Field Performance Evaluation of the Cooper Environmental Services Ambient Metals Monitor (Xact 620) for Near-Real Time PM$_{10}$ Metals Monitoring

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High Time Resolution Multi-Metals Measurements

Field sampling, laboratory analysis
• Serial collection of filter samples
• Davis Rotating-drum Unit for Monitoring (DRUM)
• Semicontinuous Elements in Aerosol Sampler (SEAS)

Online, semi-continuous measurements
• Single particle mass spectrometry (e.g. TSI ATOFMS)
• Aerosol mass spectrometer (Aerodyne AMS)
  – no refractory elements
• Cooper Environmental Services field XRF analyzer
Cooper Environmental Services (CES) Xact 620

• Xact series
  – I: Stack Sampling
  – II: Fenceline Monitoring
  – III: Ambient Monitoring
Cooper Environmental Services (CES) Xact 620
Cooper Environmental Services (CES) Xact 620
### Elements the XACT Can Measure (in Blue)

![Periodic Table Highlighted](image)

- Measured by XACT in this study
- EPA Air Toxics PM metals
Xact Performance Evaluation

LowVol PM$_{10}$ (FRM) / Teflon filter
XRF: Ca, Fe, K, Mn, Pb, Ti...

HiVol PM$_{10}$ / quartz filter
NATTS digestion protocol
ICP-MS: As, Pb, Se...
Xact vs. LowVol PM10 FRM / XRF

\[
\text{Xact} = (1.02 \pm 0.10) \times \text{filter} + (-0.1 \pm 1.8)
\]

\[
\text{Xact} = (0.84 \pm 0.21) \times \text{filter} + (28 \pm 25)
\]

\[
\text{Xact} = (1.05 \pm 0.04) \times \text{filter} + (-2.2 \pm 2.8)
\]

\[
\text{Xact} = (1.46 \pm 0.18) \times \text{filter} + (0.7 \pm 1.6)
\]

Mn: biased but highly correlated
Xact vs. LowVol PM10 FRM / XRF

Xact vs. LowVol filter / lab XRF

18-hour average Xact, ng/m³ vs. 18-hour integrated filter with offline XRF, ng/m³

Se
Selenium: Xact vs. Filter-Based Measurements

**Xact vs. LowVol filter / lab XRF**

**Xact vs. HiVol filter / lab ICP-MS**

Se: favorable comparison between Xact and PM$_{10}$ HiVol samples with analysis by ICP-MS
Collocated Study - Opportunities

• One month of collocated Xact data collected near the Doe Run primary lead smelter in Herculaneum, MO
• Examine collocated precision and practicable detection limits for various metals
• Uncertainties for source apportionment modeling (CMB, PMF)
• Missouri DNR instrument optimized for As, Hg, and Pb at remote areas
Collocated Study - Challenges

• High concentrations of lead and other elements observed
• Spectral interferences by lead and/or other elements in the plumes
• Removal of instrument-to-instrument bias for collocated precision
Collocated XACT – Vanadium (N=606)
Collocated XACT – Vanadium (N=606)

• Instrument-to-instrument Bias highlighted
• Similar trends seen for Cr, Mn, Ni and Ba
Collocated XACT – Vanadium

- Removed records with zero V concentration
- Removed records for top 25\textsuperscript{th} percentile Pb

Collocated precision = 0.42ng/m\textsuperscript{3} (29%)
Collocated XACT – Vanadium

- Regression-adjusted MDNR data
- Collocated precision = 0.17 ng/m³ (14%)
Collocated XACT – Vanadium

- Binned collocated precision (33 records/bin)
Summary

- V, As, Ba, Cd, Cr, Mn, Ni, Se, Ti, Zn
  - Relative precision better than 10% at higher concentrations (exception Cd)
  - Practicable MDL greater than reported MDL
  - No data near MDL for As, Se, Ti, Zn

- Ca, Fe, K
  - Data range well over MDL
    (e.g. 5th percentile Ca>300*MDL)
  - Relative precision better than 10% over entire data range

- Co, Hg, Sn, Sb
  - Removal of high Pb, leaves no trend in lower concentration data
Next steps ...

- XRF analysis of additional lowvol filters
- ICP analysis of lowvol filters
- Examine spectral interference due to lead on other elements
- Analysis of covariance of error
Acknowledgements

- Missouri Department of Natural Resources
  - Jim Brunnert, Celeste Koon, Will Wetherell
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  - Teri Conner, Gary Norris, Bob Willis
- U.S. EPA / Office of Air Quality Planning and Standards
  - Mike Jones
- U.S. EPA / Region VII
  - Gwen Yoshimura
- Washington University
  - Stephen Feinberg, Victoria Martin
## Xact 620 Minimum Detection Limits (ng/m³)

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic No.</th>
<th>4 hour</th>
<th>3 hour</th>
<th>2 hour</th>
<th>1 hour</th>
<th>30 min.</th>
<th>15 min.</th>
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<td>Si</td>
<td>14</td>
<td>0.018</td>
<td>0.028</td>
<td>0.051</td>
<td>0.144</td>
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<td>K</td>
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<td>0.287</td>
<td>0.811</td>
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<td>0.063</td>
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<td>0.048</td>
<td>0.137</td>
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<td>Cr</td>
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<tr>
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<td>0.019</td>
<td>0.055</td>
<td>0.16</td>
<td>0.44</td>
</tr>
</tbody>
</table>

*aBased on US EPA IO Method 3.3 one sigma interference free.*
Optimizing Sampling Time Interval

- Sampling time = analysis time (Xact operation)
- 15 minutes sampling time, various analysis times

arsenic MDL, ng/m³ vs. analysis time, hrs