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

\[ y = 1.75x + 0.59 \]
\[ R^2 = 0.999 \]
S from K$_2$SO$_4$

- (NH$_4$)$_2$SO$_4$
  - $y = 1.75x + 0.59$
  - $R^2 = 0.999$

- K$_2$SO$_4$
  - $y = 1.75x - 0.34$
  - $R^2 = 0.999$
Micromatter Standards

![Graph showing normalized counts versus S (µg/cm²)]

- (NH₄)₂SO₄
- K₂SO₄
- Micromatter Standards

<table>
<thead>
<tr>
<th>SMM Std ID</th>
<th>% Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>16501</td>
<td>+9</td>
</tr>
<tr>
<td>16845</td>
<td>-3</td>
</tr>
<tr>
<td>17129</td>
<td>+5</td>
</tr>
<tr>
<td>17133</td>
<td>+1</td>
</tr>
<tr>
<td>17973</td>
<td>-2</td>
</tr>
<tr>
<td>17974</td>
<td>-2</td>
</tr>
<tr>
<td>16523</td>
<td>-4</td>
</tr>
</tbody>
</table>
Response at high S loadings

\[ y = 1.75x + 0.59 \]
\[ R^2 = 0.999 \]
Different response by two Cu-XRF systems

Cu 2
\[ y = 1.75x + 0.59 \]
\[ R^2 = 0.999 \]

Cu 1
\[ y = 0.98x + 0.27 \]
\[ R^2 = 0.998 \]
$K_2SO_4$ response on Cu1
Normalized Counts vs. K (µg/cm²)

- K2SO4
- KCl
- Micromatter Standards

<table>
<thead>
<tr>
<th>MM Std ID</th>
<th>% Diff K (K2SO4)</th>
<th>% Diff K (KCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16296</td>
<td>+7</td>
<td>-3</td>
</tr>
<tr>
<td>16846</td>
<td>+3</td>
<td>-6</td>
</tr>
<tr>
<td>16524</td>
<td>+5</td>
<td>-5</td>
</tr>
</tbody>
</table>
Cl

![Graph showing normalized counts against Cl concentration (µg/cm²). The graph includes data points for KCl and Micromatter Standards. The table on the right shows the MM Std ID and % Diff for each data point: 16496: -6, 16841: -9, 16518: -6, 16296: -5, 16846: -9.]
Analysis of Contamination – by XRF elements
Analysis of Contamination – by FTIR water and organics

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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)
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
Spectral Change due to Added Sulfur

S/\text{Si} = 5.1 \quad \Delta \text{Si} = 29\%
% Change in Si

S added
no S added

S/Si

% Change in Si

0 2 4 6 8 10
% Change as Function of Mass

\[ y = 4.55x - 2.50 \]
\[ R^2 = 0.93 \]

\[ y = 3.38x - 11.18 \]
\[ R^2 = 0.68 \]
$\Delta Si$ vs. $\Delta S$

\[
y = 0.06x - 0.88 \\
R^2 = 0.82
\]
Aluminum

$S/Si = 5.1$  \hspace{1cm} $\Delta Si = 29\%$  \hspace{1cm} $\Delta Al = 18\%$

**SQRT Counts**

<table>
<thead>
<tr>
<th>Energy (KeV)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQRT Counts</td>
<td>0</td>
<td>50</td>
<td>100</td>
<td>250</td>
<td>300</td>
</tr>
</tbody>
</table>

**Graph:**
- S peak at 2 KeV
- Si peak at 6 KeV
- Al peak at 8 KeV
Aluminum % Difference

![Graph showing % Change in Al vs S/AI]

- % Change in Al
- S/AI
- S added
- no S added
Other Soil Elements

Ca data very similar to Fe
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
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
Acknowledgements

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  - Brian Perley
  - Krystyna Trzepla-Nagaglo
  - Paul Wakabayashi
  - Burton Mehciz
Spectra of Sulfur from Cu-XRF

![Graph showing spectra of sulfur from Cu-XRF with SQRT Counts on the y-axis, Energy (KeV) on the x-axis, and 0 - 250 μg S/cm² range. Peaks labeled S and Cu tube, with S sum peak indicated.]