Developing Single and Multi-element Reference Materials for Evaluating XRF Measurements of Atmospheric Aerosols

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Objective: To generate single and multi-element reference materials (RMs) on Polytetrafluoroethylene (PTFE, Teflon) filters using aerosol chamber at CNL-UC Davis **(Fig.1)**, and utilize them in calibration and quality control (QC) of EDXRF analyzers in order to address the limitations of available resources.

Materials & Method: High purity salts and nanoparticles for single compound RMs (SE-RMs)
Certified multi-elemental solutions containing 28 elements for multi-element RMs (ME-RMs).

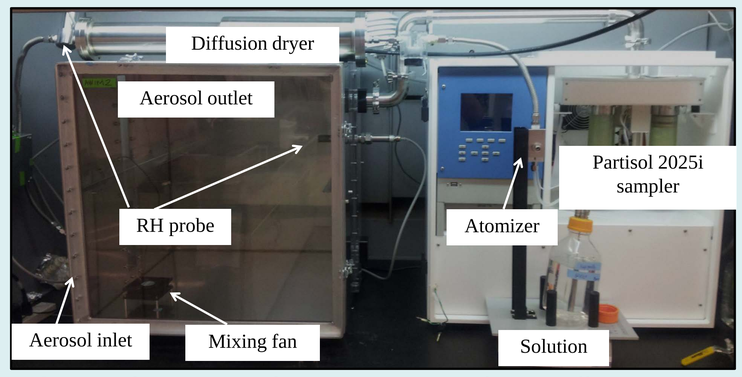

Fig.1. *The aerosol generation and sampling system*

Certified or Reference loadings of RMs:

- The loadings of SE-RMs (C_{cer}) are certified gravimetrically using a balance with 0.1 µg sensitivity
- The ME-RMs reference loading of element i ($C_{ref,i}$) was assigned assuming :
  1. The elemental ratios in solutions are preserved onto ME-RMs
  2. The potassium (K) measurement by UCD-EDXRF,$C_{K,UCD\text{-}EDXRF}$, (Epsilon 5, Panalytical Inc, the Netherlands) is accurate to be <10%. These assumptions resulted in estimated uncertainties below 10%.

$$C_{ref,i} = C_{(K,UCD-EDXRF)} * \frac{i_{solution}}{K_{solution}}$$

Data Evaluation:

1. Agreement between certified loadings of SE-RMs and EDXRF: Linear regression, bias and En number (ISO/IEC 17043, 2010):
   U:Expanded uncertainty by GUM (2008)
   When En ≤1, C_{EDXRF} and C_{cer} are equivalent

$$En = \frac{|C_{EDXRF} - C_{cer}|}{\sqrt{U^2_{C(EDXRF)} + U^2_{C(cer)}}}$$

2. Linear regression between reference loading of ME-RMs (x) and lab (y),

3. z-score (ISO 13528:2005): Loadings in µg/cm² converted to µg/g for 12 ME-RMs in interlaboratory comparison
   $\overline{C}$: outlier-excluded mean
   $\hat{\sigma}$: outlier-excluded standard deviation

$$z = \frac{C_{lab} - \overline{C}}{\hat{\sigma}}$$

For good interlaboratory comparability, |z≤3|

Results and Discussion

- The SE-RMs could be generated successfully for Na, Al, Si, S, Cl, K, Ti, Fe, Zn and Pb with loadings almost spanning the range of two large US atmospheric PM monitoring networks, namely IMPROVE (Interagency Monitoring of PROtected Visual Environments) and CSN (Chemical Speciation Network) (Fig.2.-Left) while the loadings of ME-RMs spun the range of both networks (Fig.2-Right).

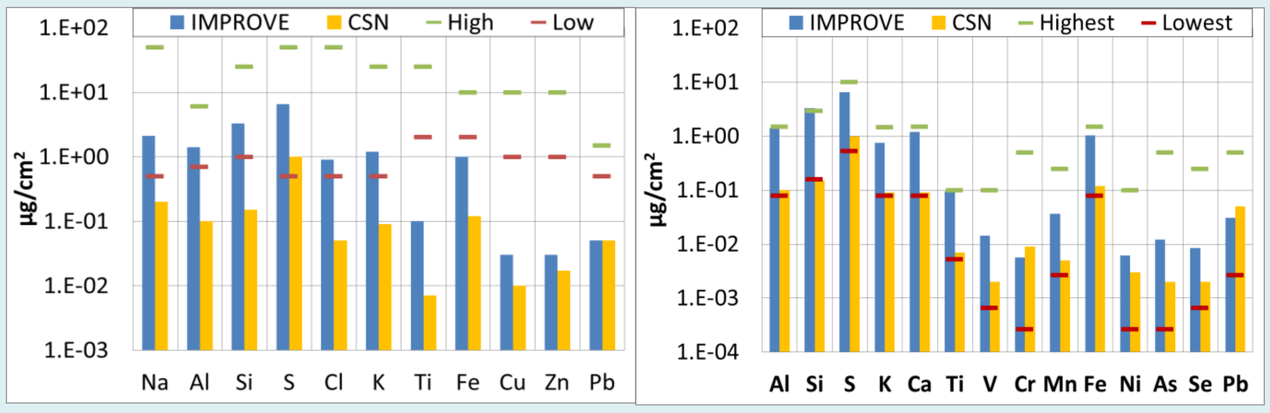

Fig.2. Left) The range of generated SE-RMs (Low and High); Right) ME-RMs (Lowest and Highest) compare to IMPROVE and CSN 90%iles for selected elements.

- The slopes between C_{ref} and C_{EDXRF} (with intercept set to zero) are within 10% of unity. The EDXRF bias remained within 10% for Al, Si, S (at >1 µg/cm²), Cl (with a few exceptions), K, Ti, Fe and Zn.
- The En number remained <1 for most of the generated SE-RMs (Fig.3)

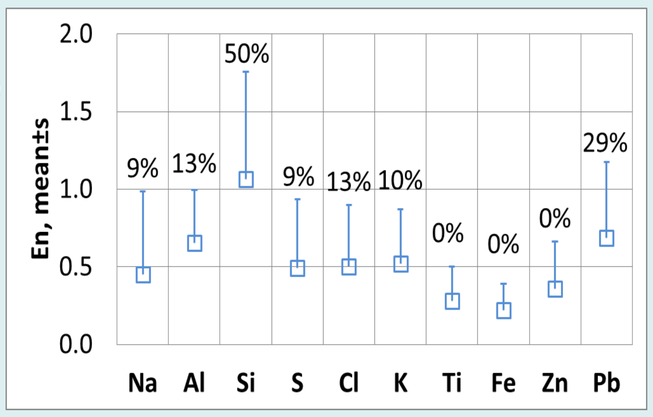

Fig.3. En number of EDXRF vs. certified loadings of SE-RMs. Numbers refer to percentages of En>1

Work in progress

- For Ca ($CaTiO_3$) and Cr (CrN)

Issues to solve:

- Disagreement between certified (ratio of Ca /Ti) vs. EDXRF (Fig.4)
  Ca enhancement effect?
- Disagreement between certified vs. EDXRF for CrN (Fig.5)

Influence of magnetic properties of CrN on gravimetric measurements?

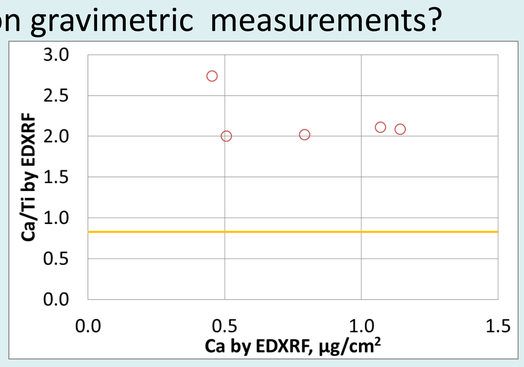

Fig.4. Ca/Ti ratio by EDXRF (points) vs. stoichiometric one (orange line)

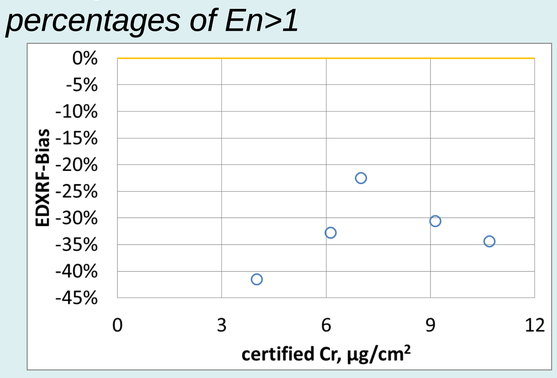

Fig.5. EDXRF bias from certified Cr loadings generated from CrN

Interlaboratory Comparison of ME-RMs

An interlaboratory comparison study of ME-RMs were conducted with participation of 9 XRF and 3 ICP-MS laboratories

- The slopes of reference vs. labs are mostly within 20% of unity (R^2>0.95) (Fig.6)
- Participating labs are mostly in good agreement (|z≤3|) (Fig.7)

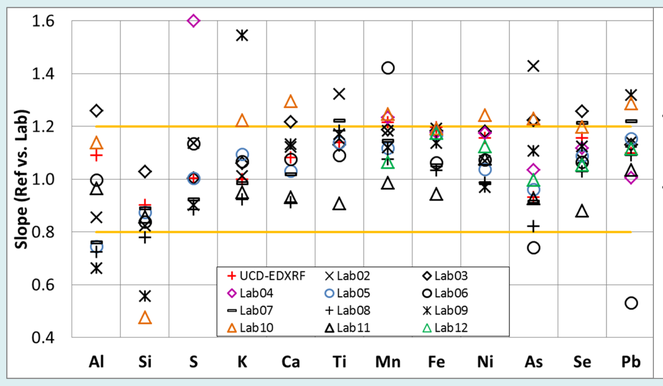

Fig.6. The slopes of reference versus labs for selected elements. Labs 10,11, and 12 are ICP-MS. The slopes higher than 1.6 were shown at 1.6 for better resolution

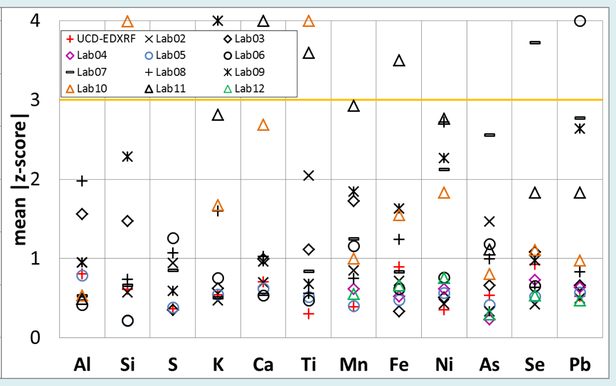

Fig.7. The absolute mean z-score of labs for selected elements. The mean z-score higher than 4 were shown at 4 for better resolution

- Selected SE-RMs were tested for short-term and long-term stability, and found to be to stable (Fig.8.)

Fig.8. Long-term reproducibility of selected SE-RMs (2011-2015). Low RSD (<3%) show good stability of generated SE-RMs.

- Generated MEs also proved to be stable (Fig.9)

Fig.9. The relative standard deviation (RSD) of a ME-RM weekly analyzed by EDXRF since 2014 (n>200). Low RSD show good stability of generated ME-RMs.

Conclusions

- **Single-element (SE)** certified reference material successfully generated on PTFE filters for Na, Al, Si, S, Cl, K, Ti, Fe, Zn and Pb
- **Multi-element (ME)** reference materials mimicking ambient aerosols are successfully generated on PTFE filters
- For most of the elements, all laboratories participating in inter-laboratory comparison compare well with each other and with established reference loadings
- Checked SEs and ME-RMs show satisfactory stability except volatile elements
- SE-RMs can serve calibration/quality control materials for XRF systems
- The unique SEs and ME-RMs can serve as quality control samples, providing valuable information about performance of XRF systems typically calibrated with single compound/element standards

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Publications

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