XRF Standards Development

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IMPROVE Steering Committee Meeting

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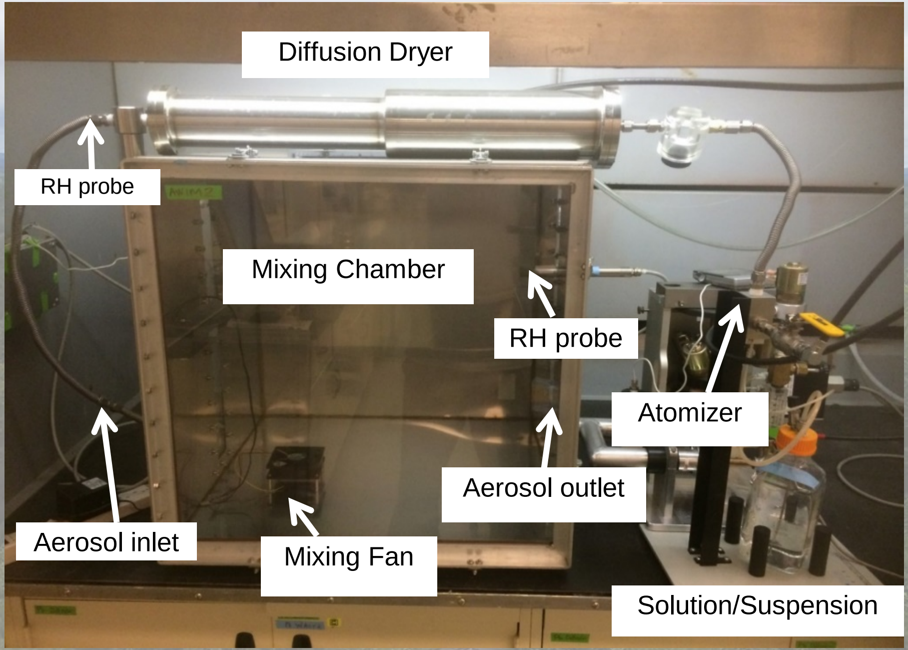
XRF Reference Materials (RMs)

- 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%

Compound	Element	Range of tested loadings, µg/cm²	Extra method for verification
NaCl	Na	0.7-34.0	Interlab comparison (IC)
	Cl	1.0-52.0	Interlab comparison (IC)
$AlCeO_3$ nanoparticles*	Al	0.6-5.5	Interlab comparison (XRF)
	Ce	3.0-29.0	
SiO_2 nanoparticles	Si	1.3-25	Interlab comparison (XRF)
$(NH_4)_2SO_4$	S	0.5-55	Interlab comparison (IC)
KCl	K	0.5-30.0	Interlab comparison (XRF, IC)
	Cl	0.5-30.0	Interlab comparison (XRF, IC)
TiO_2 nanoparticles*	Ti	0.7-23.0	Interlab comparison (XRF)
Fe_2O_3 nanoparticles*	Fe	0.7-7.0	Interlab comparison (XRF)
CuO nanoparticles*	Cu	1.7-13.0	Interlab comparison (XRF)
ZnO nanoparticles*	Zn	1.2-6.0	Interlab comparison (XRF)
Lead Acetate	Pb	0.7-14.0	Interlab comparison (XRF, ICP-MS)

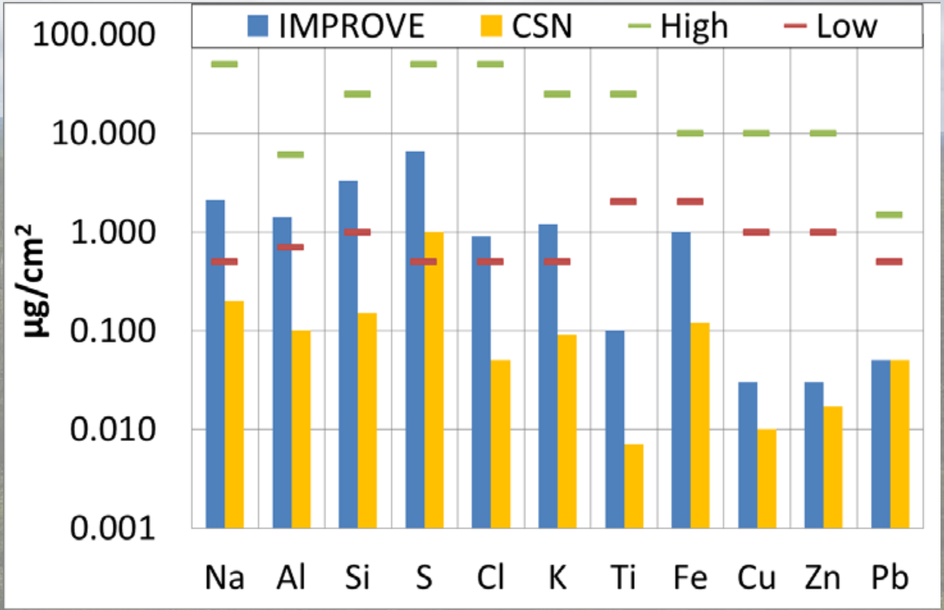
Limitations:

- 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

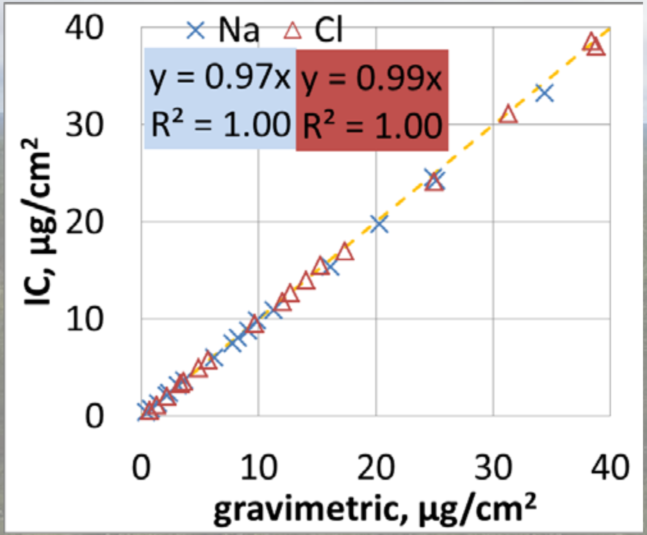
- Loadings as close to levels measured in IMPROVE as possible
- SE-RMs are stable and not affected by XRF analysis
  - Sulfate, sodium chloride, and lead standards have remained stable for >5 years
- Evaluated by other labs: Environment Canada (ECC), RTI, DRI, European JRC, International Atomic Energy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

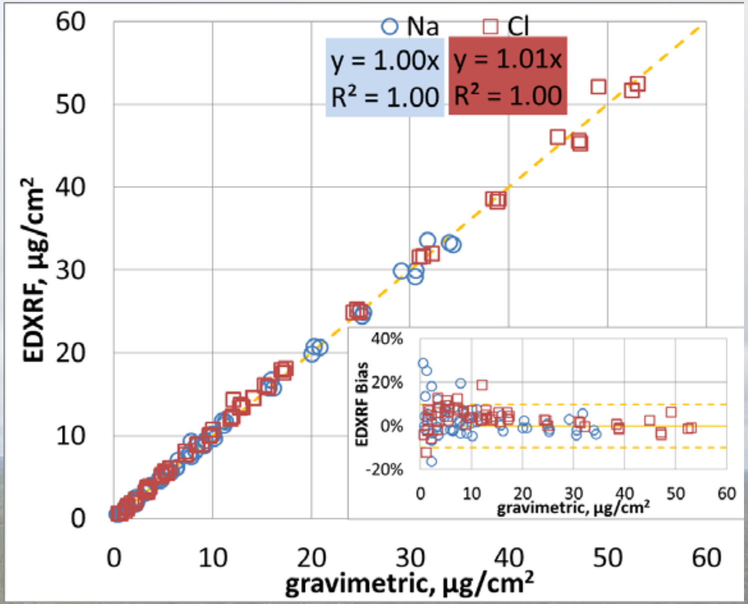
The range of generated standards (Low and High) compare to IMPROVE and CSN 90%iles for selected elements



Na & Cl

<u>NaCl salt</u>
XRF-Bias : <10%
Good IC vs. gravimetric agreement (IC bias<10%)





- XRF-bias from C_{Ref}; $[C_{XRF}/C_{Ref} - 1]$
  - C_{XRF} = Result from by EDXRF
  - C_{Ref} =Reference mass based on gravimetric

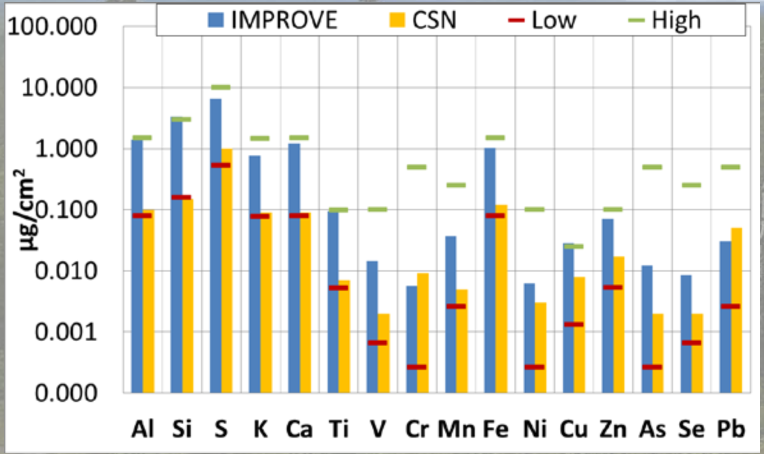
Multi-element Reference Materials (ME-RMs)

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

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

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

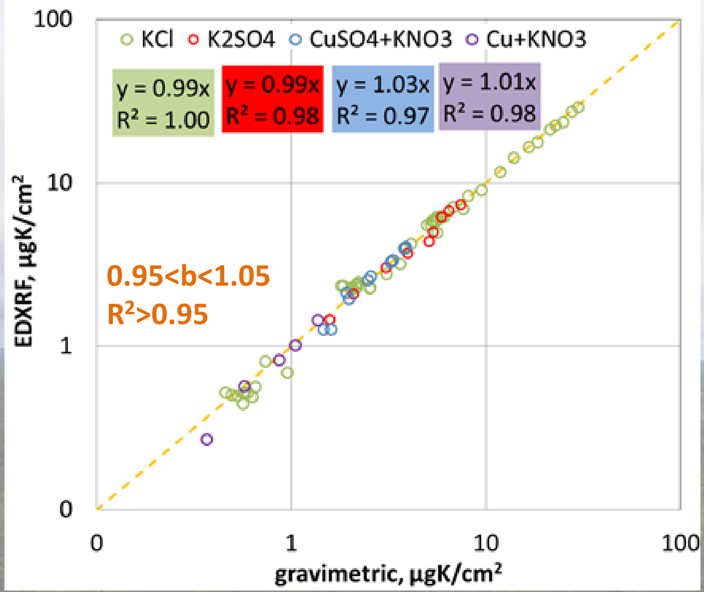
The range of ME-RMs (Low and High) compared to IMPROVE and CSN 90%iles for selected elements

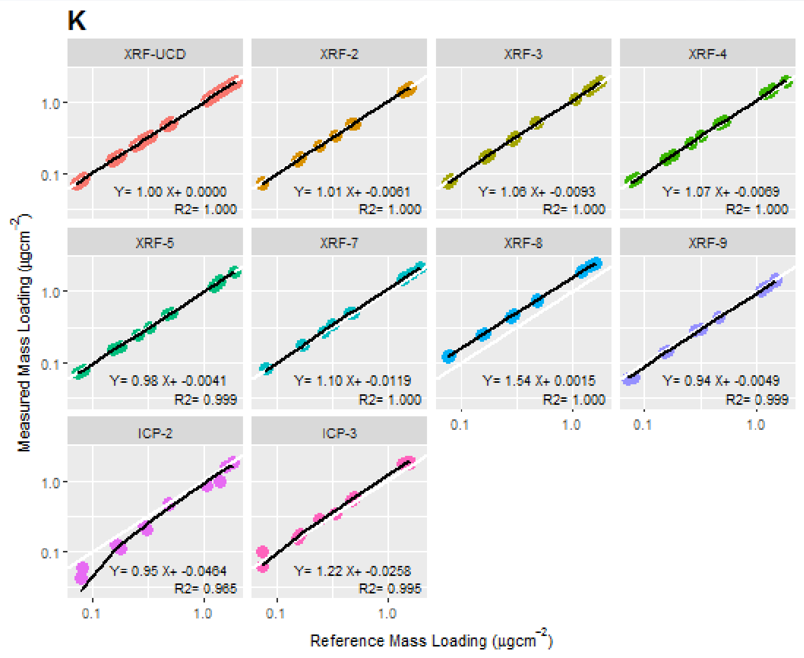


- ***Low***: Mimicking IMPROVE range (median)
- ***High***: Major elements the same as ***Low***, trace elements > 3*MDL (UCD-EDXRF)

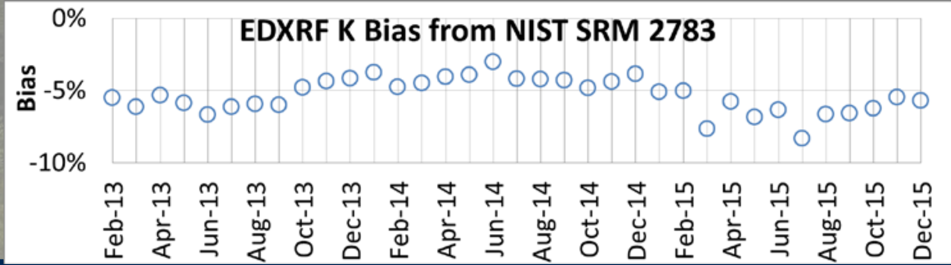
Well-Measured Element: Potassium

KCl, K_2SO_4, KNO_3+$CuSO_4$, Cu+KNO_3

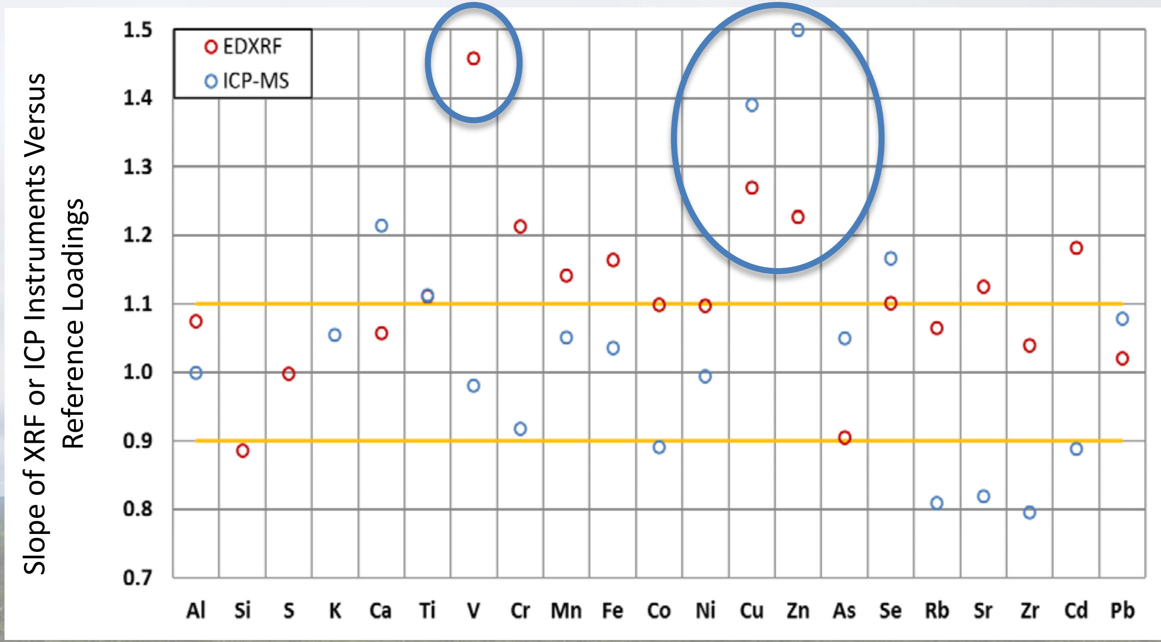




NIST SRM2783
(monthly, n=35)

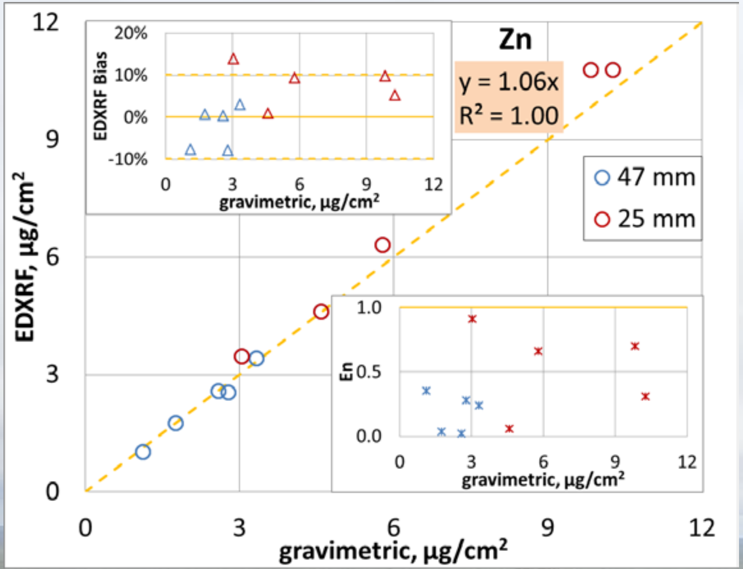


ME-RM Inter-Laboratory Comparison Results



- 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



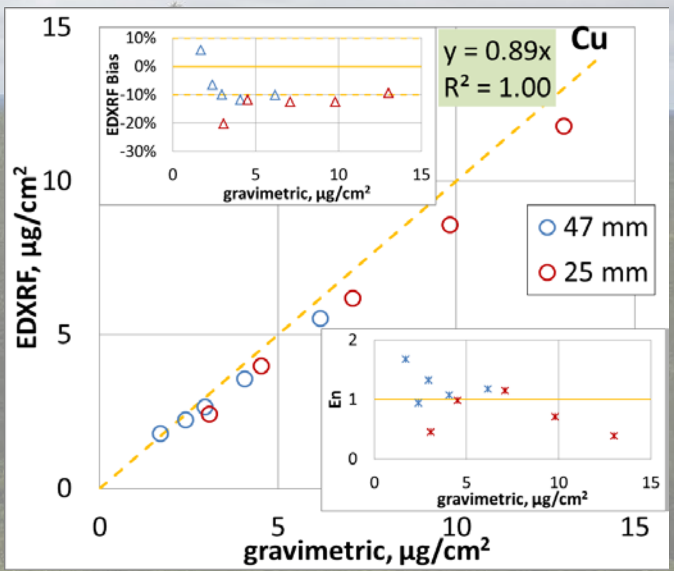
ZnO Nanoparticles

XRF-Bias: ≤10%

En: <1

Cons: Hydroscopic

Cu



En number (ISO/IEC 17043, 2010)

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

CuO Nanoparticles (>99%)

XRF-Bias : ~-10%

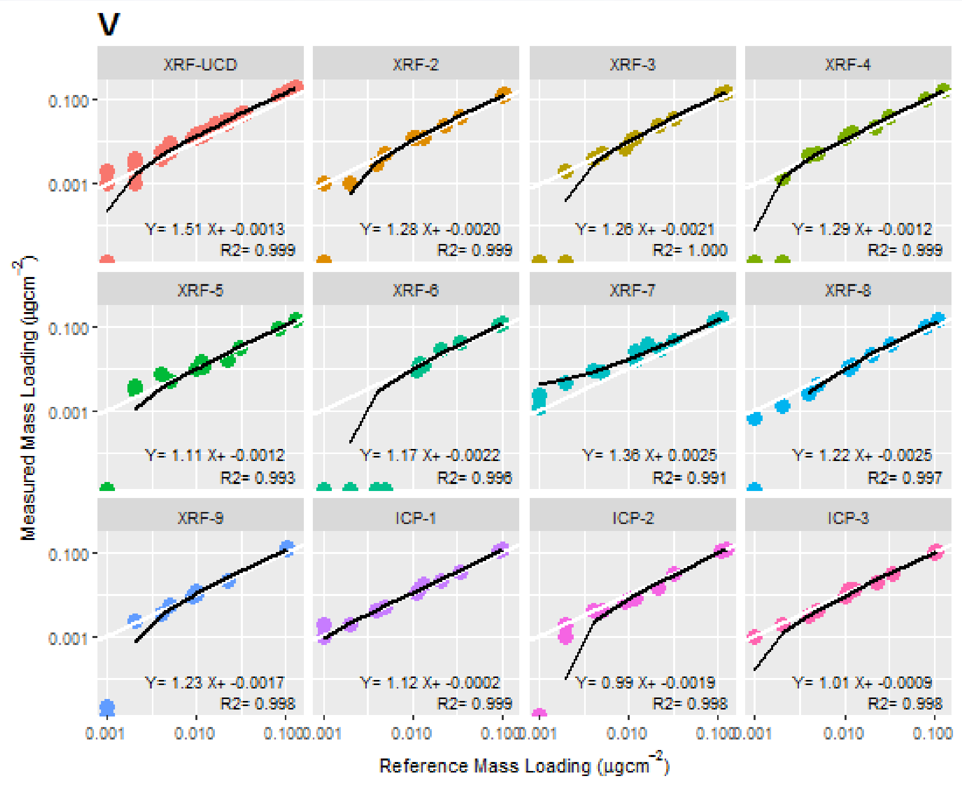
En: Variable

Cons: Hydroscopic

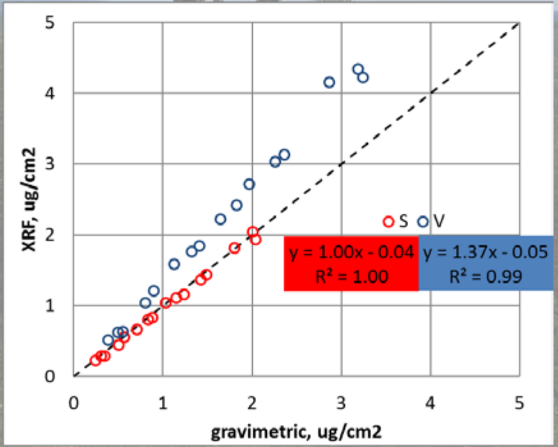
Impurity (Ca and Zn) higher than 1% in PM mass

Vanadium Biased High

Multi-Element RM Analyzed by 9 XRF and 3 ICP-MS instruments



$VOSO_4$



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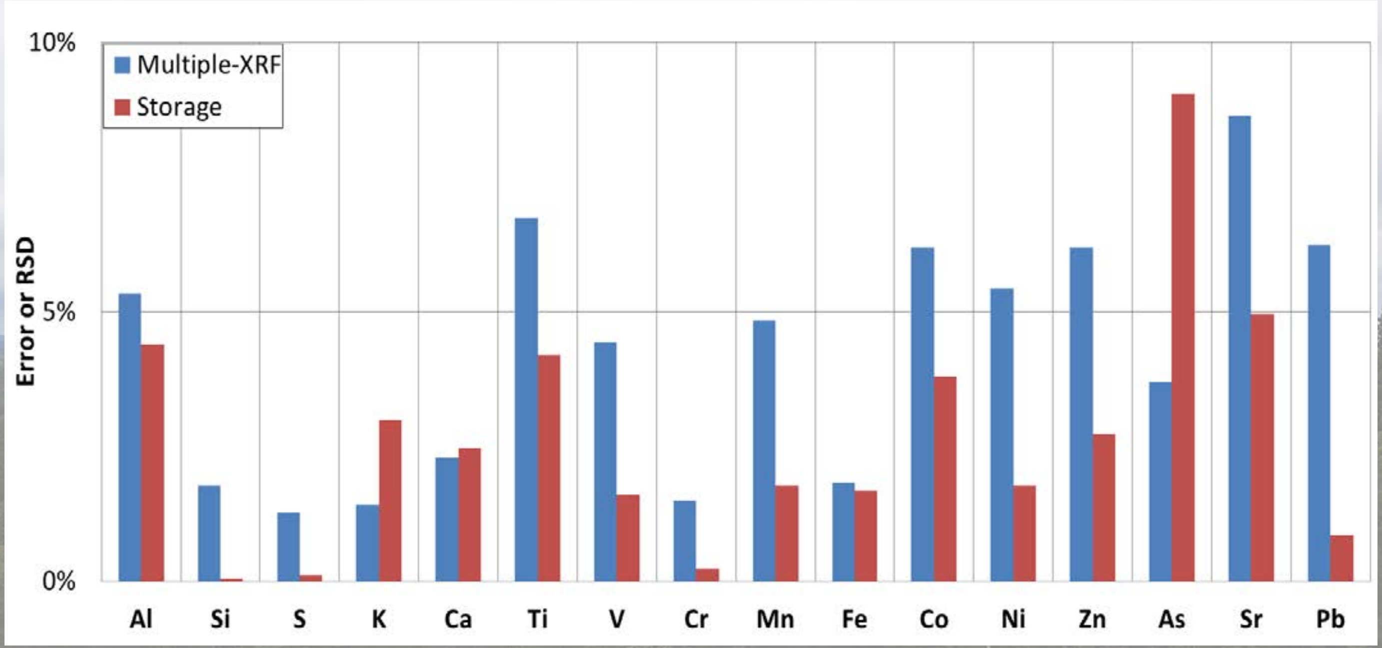
Stability of ME-RMs



Multiple-XRF: EDXRF analysis of a ME-RM every week (n~200), RSD ≤10%

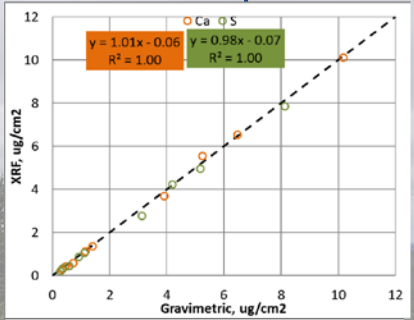
Storage: A ME-RM stored for 2 years, error≤10%

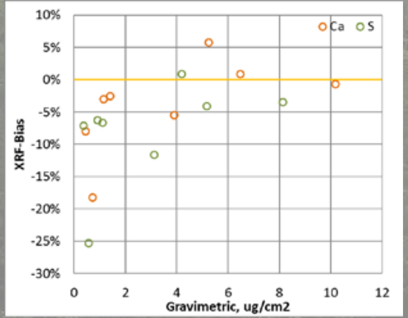
- Relative Standard Deviation (RSD) similar to EDXRF precision
- Multiple analyses by EDXRF do not alter the loadings for non-volatile elements

Single Compound Standards- In Progress

Compound	Element	Range of tested loadings, μg/cm²	Extra method for verification
NH4H2PO4+ KNO3 in 2% HNO3	P	0.07-0.23	ME-RMs approach
CaO nanoparticles	Ca	1.5-20.1	
CaCO3 salt	Ca	3.0-10.0	
CaTiO3 nanoparticles	Ca	1.0-1.5	Interlab comparison (XRF)
CaZrO3 nanoparticles	Ca	1.0-5.5	Interlab comparison (XRF)
CaSO4	Ca	0.5-10	
CaZrO3 nanoparticles	Zr	2.3-13.0	Interlab comparison (XRF)
VC nanoparticles	V	3.0-40.0	
VOSO4	V	0.3-3.3	
CrN microparticles	Cr	2.5-10.5	
Cr2O3 nanoparticles	Cr	3.0-16.0	Interlab comparison (XRF)
CuSO4	Cu	0.4-4.0	Interlab comparison (XRF, IC)
ZnSO4	Zn	0.6-4.0	Interlab comparison (XRF, IC)

$CaSO_4$





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