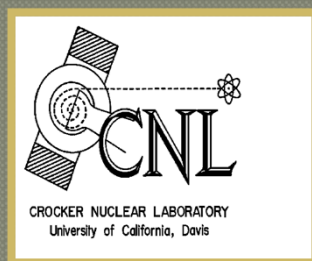
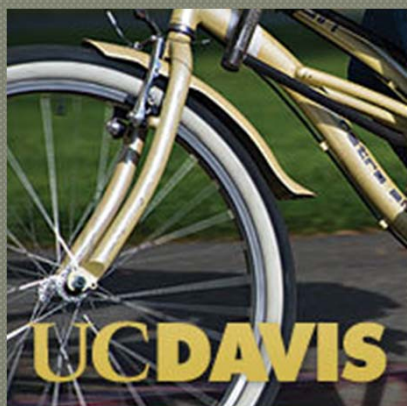


New Standards for XRF Analysis in the IMPROVE Network

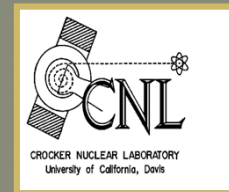
Ann M. Dillner, Hege Indresand, Warren H. White,
Chuck McDade, Brian Perley, Krystyna Trzepla-Nagaglo

Crocker Nuclear Laboratory
University of California, Davis

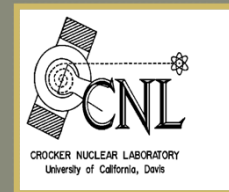


Calibration Standards for XRF

– Problem in the Scientific Community



- Ideal Standards :
 - Same matrix
 - Same substrate
 - Same mass range
 - Homogenous and stable deposit
- Commercial standards used in the XRF – PM community
 - Not made of particulate matter (metals, CuSx, CsBr)
 - Vacuum-deposited on Nuclepore or Mylar substrates
 - Higher mass than in IMPROVE samples
 - Analyzed at lower current and shorter time
 - Unsuitable for complementary analysis, i.e. IC, ICP-MS



Objectives of our work

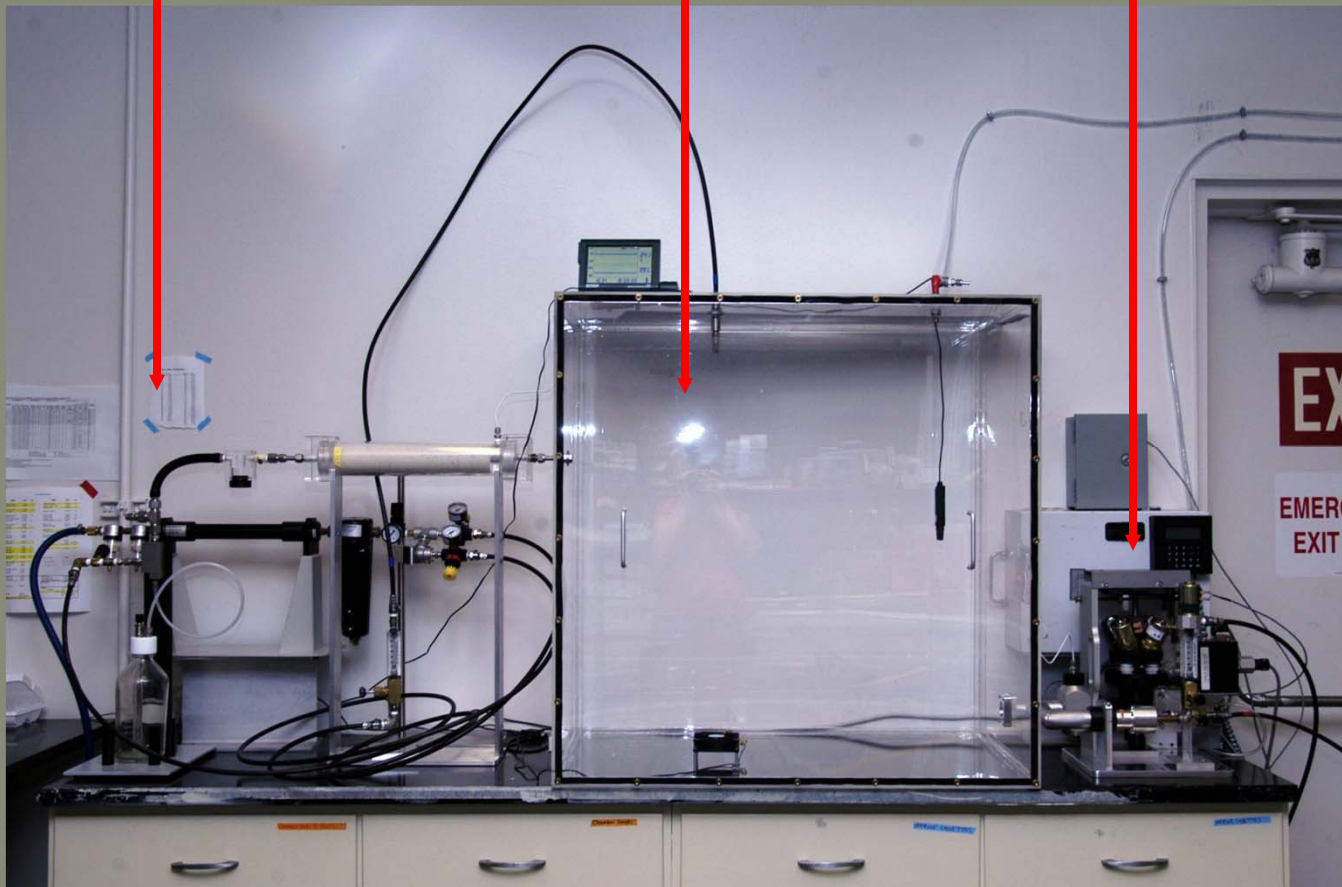
- Create S standards that mimic IMPROVE samples
 - Pure, stoichiometric particulate matter deposits of known composition
 - Mass range of IMPROVE network samples
 - on IMPROVE Teflon filters
 - using an IMPROVE sampler
- Characterize IMPROVE XRF measurement for sulfur
- Use standards in IMPROVE XRF analysis
 - Improve accuracy and precision of reported S concentrations
 - Improve S/SO₄ consistency in network

Aerosol Generation and Sampling System

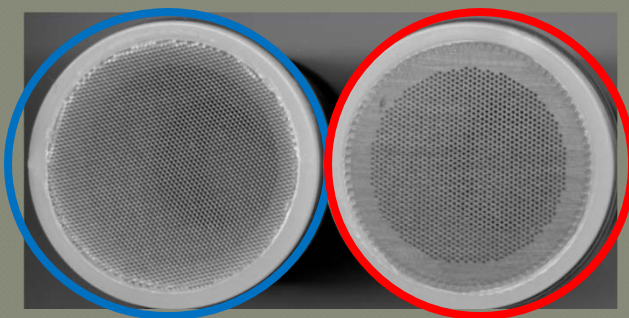
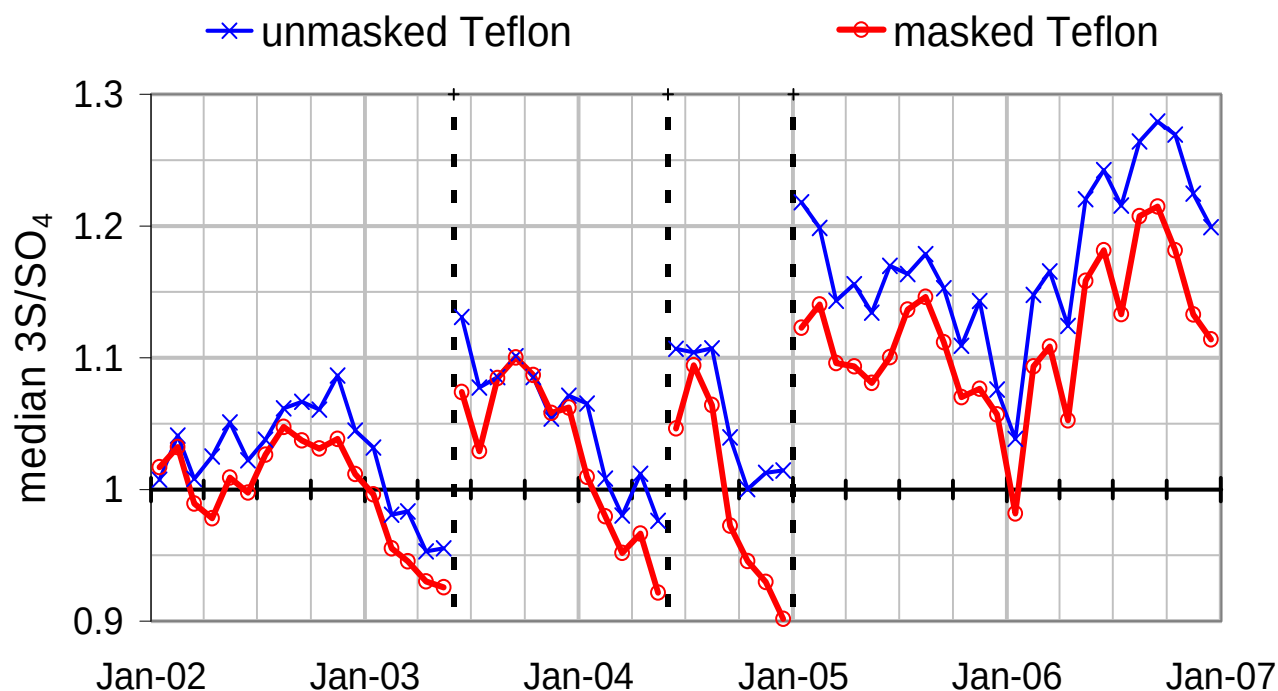
Generation System

Mixing Chamber

IMPROVE PM_{2.5} Sampler



Sulfur to Sulfate Comparisons 2002 - 2007

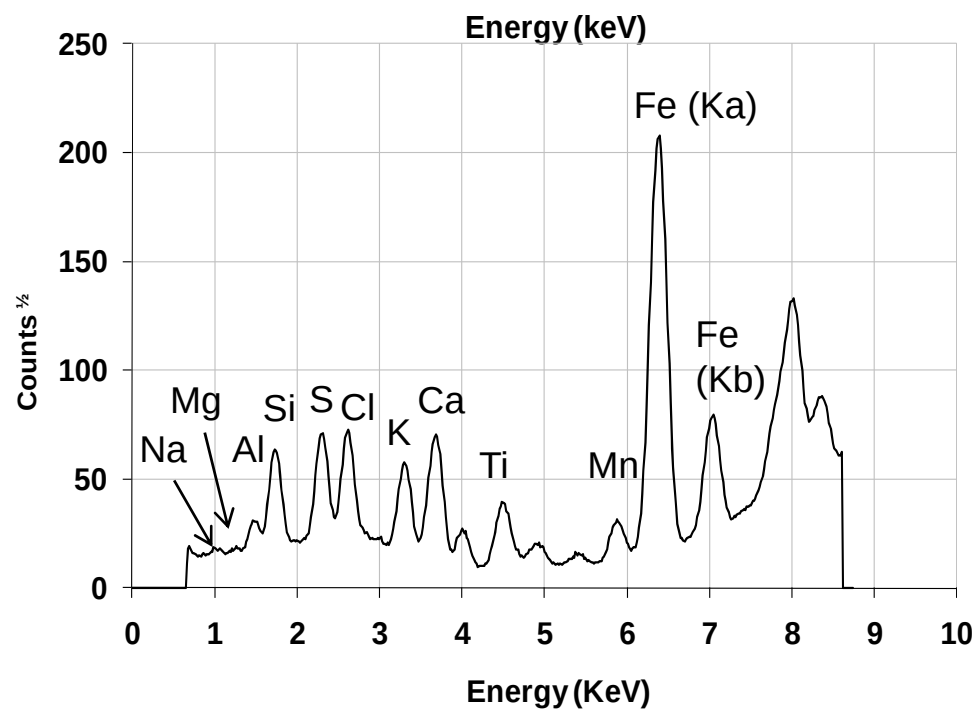
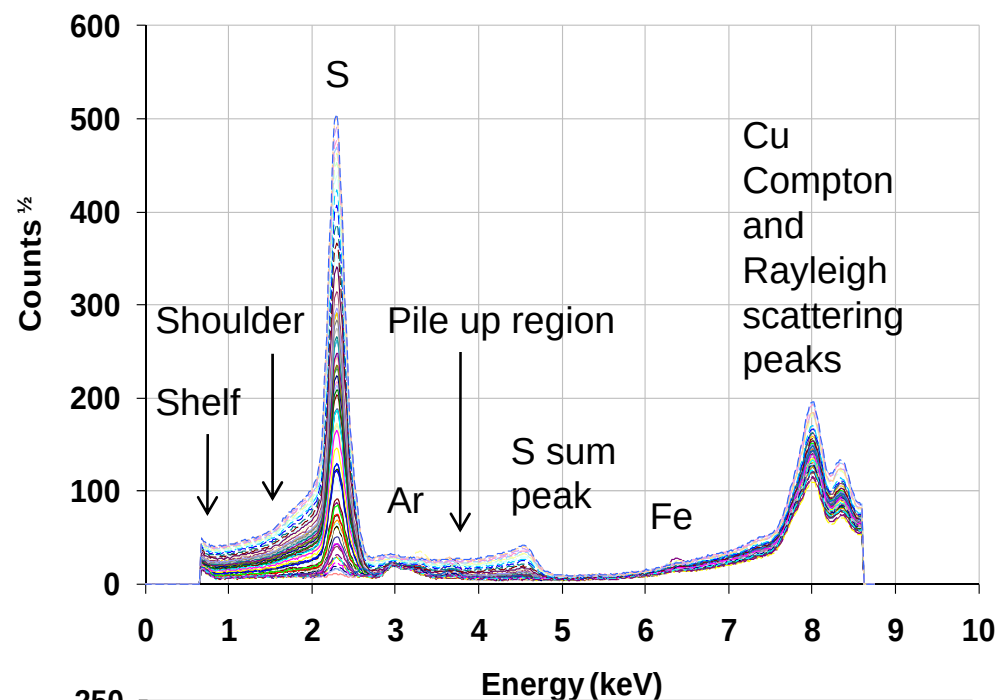


- $3 \times \text{Sulfur} / \text{sulfate} = 1$ in PM
- Dashed vertical lines indicate re-calibration
- Sulfur biased up to 20 % compared to sulfate
- 5 % Diff. in masked and unmasked filters

Aerosol S Standards to Evaluate and Calibrate XRF



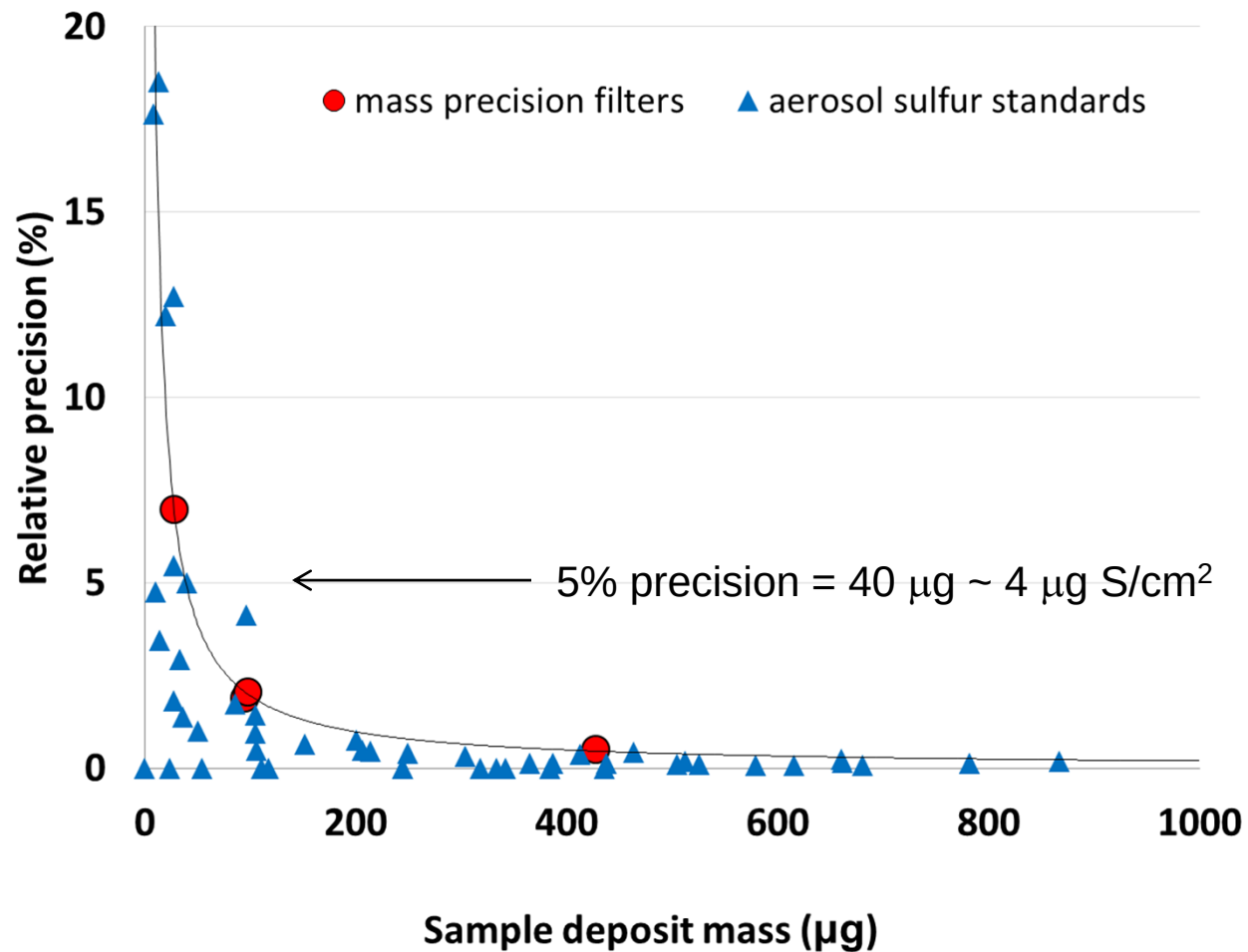
- **Created Sulfur Standards**
 - $(\text{NH}_4)_2\text{SO}_4$ (AS)
- **XRF analysis**
 - CNL CuVac2
 - DRI's PANalytical XRF instrument
- **Sulfur mass determination to compare to XRF**
 - Gravimetric analysis
 - Precision - Balance uncertainty
 - IC – for verification of gravimetric analysis
- **Evaluation of Contamination**
 - XRF – non sulfur elements
 - IC – non-sulfate ions
 - FTIR analysis – carbon and water



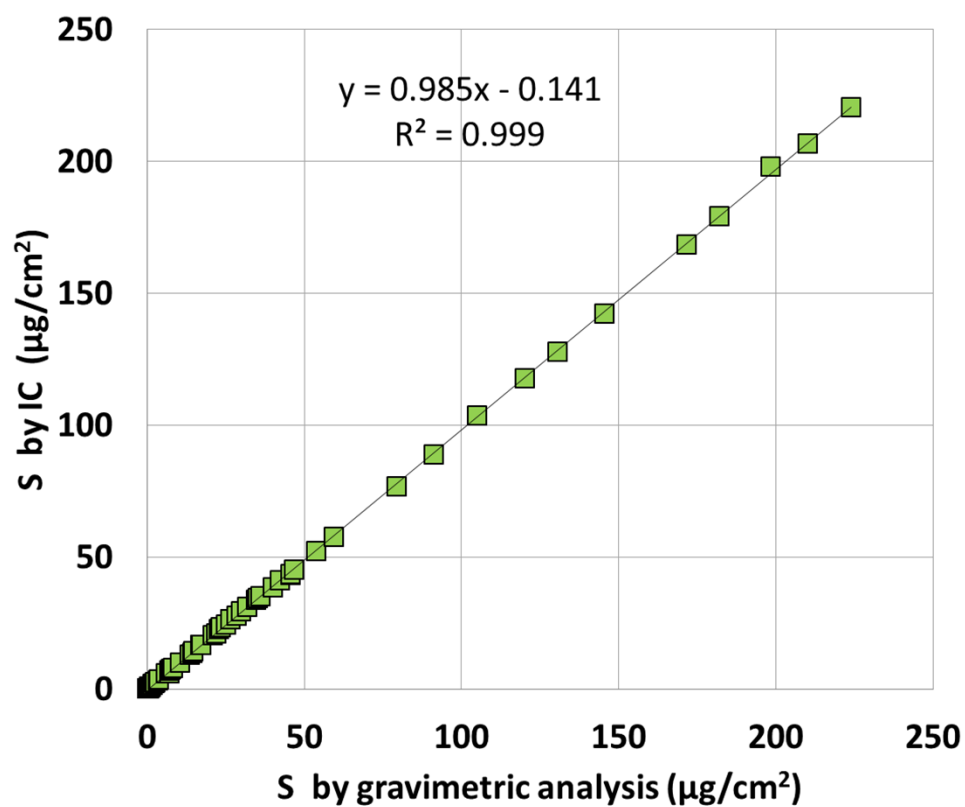
Ammonium sulfate (AS)
 RMs spectra from
 IMPROVE Cu-Vacuum
 XRF system

Typical PM2.5
 sample spectrum
 from research site in
 ag field near Davis
 CA (mostly soil)

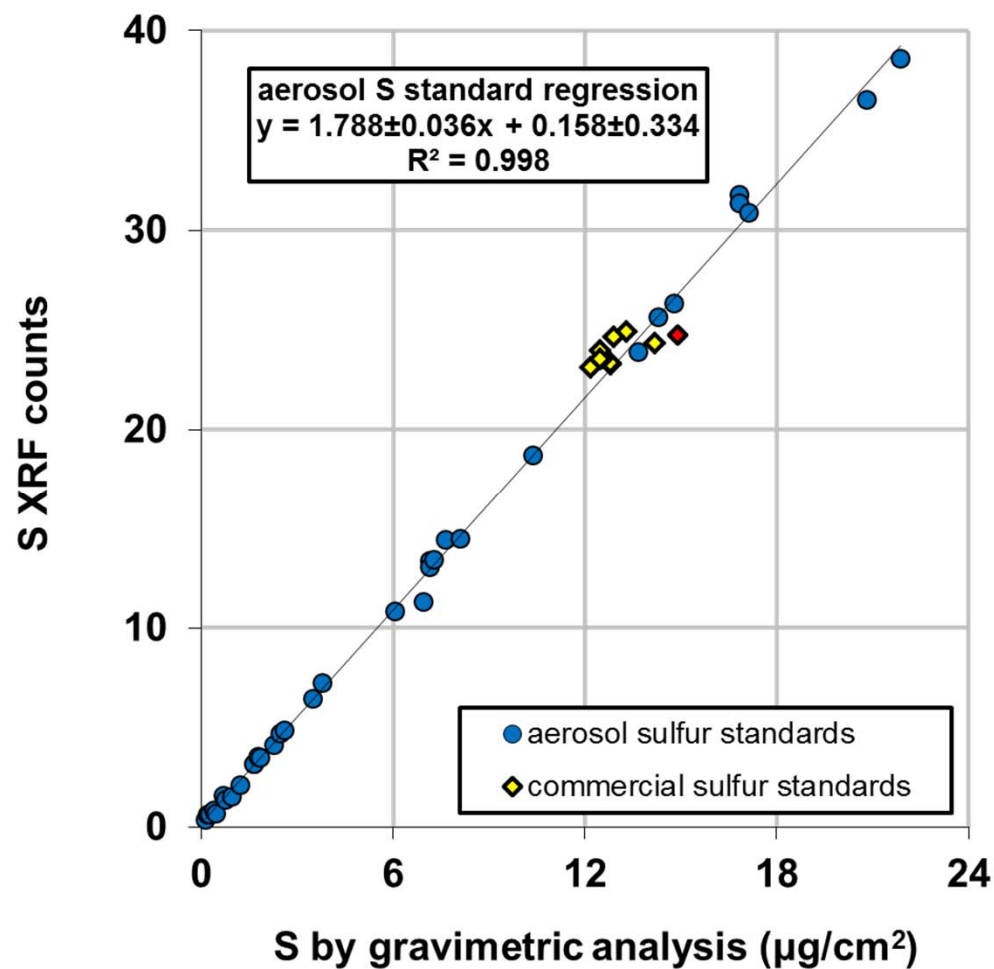
Uncertainty in Mass Precision Analysis



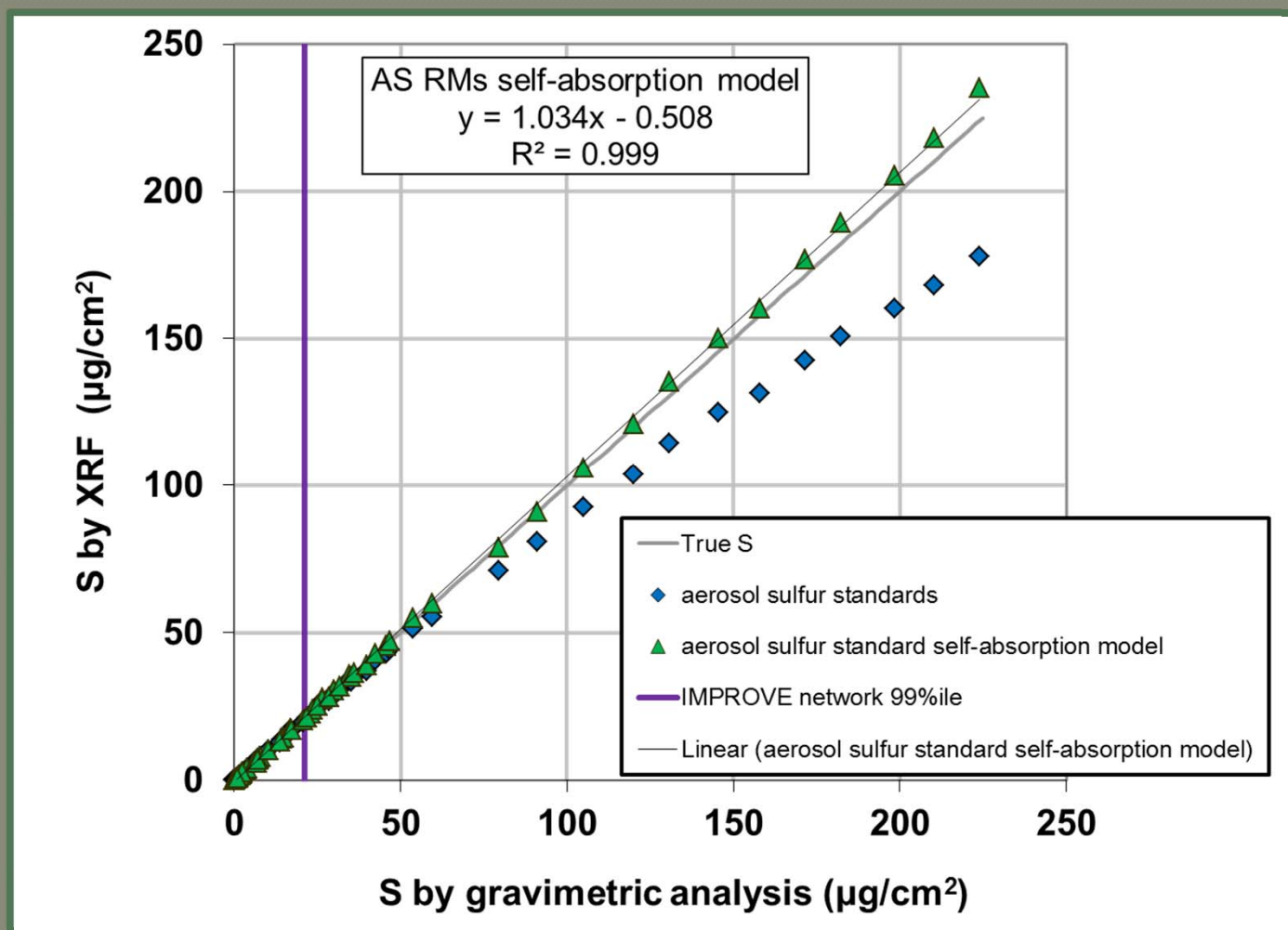
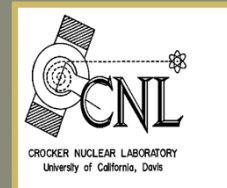
Confirmation of Mass by IC (RTI)



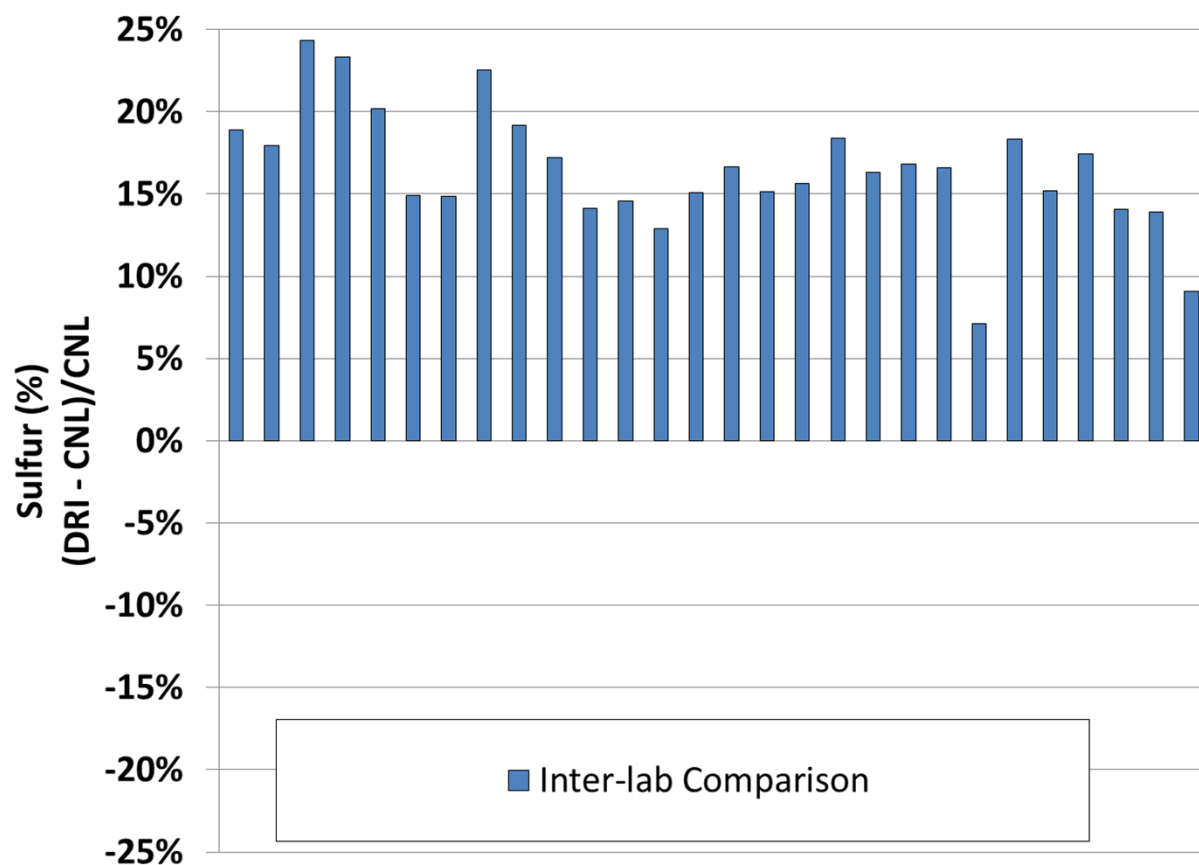
Aerosol S Standards and Commercial S Standards



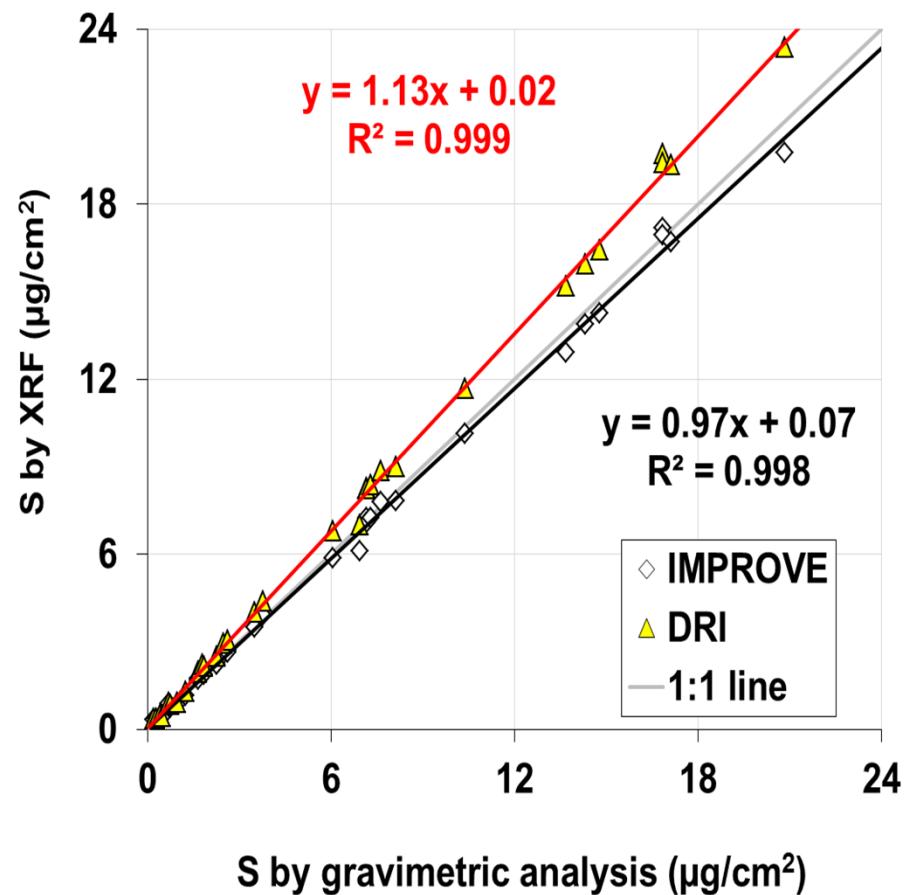
Characterizing Sulfur Response in the Cu-XRF System



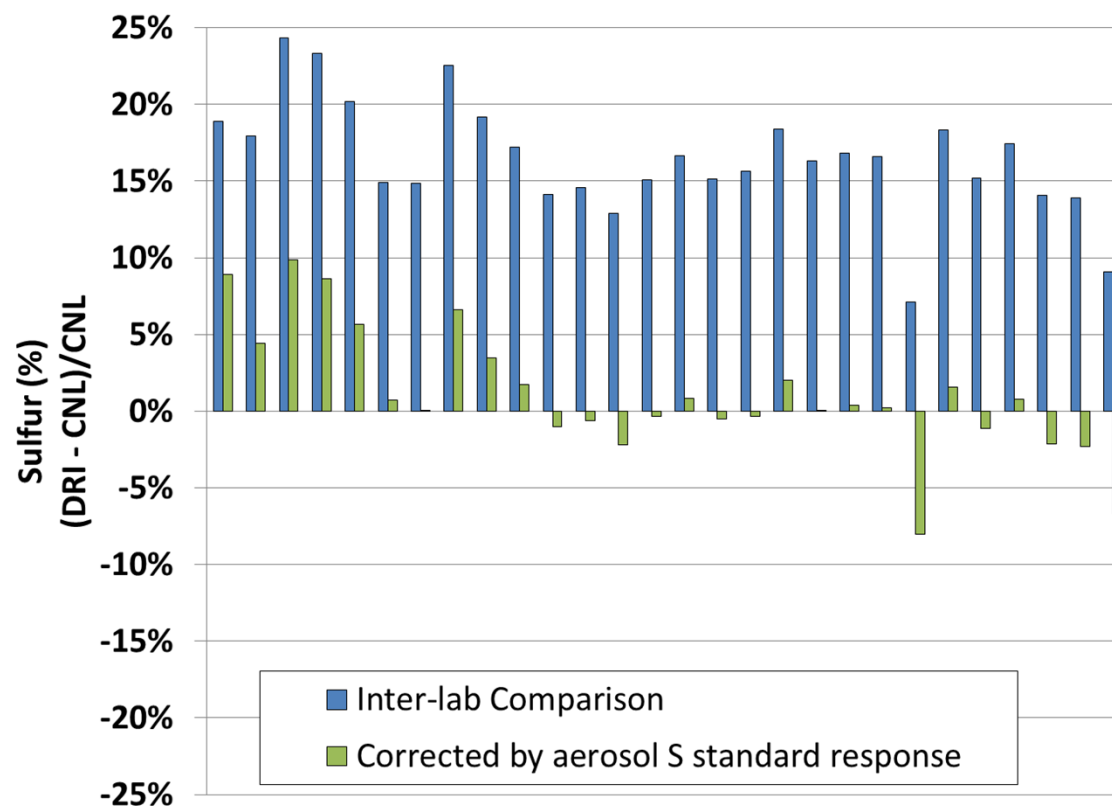
Inter-laboratory Comparison of 28 IMPROVE filters



Aerosol S Standards by CNL and DRI



28 IMPROVE samples calibrated with aerosol S standards at CNL and DRI



difference in S mass using commercial standards calibration = 16 ± 4 %

difference in S mass using aerosol S standards calibration = 1 ± 4 %

CONCLUSIONS



- Aerosol Sulfur standards
 - Sulfur mass based on primary method (gravimetry), confirmed with IC
 - Non-linearity in response revealed
 - Self-absorption is experimentally confirmed
- More precise calibration
- Improved inter-laboratory comparisons

Next Steps

- To further investigate the Sulfur/Sulfate
 - Create 200 S standards in IMPROVE range
 - Analyze by XRF
 - Send 4 to RTI for IC analysis
 - Monthly trend in Sulfur/Sulfate over 2 year period
- Create NaCl standards to evaluate potential targets in PANalytical system for Na analysis
- Incorporate aerosol S standards into calibration of IMPROVE XRF system
- Create standards of other elements and mixtures

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Dillner Research Group at UCDavis