

Pb reference materials for EPA lab audits, FEM testing and calibration

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Lead (Pb) reference materials

- Mike Papp and Joann Rice - Special project funded by EPA
- Develop reference materials for EPA Pb monitoring program
- Two purposes of filters:
 - To audit laboratories in the Pb monitoring program
 - Two mass loadings – approximately $0.1 \mu\text{g}/\text{m}^3$ and $0.3 \mu\text{g}/\text{m}^3$
 - To test Federal Equivalency Methods (FEM)
 - Current NAAQS is $0.15 \mu\text{g}/\text{m}^3$
 - Three mass loadings – 30%, 100% and 250% of NAAQS
- Additional filter prepared for XRF calibration for IMPROVE program (funded by IMPROVE)

Preparation of sulfur reference materials that reproduce atmospheric particulate matter sample characteristics for XRF calibration

H. Ind

Energy-dispersive X-ray fluorescence (EDXRF) is an important analytical technique for the determination of sulfur in atmospheric particulate matter (PM) samples. However, the lack of standardized reference materials (RMs) for sulfur in PM samples has led to significant uncertainties in the measurement of sulfur in PM samples. These differences are due to the different sampling methods used in the different networks. Continuous flow samplers are used in the IMPROVE network and a calibration method to correct for the differences in PM sampling geometry and deposition efficiency is used. This method is not applicable to the IMPROVE network and a new method is needed to produce RMs that reproduce the characteristics of the IMPROVE samples.

- Highlights of method
 - Reference material that physically mimic ambient samples
 - Material is particles
 - Support is same filter material as samples
 - Particles collected using PM sampler
 - Mass range of samples

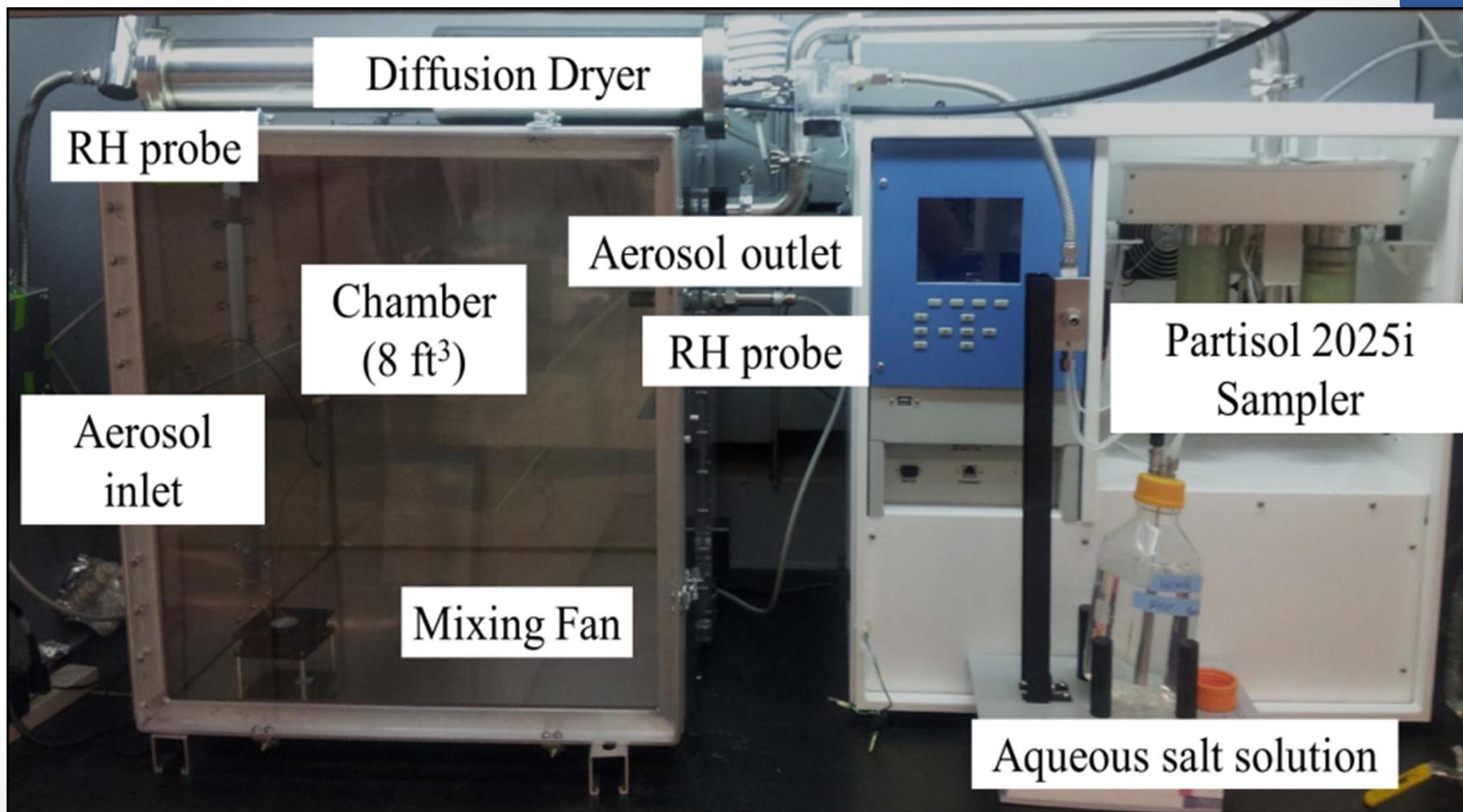
acceptable uncertainty in the measurement range. The XRF response of the sulfur reference materials is similar to other commercial standards and is linear in the measurement range, and the slope of the multipoint calibration curve has very low uncertainty. These reference materials are valid for the calibration of XRF systems, and they bring improved transparency and credibility to the IMPROVE calibration. Copyright © 2013 John Wiley & Sons, Ltd.

Introduction

Energy-dispersive X-ray fluorescence (EDXRF) is an important

(Micromatter, Vancouver, BC, Canada) are typically produced with a $50 \mu\text{g}/\text{cm}^2$ areal density of a deposit containing element(s) and are certified with an uncertainty of $\pm 1.5\%$. Attributes of the commercial

Experimental Apparatus

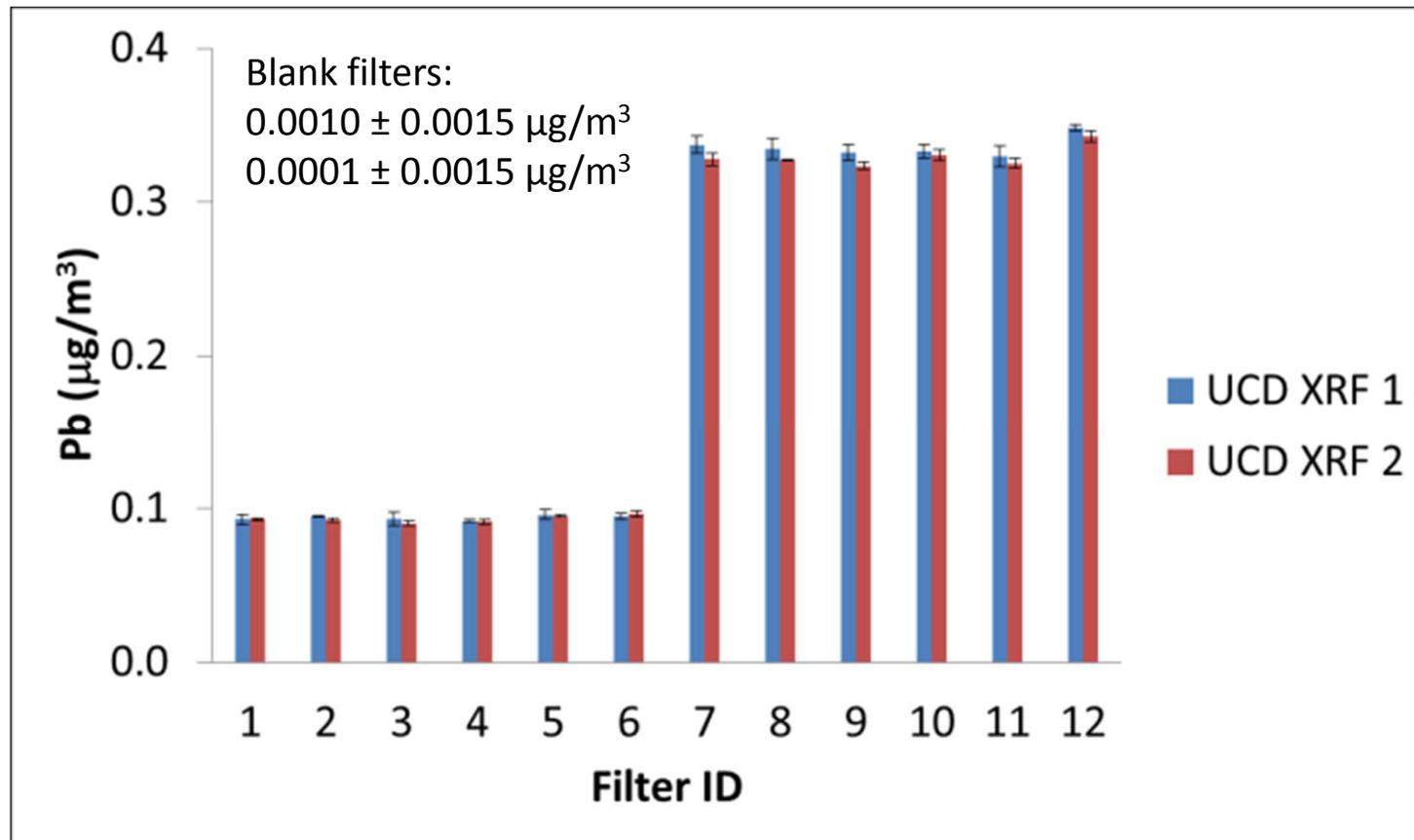


Lead acetate trihydrate, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$
Apparatus in fumehood

Analysis of Filters for EPA project

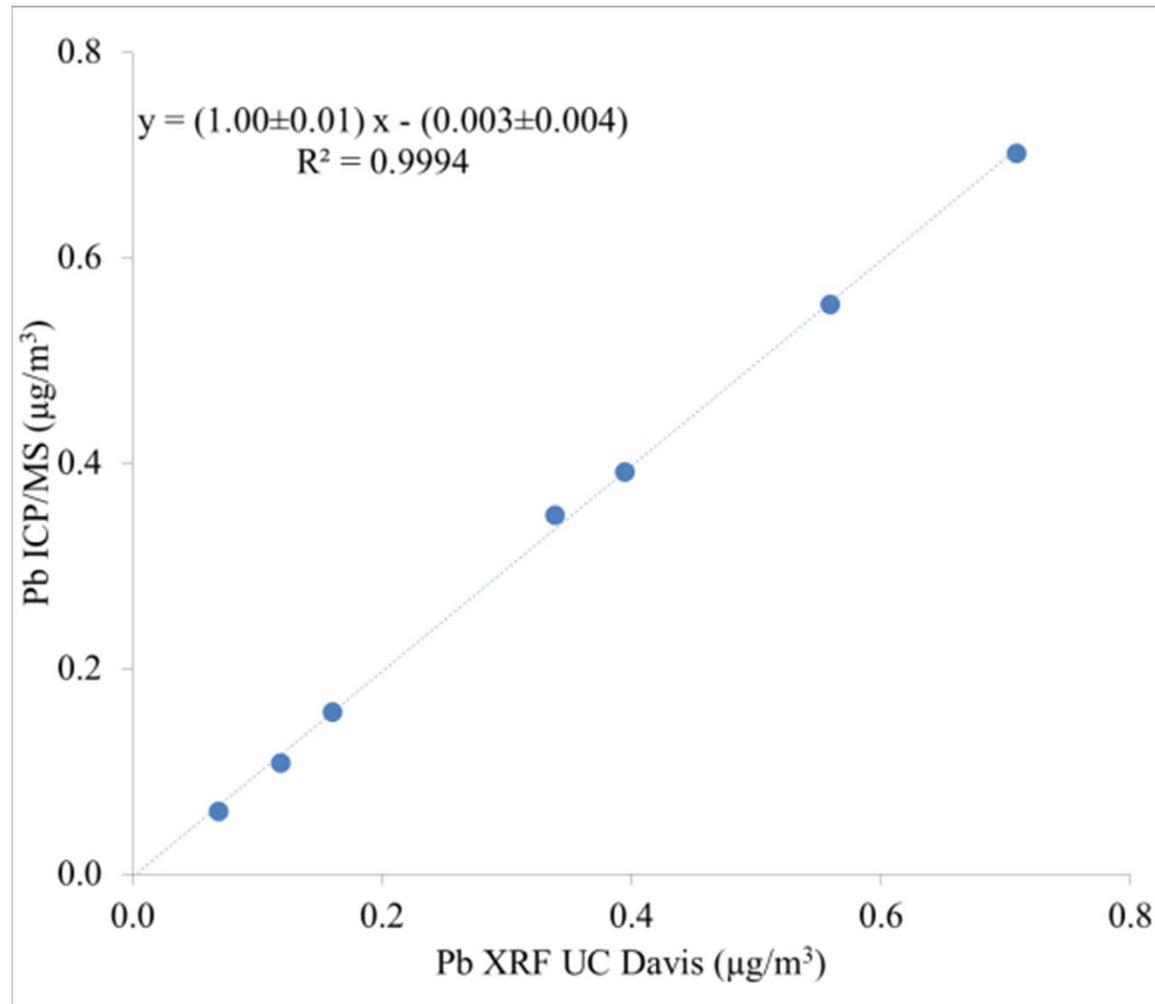
- 47 mm MTL “Teflon” filters – used for Pb monitoring
- XRF at UC Davis - PANalytical Epsilon 5
 - Calibrated with commercial standards
 - Triplicate measurements on two instruments for some samples
- XRF at RTI – Thermo Quant’X
 - Calibrated with commercial standards
 - Analyzed four times, rotating the sample 45 degrees
- ICP-MS at UC Davis - Agilent 7500ce
 - solvent extraction method using acetone and nitric acid followed by sonication and bubbling nitrogen through extract
 - developed by Mike Kleeman’s group at UC Davis
 - Less toxic than most ICPMS methods (no HF)
 - Pb isotopes monitored 204, 205, 206 and 208 m/z.

Triplicate Pb measurements

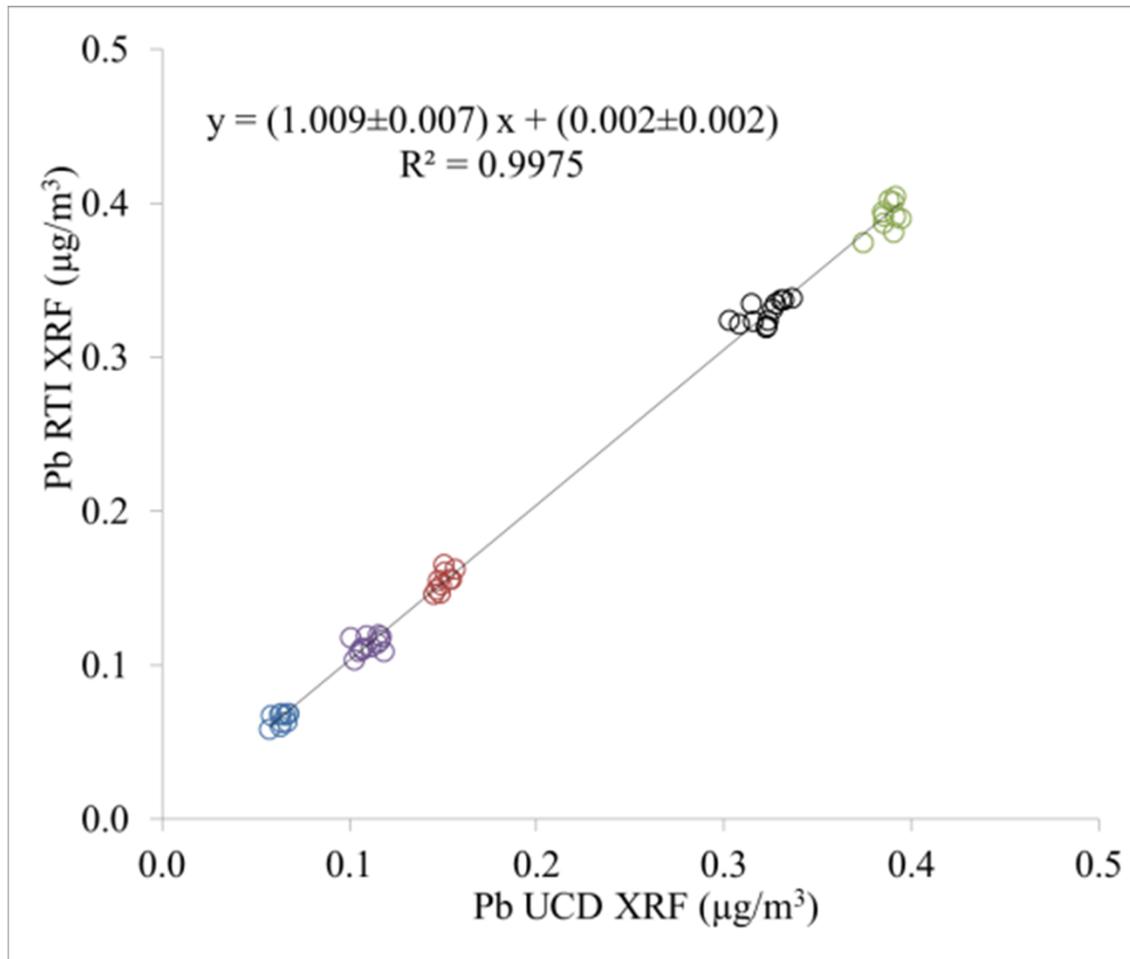


Sampled filter masses are nominally $2 \mu\text{g Pb}/\text{filter}$ and $8 \mu\text{g Pb}/\text{filter}$

ICP-MS vs. XRF



RTI XRF vs. UC Davis XRF



Four sets (24 filters) of audit filters (purple and black markers) and ten sets (30 filters) of FEM Pb filters (blue, red and green markers)

EPA project completed

- Within less than one year of start of project, delivered
 - Four sets of audit filters (24 filters)
 - Ten sets FEM Pb filters (30 filters)
- Article for EPA's OAQPS QA EYE newsletter
- Capability of producing additional filters for future needs

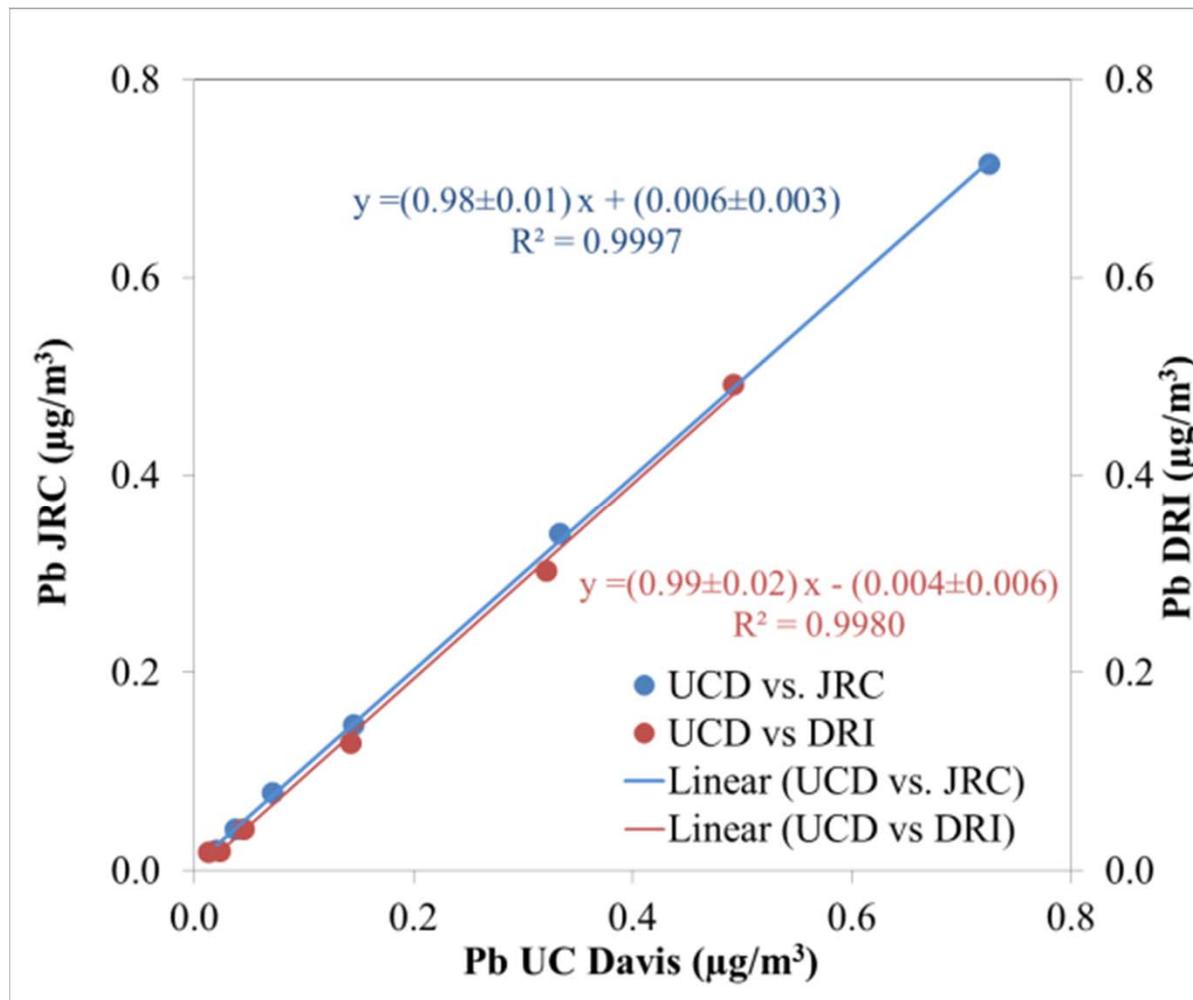
Pb standards for IMPROVE

- Funded via National Park Service
- Develop Pb standards to calibrate XRF instruments used to analyze IMPROVE filters
- Same experimental set-up as EPA project
- 47 mm Teflo filters (same material as IMPROVE 25 mm filters)
- Reference materials produced that span the mass range of IMPROVE samples

Analysis of Filters

- XRF at UC Davis - PANalytical Epsilon 5
- XRF at DRI - PANalytical Epsilon 5
 - Calibrated slightly differently than UC Davis
- XRF at European Commission Joint Research Center (JRC), Air Climate Unit, Ispra (VA), Italy - Quant'X
 - Standardless quantification method
 - Collaboration made possible by new IMPROVE staff person

Pb measurements



Summary

- Special project to deliver Pb reference materials to EPA completed with one year
 - Reference materials made with particles collected with an FRM sampler on filters used in Pb ambient sampling program
 - Filters with required mass loadings for audit filters and FEM development produced
 - Multiple analyses showed good agreement indicating strong confidence in Pb mass on the filter
- Additional Pb reference materials produced for IMPROVE XRF calibration
 - Reference materials made using IMPROVE filter material
 - IMPROVE mass range
 - Good agreement in Pb loadings across labs
 - To be included in XRF calibration