XRF Standards Development

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IMPROVE Steering Committee Meeting

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Ely, Minnesota
XRF Reference Materials (RM)s

- Use for calibration and quality control
  - Add to existing calibration reference materials from MicroMatter and NIST
  - Started using our in-house single-element RMs in 2011
  - Started using our in-house multi-element RMs in 2014
- Commercially available RMs are very limited
  - Not at concentrations relevant to atmosphere
  - Not on appropriate media
  - Only one NIST standard RM available
Generating XRF Reference Materials (RM)

- Materials
  - High purity salts (>99.9%) and nanoparticles (>99%) for single-element (SE-RMs)
  - Certified multi-element solutions for Multi-element RM (ME-RMs)

- Sample Collection
  - PTFE filters, 3 µm pore size, 25mm and 37mm (IMPROVE sampler) and 47mm (Partisol, MetOne SASS)

- Determining Reference Loadings
  - Ultra-microbalance for salts and nanoparticles
  - Inter-laboratory comparisons and ratios to well-measured elements for ICP calibration solutions
## Single Compound Standards

**Completed** (*indicates completed in 2016-2017, half way through list of elements)*

**Acceptance Criteria:** gravimetric uncertainty < 10% & XRF-Bias < 10%

<table>
<thead>
<tr>
<th>Compound</th>
<th>Element</th>
<th>Range of tested loadings, µg/cm²</th>
<th>Extra method for verification</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Na</td>
<td>0.7-34.0</td>
<td>Interlab comparison (IC)</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>1.0-52.0</td>
<td>Interlab comparison (IC)</td>
</tr>
<tr>
<td><strong>AlCeO₃ nanoparticles</strong>*</td>
<td>Al</td>
<td>0.6-5.5</td>
<td>Interlab comparison (XRF)</td>
</tr>
<tr>
<td></td>
<td>Ce</td>
<td>3.0-29.0</td>
<td></td>
</tr>
<tr>
<td><strong>SiO₂ nanoparticles</strong></td>
<td>Si</td>
<td>1.3-25</td>
<td>Interlab comparison (XRF)</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>S</td>
<td>0.5-55</td>
<td>Interlab comparison (IC)</td>
</tr>
<tr>
<td>KCl</td>
<td>K</td>
<td>0.5-30.0</td>
<td>Interlab comparison (XRF, IC)</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.5-30.0</td>
<td>Interlab comparison (XRF, IC)</td>
</tr>
<tr>
<td><strong>TiO₂ nanoparticles</strong>*</td>
<td>Ti</td>
<td>0.7-23.0</td>
<td>Interlab comparison (XRF)</td>
</tr>
<tr>
<td><strong>Fe₂O₃ nanoparticles</strong>*</td>
<td>Fe</td>
<td>0.7-7.0</td>
<td>Interlab comparison (XRF)</td>
</tr>
<tr>
<td><strong>CuO nanoparticles</strong>*</td>
<td>Cu</td>
<td>1.7-13.0</td>
<td>Interlab comparison (XRF)</td>
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<tr>
<td><strong>ZnO nanoparticles</strong>*</td>
<td>Zn</td>
<td>1.2-6.0</td>
<td>Interlab comparison (XRF)</td>
</tr>
<tr>
<td>Lead Acetate</td>
<td>Pb</td>
<td>0.7-14.0</td>
<td>Interlab comparison (XRF, ICP-MS)</td>
</tr>
</tbody>
</table>

**Limitations:**
- Availability of high-purity raw materials to generate desired standards
- Balance capability: accurate measurements require ~10 µg material deposit on filter
Single Compound RM Status

- Loadings as close to levels measured in IMPROVE as possible
- SE-RMs are stable and not affected by XRF analysis
  - Sulfate, sodium chloride, and lead standards have remained stable for >5 years
- Evaluated by other labs: Environment Canada (ECC), RTI, DRI, European JRC, International Atomic Energy Agency (IAEA), New Zealand Isotope Centre

The range of generated standards (Low and High) compare to IMPROVE and CSN 90%iles for selected elements
Na & Cl

**NaCl salt**

XRF-Bias: <10%

Good IC vs. gravimetric agreement (IC bias<10%)

- XRF-bias from $C_{\text{Ref}}$: \( \frac{C_{\text{XRF}}}{C_{\text{Ref}}} - 1 \)
- \( C_{\text{XRF}} \) = Result from by EDXRF
- \( C_{\text{Ref}} \) = Reference mass based on gravimetric
Multi-element Reference Materials (ME-RMs)

- Generated from certified multi-element solutions
- Reference loadings determined from ratios with $K$

$$[\text{Element}]_{RM} = [\text{Element}]_{solution} \times \frac{[K]_{RM}}{[K]_{solution}}$$

- An inter-laboratory comparison study with 9 XRF+3 ICP-MS at 12 levels

The range of ME-RMs (Low and High) compared to IMPROVE and CSN 90%iles for selected elements

- **Low**: Mimicking IMPROVE range (median)
- **High**: Major elements the same as Low, trace elements $> 3 \times \text{MDL (UCD-EDXRF)}$
Well-Measured Element: Potassium

KCl, K$_2$SO$_4$, KNO$_3$+CuSO$_4$, Cu+KNO$_3$

NIST SRM2783 (monthly, n=35)

$0.95 < b < 1.05$

$R^2 > 0.95$
ME-RM Inter-Laboratory Comparison Results

- Interlab results comparable with each other and with reference values for most elements
- Correlations for each lab were excellent ($R^2>0.95$) with very few exceptions
- ME-RMs helped identify some problems with the system and with existing calibration materials
- Provide quick check on instrument stability
  - At UCD since 2014, daily analysis on 4 analyzers
  - At Environment Canada since 2016, daily analysis on 2 analyzers
  - At IAEA and member labs since 2016
Zn

ZnO Nanoparticles

XRF-Bias: ≤10%

En: <1

Cons: Hydroscopic

Cu

CuO Nanoparticles (>99%)

XRF-Bias: ~-10%

En: Variable

Cons: Hydroscopic

Impurity (Ca and Zn) higher than 1% in PM mass

En number (ISO/IEC 17043, 2010)

\[ En = \frac{|C_{XRF} - C_{Ref}|}{\sqrt{U^2_{C(XRF)} + U^2_{C(Ref)}}} \]
Vanadium Biased High
Multi-Element RM Analyzed by 9 XRF and 3 ICP-MS instruments

VOSO₄
Stability of ME-RMs

- Relative Standard Deviation (RSD) similar to EDXRF precision
- Multiple analyses by EDXRF do not alter the loadings for non-volatile elements

**Multiple-XRF:** EDXRF analysis of a ME-RM every week ($n \sim 200$), $\text{RSD} \leq 10\%$

**Storage:** A ME-RM stored for 2 years, $\text{error} \leq 10\%$
### Single Compound Standards - In Progress

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<tr>
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<tbody>
<tr>
<td>NH₄H₂PO₄+ KNO₃ in 2% HNO₃</td>
<td>P</td>
<td>0.07-0.23</td>
<td>ME-RMs approach</td>
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<tr>
<td>CaO nanoparticles</td>
<td>Ca</td>
<td>1.5-20.1</td>
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<tr>
<td>CaCO₃ salt</td>
<td>Ca</td>
<td>3.0-10.0</td>
<td></td>
</tr>
<tr>
<td>CaTiO₃ nanoparticles</td>
<td>Ca</td>
<td>1.0-1.5</td>
<td>Interlab comparison (XRF)</td>
</tr>
<tr>
<td>CaZrO₃ nanoparticles</td>
<td>Ca</td>
<td>1.0-5.5</td>
<td>Interlab comparison (XRF)</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>Ca</td>
<td>0.5-10</td>
<td></td>
</tr>
<tr>
<td>CaZrO₃ nanoparticles</td>
<td>Zr</td>
<td>2.3-13.0</td>
<td>Interlab comparison (XRF)</td>
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<tr>
<td>VC nanoparticles</td>
<td>V</td>
<td>3.0-40.0</td>
<td></td>
</tr>
<tr>
<td>VO₂SO₄</td>
<td>V</td>
<td>0.3-3.3</td>
<td></td>
</tr>
<tr>
<td>CrN microparticles</td>
<td>Cr</td>
<td>2.5-10.5</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃ nanoparticles</td>
<td>Cr</td>
<td>3.0-16.0</td>
<td>Interlab comparison (XRF)</td>
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<tr>
<td>CuSO₄</td>
<td>Cu</td>
<td>0.4-4.0</td>
<td>Interlab comparison (XRF, IC)</td>
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<tr>
<td>ZnSO₄</td>
<td>Zn</td>
<td>0.6-4.0</td>
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</tbody>
</table>