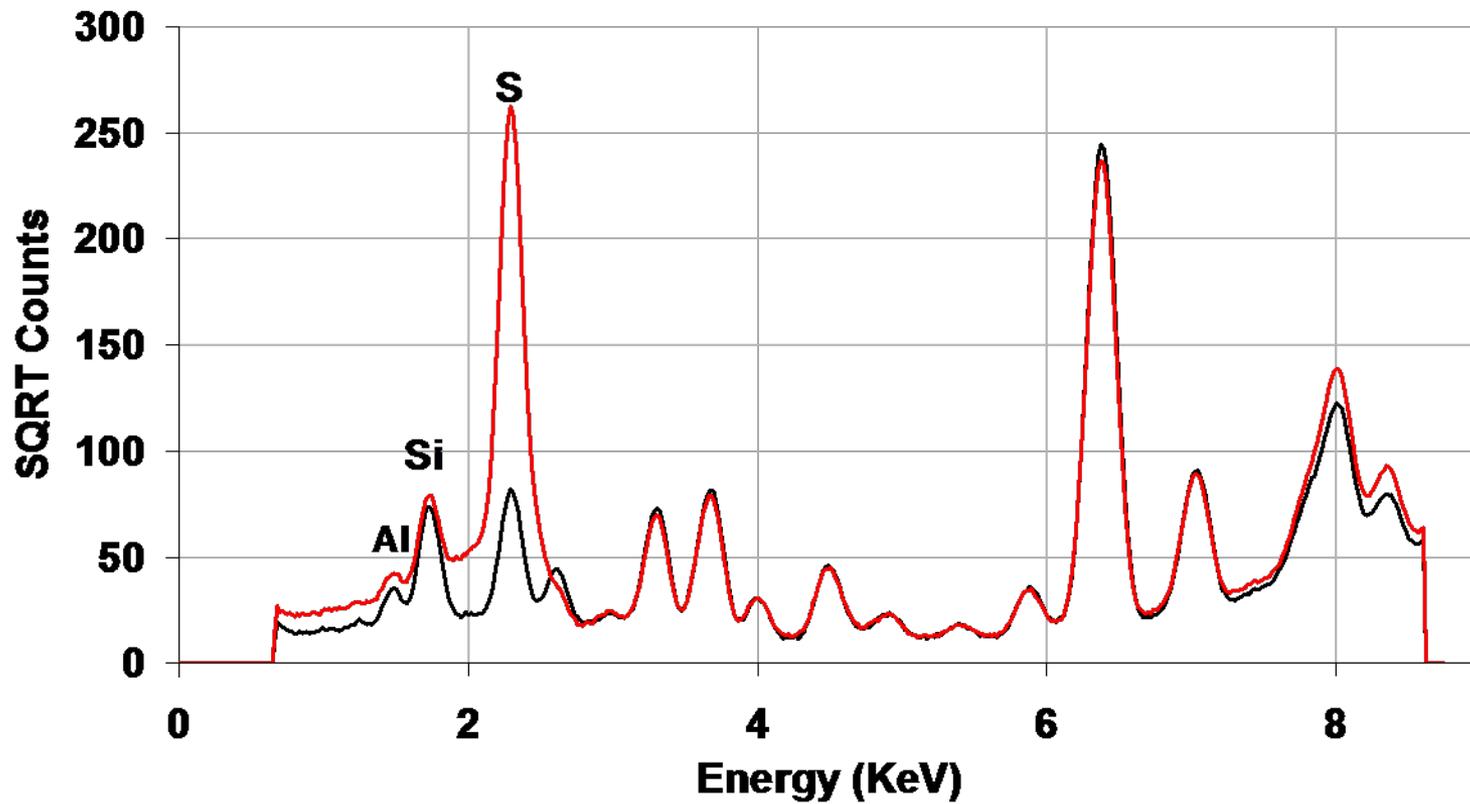


Aluminum

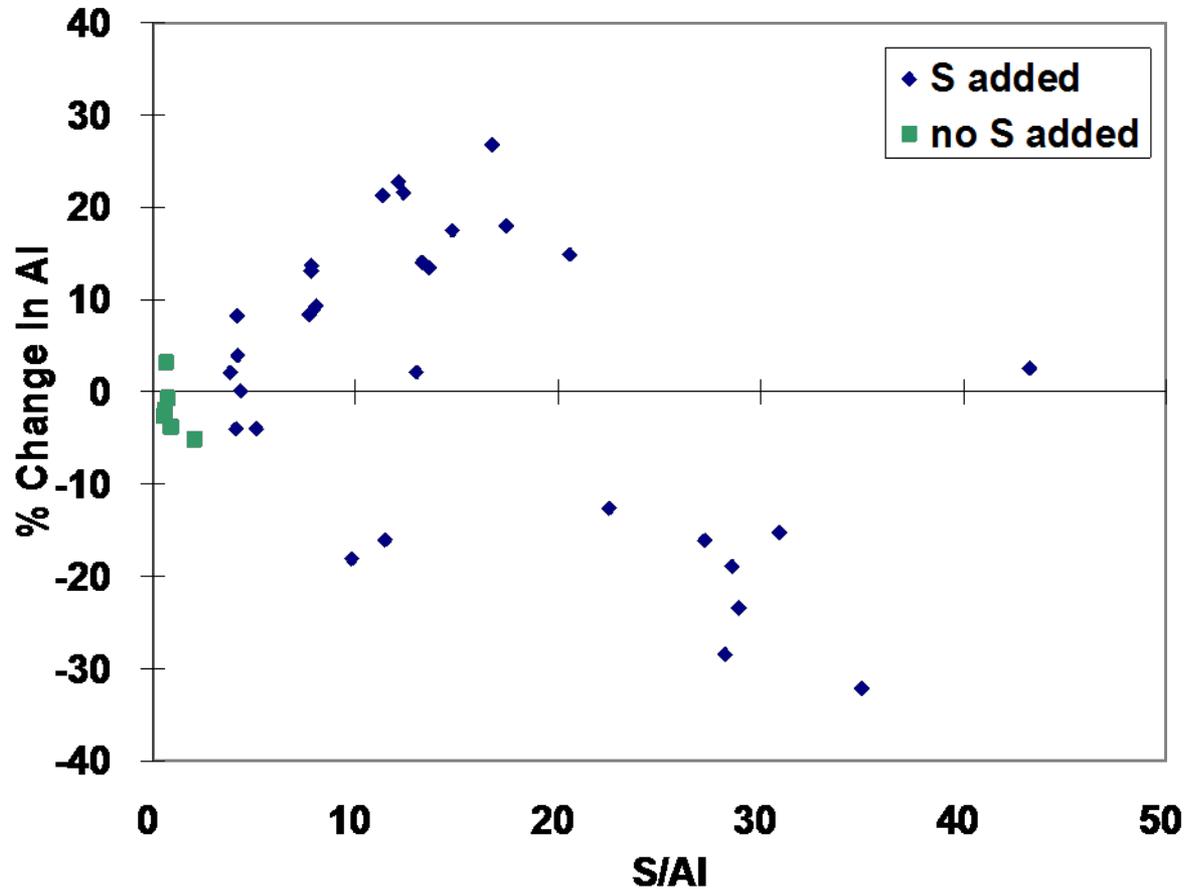
S/Si = 5.1

Δ Si = 29%

Δ Al = 18%

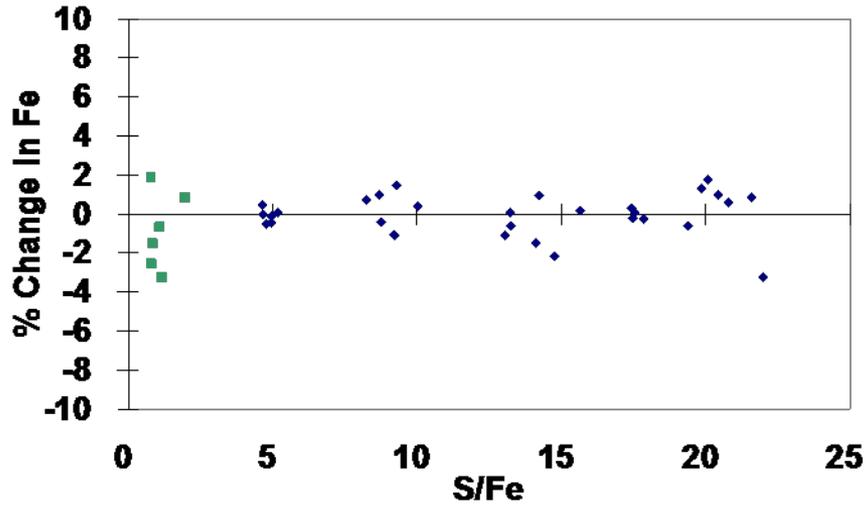


Aluminum % Difference



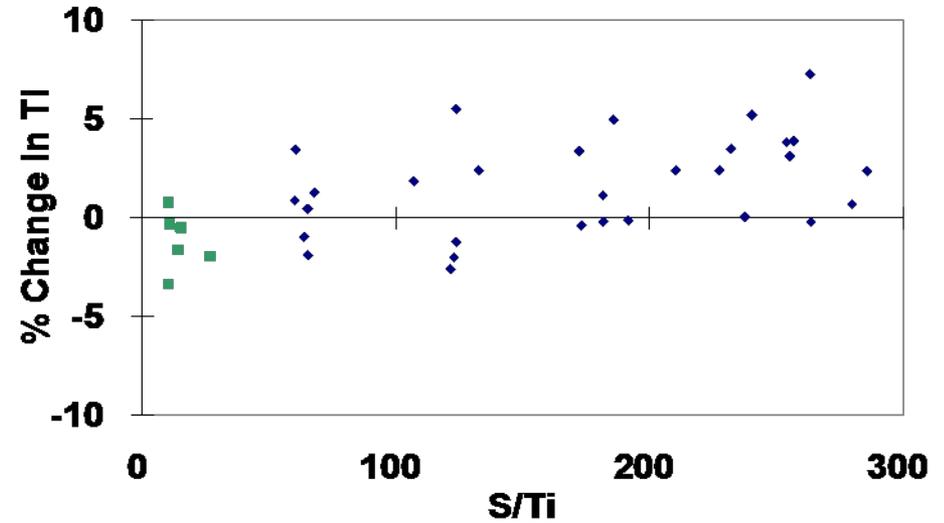
Other Soil Elements

Fe



Ca data very similar to Fe

Ti



Summary/Solutions of Interference

- At $S/Si > 3$, Si is inaccurately measured by XRF
 - Al is also inaccurately measured by XRF
 - other soil elements not impacted
 - Solution
 - Multi-element calibration standards
 - Range of S/Si , S/Al
 - New calibration algorithm
 - Improve XRF quantification
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Future Work

- Create reference filters of other elements
 - Use ICP-MS as reference method
 - Investigate other interferences
 - Have reference filters analyzed by other labs
 - **Improve XRF quantification**
 - **Create multi-element standards**
 - **Focus on soil elements**
 - **Focus on interferences**
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- Post-Doctoral researcher
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Nagaglo
 - Paul Wakabayashi
 - Burton Mehciz



Dillner/White Research Group Meeting
at UC Davis

Spectra of Sulfur from Cu-XRF

