



## An inter-laboratory evaluation of new multi-element reference materials for atmospheric particulate matter measurements

Nicole Pauly Hyslop, Krystyna Trzepla, Sinan Yatkin, Warren H. White, Travis Ancelet, Perry Davy, Owen Butler, Michel Gerboles, Steven Kohl, Andrea McWilliams, Laura Saucedo, Marco Van Der Haar & Armand Jonkers

To cite this article: Nicole Pauly Hyslop, Krystyna Trzepla, Sinan Yatkin, Warren H. White, Travis Ancelet, Perry Davy, Owen Butler, Michel Gerboles, Steven Kohl, Andrea McWilliams, Laura Saucedo, Marco Van Der Haar & Armand Jonkers (2019) An inter-laboratory evaluation of new multi-element reference materials for atmospheric particulate matter measurements, *Aerosol Science and Technology*, 53:7, 771-782, DOI: [10.1080/02786826.2019.1606413](https://doi.org/10.1080/02786826.2019.1606413)

To link to this article: <https://doi.org/10.1080/02786826.2019.1606413>

 View supplementary material 

 Accepted author version posted online: 11 Apr 2019.  
Published online: 25 Apr 2019.

 Submit your article to this journal 

 Article views: 216

 View related articles 

 View Crossmark data 



## An inter-laboratory evaluation of new multi-element reference materials for atmospheric particulate matter measurements

Nicole Pauly Hyslop<sup>a</sup>, Krystyna Trzepla<sup>a</sup>, Sinan Yatkin<sup>a</sup>, Warren H. White<sup>a</sup>, Travis Ancelet<sup>b</sup>, Perry Davy<sup>b</sup>, Owen Butler<sup>c</sup>, Michel Gerboles<sup>d</sup>, Steven Kohl<sup>e</sup>, Andrea McWilliams<sup>f</sup>, Laura Saucedo<sup>g</sup>, Marco Van Der Haar<sup>h</sup>, and Armand Jonkers<sup>h</sup>

<sup>a</sup>Air Quality Research Center, University of California, Davis, California, USA; <sup>b</sup>Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand; <sup>c</sup>Health and Safety Laboratory, Buxton, United Kingdom; <sup>d</sup>European Commission, Joint Research Centre, Directorate for Energy, Transport and Climate, Ispra, Italy; <sup>e</sup>Desert Research Institute, Reno, Nevada; <sup>f</sup>Research Triangle Institute, Research Triangle Park, North Carolina, USA; <sup>g</sup>South Coast Air Quality Management District, Diamond Bar, California, USA; <sup>h</sup>Malvern Panalytical, Almelo, The Netherlands

### ABSTRACT

Eight institutes using 12 different instruments analyzed newly developed multi-element reference materials (RM) for atmospheric particulate matter (PM) measurements. These RM have the potential to fill a gap in the currently available quality assurance resources for element analysis of PM samples such as X-ray fluorescence and inductively-coupled plasma mass spectrometry. This study evaluates the performance of these new RM generated by the University of California, Davis. The methodological challenge was to determine the reference loadings on the RM. Gravimetry is the most robust method to determine the sample deposit mass but cannot be used for these RM because some solution components are volatile and result in unpredictable total mass loadings on the RM. Instead of using gravimetry, a single well-measured element, along with the assumption that the relative mass fractions in the solutions were maintained in the aerosol deposited on the filters, was used to determine the reference loadings on the RM. This assumption appears to be valid for most elements in the solutions; notable exceptions include volatile species such as chlorine and bromine. Results from the 12 different instruments in the inter-laboratory evaluation agreed very well with the reference loadings (adjusted  $R^2 > 0.9$  and slope between 0.7 and 1.3) for 17 of the 28 elements. In many cases, one or two instruments did not meet the performance criteria, which points to individual instrument calibration problems. For the 11 elements that did not perform as well, development work continues, and this intercomparison helped identify and fix a source of contamination in the system used to create the RM.

### ARTICLE HISTORY

Received 14 November 2018  
Accepted 14 March 2019

### EDITOR

Pramod Kulkarni

## Introduction

Most chemical measurements are made using comparative techniques by which an instrument response for an unknown sample is compared with the responses to samples of known composition. The samples with known concentrations are referred to as reference materials (RM) (Taylor 1985; ISO 2000; Kane 2000) and are referred to as “standards” when used to calibrate the instrument. By comparing the measured instrument response to the RM known concentrations, a calibration curve is developed.

Then the developed calibration curve equation is applied to all subsequent instrument responses to determine unknown concentrations. A calibration curve is generally only valid for the range of measurements used to develop it (Taylor 1985; ISO 2000). Ideally, calibrations are performed using multiple RM with concentrations spanning the range of expected sample concentrations in the planned study. Spanning the range is important for determining the appropriate relationship between the instrument

**CONTACT** Nicole Pauly Hyslop  [nmhyslop@ucdavis.edu](mailto:nmhyslop@ucdavis.edu)  Air Quality Research Center, University of California, Davis, One Shields Ave, Davis, CA 95616, USA.

Color versions of one or more of the figures in the article can be found online at [www.tandfonline.com/uast](http://www.tandfonline.com/uast).

 Supplemental data for this article is available online at <https://doi.org/10.1080/02786826.2019.1606413>.

This article was originally published with errors, which have now been corrected in the online version. Please see Correction (<https://doi.org/10.1080/02786826.2019.1606413>).

response and concentrations because sometimes responses are not linear throughout the measurement range (i.e., become non-linear at low or high concentrations). It is also important to use RM with the same sample matrix and media as the unknown samples that will be analyzed to properly account for interferences.

RM are readily available for many analytical techniques but are not directly applicable to atmospheric particulate matter (PM) measurements. Several large PM measurement networks collect samples on polytetrafluoroethylene (PTFE) membranes for laboratory analysis; energy dispersive X-ray fluorescence (ED-XRF) or inductively coupled plasma mass spectrometry (ICP-MS) are used to measure the elemental content of these samples (Hansen et al. 2003; Dabek-Zlotorzynska et al. 2011; Hand et al. 2012; Solomon et al. 2014). ED-XRF is most commonly used because it does not require any sample preparation, is nondestructive, and is not affected by the molecular or atomic structure of the elements. No RM are shared between ED-XRF and ICP-MS, and biases exist between concentrations reported by the two techniques (Brown et al. 2010; Yatkin, Gerboles, and Borowiak 2012; Kang et al. 2014).

Most ED-XRF measurements of atmospheric PM samples rely on a limited range of RM: one multi-element standard reference material (SRM2783) produced by the National Institute of Standards and Technology (NIST) along with a variety of thin film RM produced by Micromatter<sup>TM</sup> (Vancouver, Canada). NIST SRM2783 was prepared by filtration of a homogenous liquid suspension of urban dust from Vienna, Austria, onto Nuclepore polycarbonate membrane (0.4  $\mu\text{m}$  pore size) filters (Wise and Watters 2002). SRM2783 represents a specific location and emissions mix, and certified loadings are not provided for some elements of interest. The SRM2783 certificate of analysis provides uncertainties for the certified elements varying from 2% to 19% with an average of 10%, and a reference rather than certified value is given for some elements including S with an uncertainty of 25%. Therefore, for several elements, the XRF calibration curves are based solely on Micromatter RM. Both the NIST and Micromatter RM are deposited on Nuclepore membranes not PTFE, which means that the spectral background subtraction is quite different than for the PM samples. The NIST SRM2783 membrane does not have a support ring, making it difficult to keep flat and achieve consistent radiation exposure on the surface. In addition, the available RM do not adequately cover the

range of measurements experienced in the sampling networks; most Micromatter RM have loadings that are orders of magnitude higher than typical atmospheric samples. The Micromatter RM are vacuum-deposited thin films, and are thus not similar to the PM samples in physical composition. Significant differences between the NIST and Micromatter standards are observed for some elements (e.g., Zn, likely because the Micromatter standards are non-stoichiometric).

Most ICP-MS measurements of atmospheric PM samples are calibrated using reference solutions produced by chemical manufacturers (Sigma, Pure Standards, etc.). ICP-MS labs check their digestion efficiency using certified dusts (e.g. NIST SRM 1648 and ERM-CZ120 by European Union) instead of filter-based RM. The RM developed herein are highly soluble in dilute acid and while they do require the extraction step, they do not challenge the extraction efficiency (Yatkin et al. 2018).

Measurement interferences complicate results and can be difficult to address; ED-XRF calibrations are often performed with pure, single-species RM that lack the complicated matrix of real samples, particularly environmental samples. Multi-element RM are particularly important for evaluating nonselective analysis techniques, such as ED-XRF which generates energy emission spectra from all the excited elements simultaneously and the resulting spectra typically have several overlapping, escape, and sum peaks. In ICP-MS, spectral overlaps and sample preparation may cause interferences, loss of elements, and/or contamination. In addition, multi-element RM are the most efficient way to evaluate instrument stability as it is not practical to analyze 20–40 single-element reference filters (one for each measured element) frequently.

Many XRF laboratories have generated RM mimicking ambient or work place PM compositions, mainly for specific studies (Foster 2000; Vanhoof, Corthouts, and De Brucker 2000; Szilagyi and Hartyani 2005; Stacey and Butler 2008; Canepari et al. 2009; Brown et al. 2010; Oztürk et al. 2011; Yatkin, Gerboles, and Borowiak 2012; Oster, Labarraque, and Fiscaro 2015). The Air Quality Research Center (AQRC) at the University of California Davis (UCD) has successfully created and distributed RM for atmospheric PM measurements using a system consisting of an atomizer, aerosol chamber, and sampler (Indresand et al. 2013). The RM are prepared by aerosolizing a solution containing elements of interest, drying the aerosols, mixing the aerosols in a chamber, and then sampling PM from the chamber using the

**Table 1.** Participating laboratories and their analytical techniques.

Laboratory	Analytical techniques
University of California, Davis, Air Quality Research Center, USA	ED-XRF – PANalytical Epsilon 5
Desert Research Institute, USA	ED-XRF – PANalytical Epsilon 5
ICP-MS – Perkin Elmer Nexlon 300D	
Research Triangle Institute, USA	ED-XRF – Thermo Quant’X
European Commission, Joint Research Center, Directorate for Energy, Transport and Climate, Ispra, Italy	ED-XRF – Thermo Quant’X
Health and Safety Lab, UK	ED-XRF – PANalytical Epsilon 5
	ICP-MS – Thermo ICAP-Q
South Coast Air Quality Management District, USA	ED-XRF – PANalytical Epsilon 5
	ICP-MS – Perkin Elmer ELAN DRC-e
Institute of Geological and Nuclear Sciences, New Zealand	ED-XRF – PANalytical Epsilon 5
	Proton Induced X-ray Emission (PIXE) <sup>a</sup>
Malvern Panalytical, Almelo, The Netherlands	ED-XRF – PANalytical Epsilon 5

<sup>a</sup>The PIXE results are labeled as XRF to keep the results anonymous and because the techniques are similar.

same PM sampler and substrates as used in major aerosol sampling networks. This system has successfully been used to generate single-element RM from pure salt solutions or suspensions of nanoparticles (Indresand et al. 2013; Yatkin et al. 2016). AQRC performs ED-XRF measurements for the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network and Chemical Speciation Network (CSN), and our primary goal in this work is to create RM to support the measurements in these networks. IMPROVE is a PM monitoring network with over 160 sites located in rural areas throughout the United States (<http://vista.cira.colostate.edu/IMPROVE/Publications/SOPs/ucdsop.asp>), and CSN is a PM monitoring network with over 130 sites located in urban areas throughout the United States (<https://www3.epa.gov/ttnamti1/speciepg.html>). Both networks collect PM samples with aerodynamic diameter less than 2.5  $\mu\text{m}$  (PM<sub>2.5</sub>) on PTFE filters and analyze them by ED-XRF for element content. Wet chemistry analytical techniques, such as ICP-MS, are calibrated using acidic reference solutions, which can be customized to a wide range of concentrations and compositions. We recently produced RM from these reference solutions at concentrations relevant to atmospheric PM monitoring networks and on filter media commonly used in PM monitoring networks (Yatkin et al. 2018).

This study describes an inter-laboratory comparison to evaluate the performance of these new multi-element RM. Assigning reference loadings for the RM was a methodological challenge, and this inter-comparison further evaluates the approach to assigning the reference loadings. The RM were analyzed by 12 different instruments at eight different institutes. The analytical results are compared against the assigned reference loadings. In addition to evaluating the RM, this study provides a rare opportunity to compare

XRF and ICP-MS results from several instruments. International laboratory (and instrument) inter-comparisons such as this are important for confidence in the elemental concentration results and subsequent data analytics (e.g., receptor modeling) being reported across the literature.

## Materials and methods

The system used to generate the RM consists of a constant output atomizer (TSI-3076, TSI Incorporated, MA, USA), filtered air supply, diffusion dryer, mixing chamber, and sampler (Indresand et al. 2013; Yatkin et al. 2016). The RM were collected on PTFE membrane filters (Teflo, 47 mm, 3.0  $\mu\text{m}$  pore size; Pall Life Sciences, Ann Arbor, MI, USA) using a Partisol sampler (Thermo Inc., USA). Further details on the UCD aerosol generation system and sampler can be found in the work by Yatkin et al. (2016).

Two mixtures containing 28 elements of interest were prepared from certified multi-element solutions (High Purity Standards, the USA) by micro-pipetting the certified solutions into 350 mL de-ionized water (MilliQ Academic, Millipore, USA) in pre-cleaned glass bottles. Contamination from the glass bottles was ruled out by verifying that the ratios of Si to other elements were stable on the RM and the same as in the solution itself. The first mixture, hereafter called *atmospheric*, was designed to simulate the IMPROVE range of elemental concentrations and had elemental ratios close to the median IMPROVE values. On the *atmospheric* RM, the mass loadings of major elements (Na, Mg, Al, Si, S, K, Ca, Ti, Fe, and Zn) were higher than three times the UCD XRF detection limits whereas the mass loadings of trace elements (P, Cl, V, Cr, Mn, Co, Ni, Cu, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Ba, and Pb) were below or close to the UCD XRF detection limits. To make trace

**Table 2.** Summary of the linear regressions on the measured versus reference mass loadings for all participating instruments.

Element	No. inst.	Regression coefficient (adjusted $R^2$ )		Slopes		No. of instruments meeting criteria			
		Minimum	Maximum	Minimum	Maximum	Coef ( $R^2$ )	Slope	Both criteria	Fraction meeting both criteria
Na	10	0.58	1.00	0.62	1.77	9	8	7	0.70
Mg	10	-0.01	0.99	0.22	1.85	4	4	2	0.20
Al	10	0.95	1.00	0.68	1.27	10	9	9	0.90
Si	10	0.93	1.00	0.47	1.03	10	8	8	0.80
P	6	0.87	1.00	0.21	5.20	5	2	2	0.33
S	9	1.00	1.00	0.88	1.63	9	8	8	0.89
Cl <sup>a</sup>	8	-0.10	0.60	0.08	0.18	0	0	0	0
K	10	0.96	1.00	0.91	1.54	10	9	9	0.90
Ca	10	0.91	1.00	0.93	1.29	10	10	10	1
Ti	10	0.95	1.00	0.53	1.30	10	9	9	0.90
V	12	0.99	1.00	0.96	1.39	12	11	11	0.92
Cr	12	1	1.00	0.95	1.27	12	12	12	1
Mn	12	1	1.00	0.95	1.39	12	11	11	0.92
Fe	12	0.95	1.00	0.91	1.18	12	12	12	1
Co	10	0.95	1.00	0.85	1.32	10	9	9	0.90
Ni	12	0.98	1.00	0.95	1.28	12	12	12	1
Cu <sup>b</sup>	12	0.62	0.86	1.79	2.59	0	0	0	0
Zn <sup>b</sup>	12	0.54	1.00	0.89	1.51	11	6	5	0.42
As	12	0.99	1.00	0.74	1.43	12	11	11	0.92
Se	12	0.99	1.00	0.87	1.24	12	12	12	1
Br <sup>a</sup>	8	0	0.80	0.06	0.31	0	0	0	0
Rb	9	0.85	1.00	1.04	1.26	8	9	8	0.89
Sr	10	0.78	1.00	0.98	1.33	9	9	8	0.80
Zr	9	0.62	1.00	0.68	1.51	8	6	6	0.67
Mo	9	0.04	1.00	0.52	1.34	8	7	6	0.67
Cd	12	0.86	1.00	0.96	1.65	11	10	9	0.75
Ba	11	0.12	0.99	0.01	2.49	5	6	3	0.27
Pb	12	0.79	1.00	0.64	1.31	11	10	10	0.83

<sup>a</sup>Volatile element, not stable on RM.

<sup>b</sup>Contamination discovered in aerosol generation system.

The columns list the element, number of instruments that measured the element, minimum and maximum regression coefficients for all the instruments, minimum and maximum slopes for all the instruments, and fraction of the instruments meeting both criteria. Rows highlighted in yellow are elements that passed the criteria for at least 80% of the participating instruments.

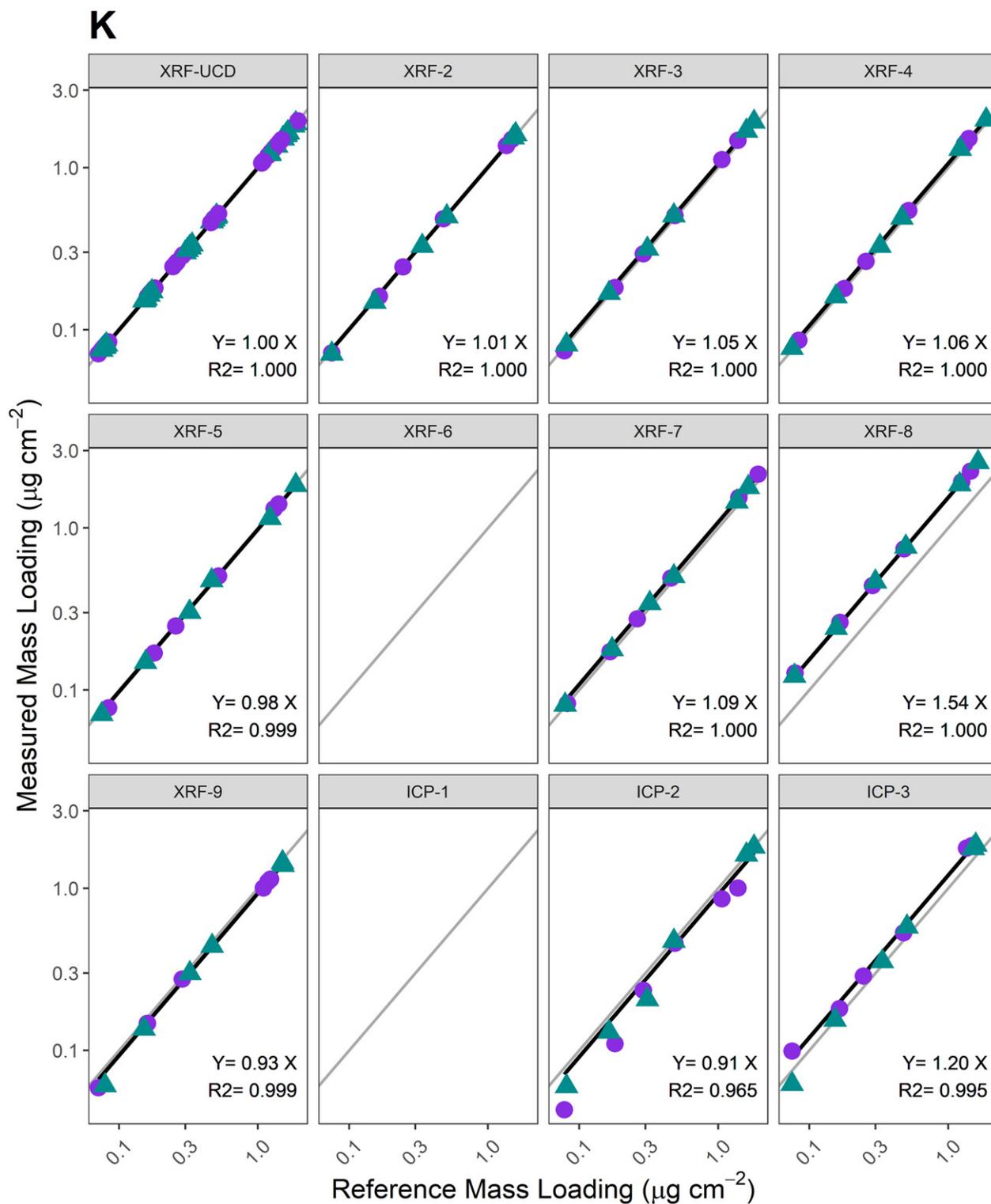
elements quantifiable, another mixture, hereafter called *augmented*, was prepared keeping the major element ratios the same as in the *atmospheric* mixture but increasing the concentrations of the trace elements. While the compositions of the mixtures do not mimic the composition of particles in the natural atmosphere, they do contain ammonium salts and carbon species which are prevalent in the atmosphere (Yatkin et al. 2018).

Each mixture was then aerosolized in the UCD aerosol generation system and samples were collected from the chamber to create sets of *atmospheric* and *augmented* RM. The sample collection durations were varied to provide a range of element loadings on the RM. Samples were collected over 5, 10, 15, 30, 60, and 90 min from the UCD chamber using both the *atmospheric* and *augmented* mixtures, resulting in sets of RM at 12 different loading levels. The RM samples consist of particles collected from the chamber using a Thermo Scientific 2025i Partisol sampler (Franklin, MA, USA). The filters were weighed pre- and post-sampling using a microbalance (Mettler Toledo, XP6, 1  $\mu$ g sensitive, the USA) to determine

the net PM mass. All the RM were then analyzed by ED-XRF at UCD. More details on the generation of these RM can be found in the work by Yatkin et al. (2018).

Note the element composition (in terms of inter-element ratios) at the various levels in the *atmospheric* and *augmented* sets of reference filters is identical because they are made from the same solutions. Therefore, these sets of reference filters alone cannot fully characterize interferences among elements resulting from peak overlaps. The first step in the development process was to evaluate the linearity of the RM loadings, and to focus on that goal, the number of variables needed to be limited. That said, sets of RM could easily be developed to characterize peak interferences using this technique.

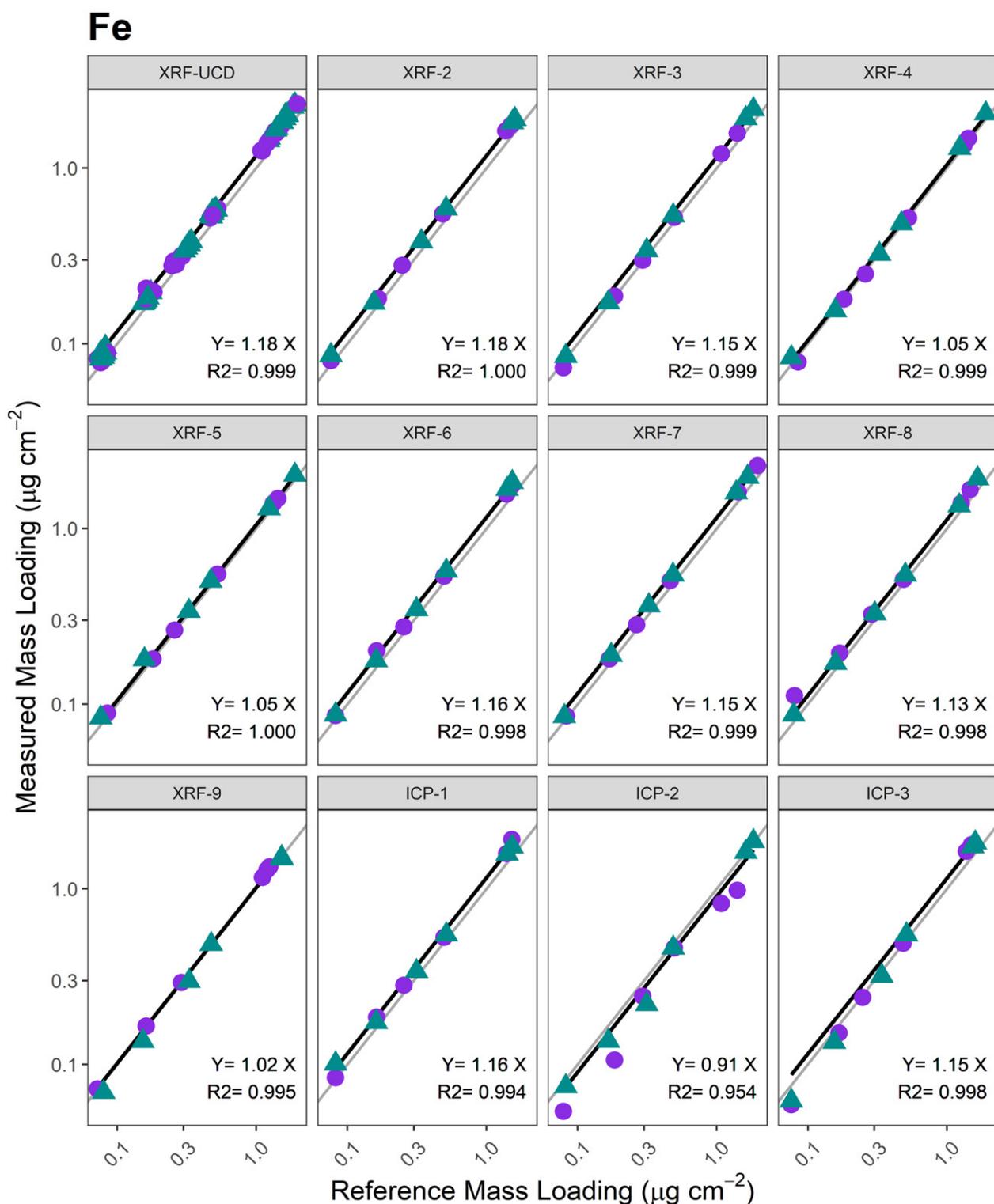
Eight laboratories agreed to participate in the inter-laboratory comparison, and four labs analyzed the RM with two different techniques as shown in Table 1. Each lab was sent 12 RM – six from the *atmospheric* and six from the *augmented* mixture – and a blank PTFE filter for background correction was applied. Details about the data processing, including blank



**Figure 1.** Measured ( $Y$ ) versus reference mass loadings ( $X$ ) for the ten labs that measure  $K$ . Thin, gray diagonal lines are 1-to-1, and thick, black lines are least-squares regression models forced through zero. Atmospheric RM (purple circles) are distinguished from the augmented RM (green triangles). The regression equation and coefficient (adjusted  $R^2$ ) are printed on each graph. Empty graphs indicate instruments that did not quantify  $K$ .

correction, were not collected from the labs. The RM were identified only with unique numbers; no information about the content of the deposits was provided

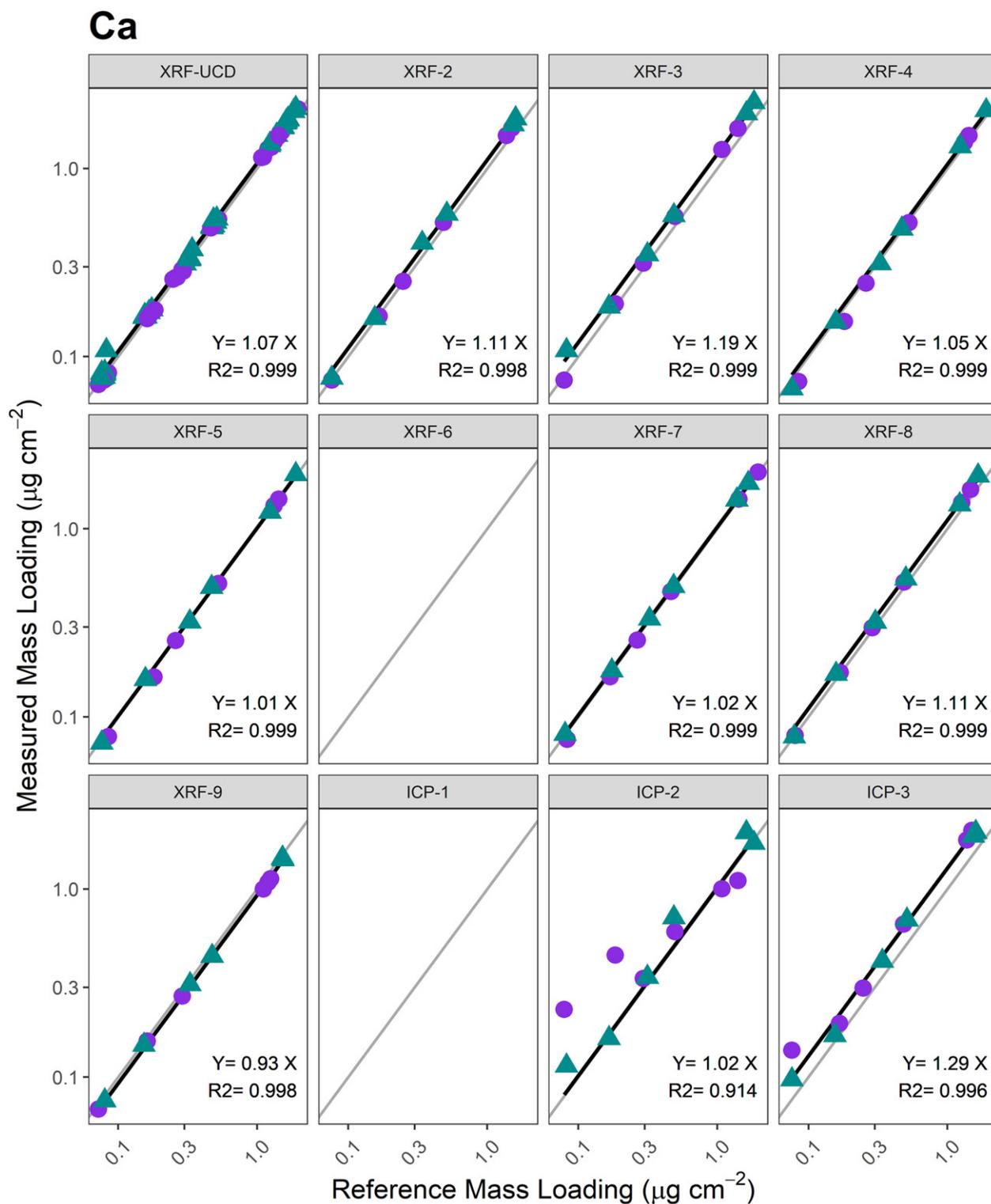
to the participating labs. The labs were instructed to follow their routine procedures for atmospheric PM sample analysis, analyze each sample three times, and



**Figure 2.** Measured versus reference Fe mass loadings for all 12 instruments.

report the measured concentrations along with analytical detection limits and uncertainties. The averages of the multiple measurements are used for the graphs and statistics herein. Not all the labs measure all the elements on the RM, and each lab reported only the

elements that they routinely report. The laboratories used several different approaches to estimate their detection limits and uncertainties, limiting their comparability, so the detection limits and uncertainties are not presented herein.

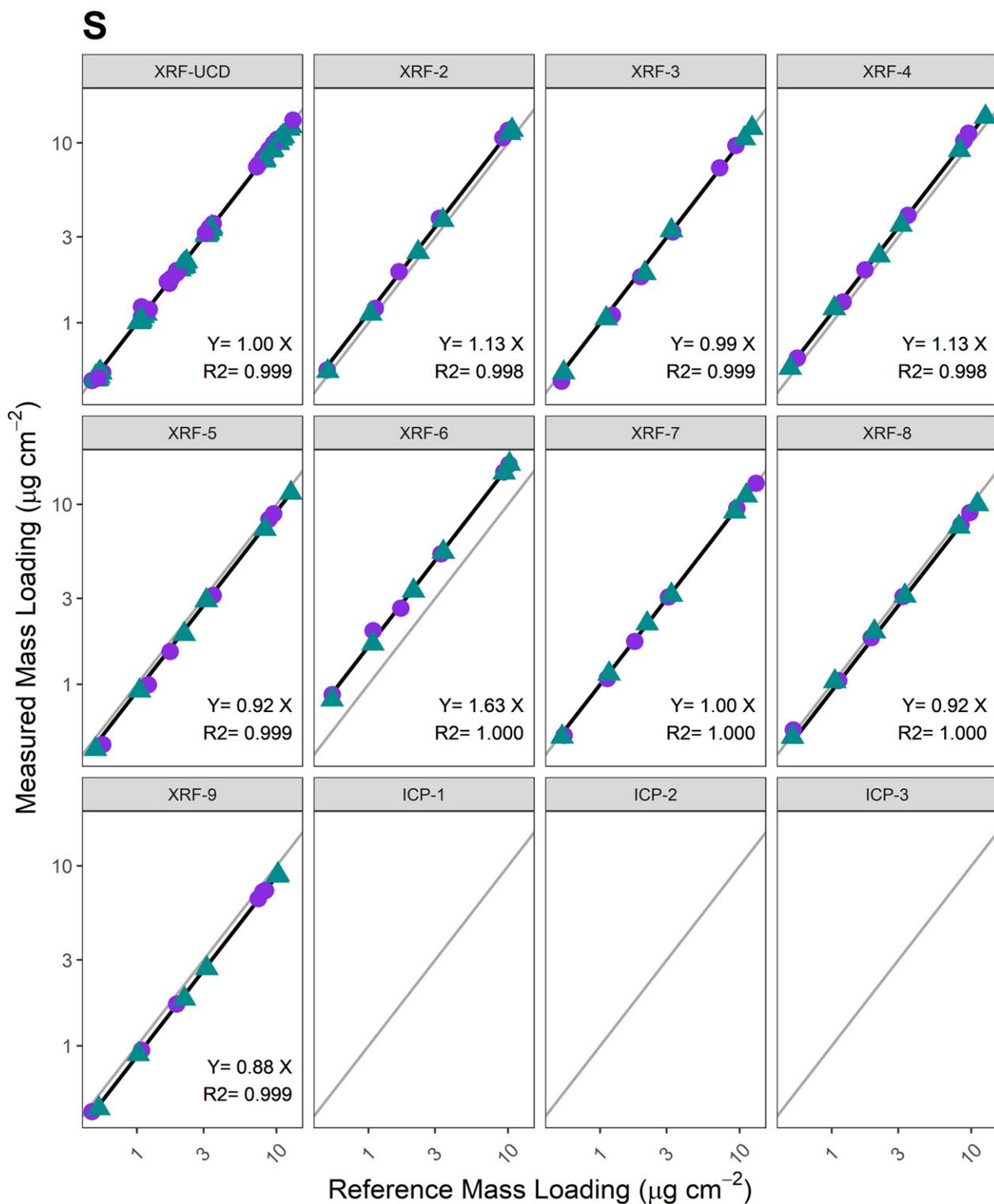


**Figure 3.** Measured versus reference Ca mass loadings. Two of the 12 instruments did not report Ca, reflected by the blank graphs.

## Results and discussion

To determine the RM reference loadings, we made two assumptions: (1) potassium (K) is measured well enough by XRF-UCD to be used as a reference value

and (2) the element-to-potassium ratios in the liquid solutions are maintained in the RM,  $\frac{[\text{Element}]_{\text{RM}}}{[\text{K}]_{\text{RM}}} = \frac{[\text{Element}]_{\text{solution}}}{[\text{K}]_{\text{solution}}}$ . If these assumptions are correct, we can

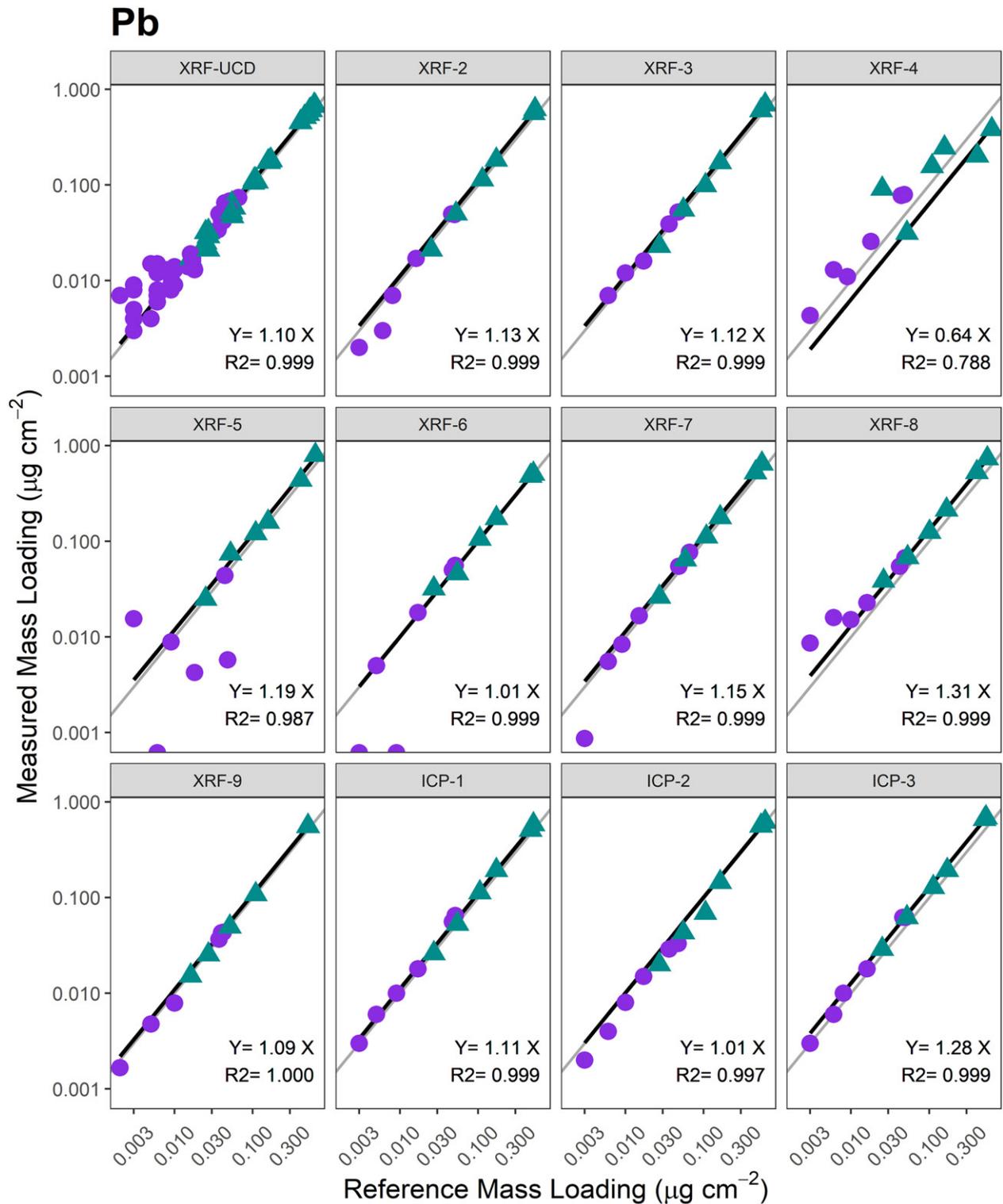


**Figure 4.** Measured versus reference S mass loadings. The three ICP-MS instruments did not report S, reflected by the blank graphs.

determine the reference loading of any element,  $[\text{Element}]_{\text{RM}}$ , by multiplying its known concentration in the solution,  $[\text{Element}]_{\text{solution}}$ , by the ratio of measured K loading on the reference material,  $[K]_{\text{RM}}$ , to the known K concentration in the solution,  $[K]_{\text{solution}}$

$$[\text{Element}]_{\text{RM}} = [\text{Element}]_{\text{solution}} * \frac{[K]_{\text{RM}}}{[K]_{\text{solution}}} \quad (1)$$

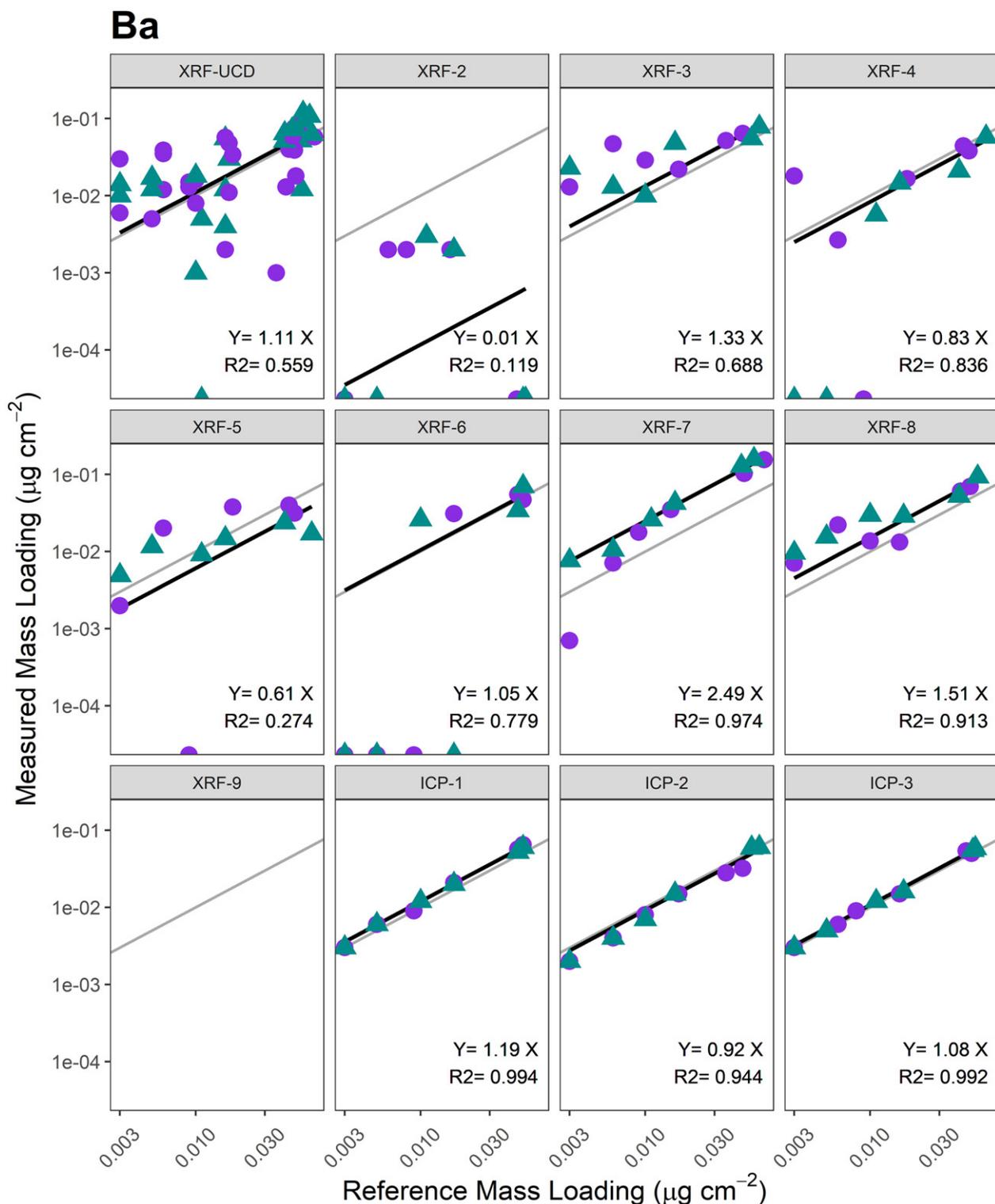
These assumptions were evaluated with multiple tests prior to this inter-laboratory comparison (Yatkin



**Figure 5.** Measured versus reference Pb mass loadings for all 12 instruments. Points plotted at the bottom of the y-axis reflect measured loadings of zero.

et al. 2018), but are further vetted with this study. To evaluate the RM, the reference loadings, based on Equation (1), were compared to the loadings reported by each instrument. Figure 1 shows the measured  $K$  versus reference loadings for the ten participating labs

that routinely quantify  $K$ . Most labs measured the RM three times, and for those labs, the average measured values are shown in the figures; XRF-3 and ICP-2 measured the RM two times, XRF-6 and ICP-1 measured the RM one time, and UCD measured all the



**Figure 6.** Measured versus reference Ba mass loadings for all 12 instruments.

RM one time. The XRF-UCD slope is by definition 1 because of our first assumption; note that the XRF-UCD plot has many more points than the other labs because XRF-UCD analyzed all the RMs before sending them to the external laboratories. To minimize the influence of the low concentration values – which are

often below the detection limits – on the regressions, we regressed the linear loadings, rather than their logarithms, on each other using the equation  $MM = b \times RM$ , where MM is the measured mass loading, RM is the reference mass loading, and  $b$  is the regression slope. The results are all plotted on log scales, so

changes in the slope are displayed as a change in intercept on the log axis,  $\log(\text{MM}) = \log(b) + \log(\text{RM})$ . While the regression model is heavily influenced by the high concentrations, the log scales on the plots allow the reader to evaluate performance at the low concentrations. The agreement between the reference and measured  $K$  loadings is excellent for all the labs except XRF-8; the least-squares regression slopes are all within 20% of unity (0.91–1.2) except for XRF-8 lab which has a slope of 1.54, and the correlations (adjusted  $R^2$ ) are all greater than 0.99, except for ICP-2 which has a correlation of 0.965. This agreement provides further evidence that the first assumption is valid. The second assumption must be evaluated for each element independently.

Figures 2–5 compare the measured versus reference Fe, Ca, S, and Pb loadings for all 12 participating instruments. Graphs for all 28 elements on the RM are included in the online [supplementary information](#). Fe agreement is excellent for all 12 instruments throughout the range of RM loadings. Ca agreement is excellent for the XRF instruments, but not as good for the ICP-MS instruments. S agreement is excellent for the XRF instruments, but S is not quantified by any of the ICP-MS instruments; XRF-6 has a high S slope (1.63), suggesting a calibration issue with that instrument. Pb shows more variation across the instruments, yet the  $R^2$  values are greater than 0.98 for every instrument except XRF-4. The measured Pb concentrations for many instruments showed more scatter at concentrations below or close to the detection limits. To minimize the influence of the low concentrations on the overall fit, we utilized least-squares regression.

It is impossible to evaluate which technique or instrument is most accurate for measuring atmospheric PM deposits on filters with currently available RM or these RM. In this study, the calibration details are not evaluated for each instrument, but those details may illuminate some of the observed measurement differences. For most elements, one or two instruments showed poor agreement (e.g., XRF-8 for K and XRF-4 for Pb); these isolated cases more likely reflect an inaccurate calibration, contamination, or missing/incorrect interference correction for that particular instrument than a problem with the RM. Therefore, in evaluating the performance of these RMs, the most important attribute wasn't accuracy but linearity. Two criteria were used to evaluate the regression results: (1) a regression coefficient (adjusted  $R^2$ ) greater than 0.9 and (2) a slope between 0.7 and 1.3. Of the 28 elements on the RM, five met both the

slope and correlation coefficient criteria for all the reporting instruments and 17 met both criteria for at least 80% of the reporting instruments. Table 2 summarizes the inter-laboratory comparison results for all the elements in the RM. The regression coefficients were quite high in almost all cases, and the results are promising.

Of the elements that failed the criteria, some have known issues and others are difficult to measure by one of the two techniques. For example, Cl and Br were not stable on the RM, and the results did not pass the performance criteria for any of the measuring instruments (Table 1); previous work documented the instability of Cl and Br on the RM and ambient aerosol samples (Hyslop, Trzepla, and White 2015; Yatkin et al. 2018). The poor performance of Cu and Zn has been resolved. The Cu slopes were consistently high on all instruments, which pointed to contamination on the RM. Investigation led to the discovery that a brass ferrule in the aerosol generation system was causing Cu and Zn contamination when exposed to nitric acid, which is the solvent for the multi-element solutions. The brass ferrule was replaced after these RM were produced (Yatkin et al. 2018); Cu and Zn loadings measured by XRF on RM generated subsequent to the change agree well with the reference loadings. Ba, Cd, and Mo were not well-measured by most of the XRF instruments; Figure 6 shows that the ICP-MS results for Ba were very good while the XRF results were erratic. The erratic XRF behavior results from low loadings and non-optimized analytical conditions for these elements (e.g., spectral interferences between Ba and Ti). These multi-element RM could help improve the correction algorithms for spectral interferences such as this by providing RM with varying levels of interfering elements for evaluation. Finally, there were a few elements – Na, Mg, P, and Zr – with widely varying slopes that were not measured consistently by either analytical technique.

RM were developed from certified multi-element solutions for quality assurance and characterization of elemental measurements on atmospheric PM samples. These RM offer many advantages over existing RM including that they cover the range of elemental loadings measured in major PM monitoring networks, are deposited on the same sample media used in major PM monitoring networks, contain a mixture of elements at concentrations representative of real atmospheric samples, and are easy to handle. The reference values assigned to the RM compared very well to the measured values for most elements. Agreement among the various instruments was also very good. For most

elements, one or two instruments often showed a bias >30%, which suggests a calibration, contamination, or interference problem for that particular instrument. These RM are a useful resource for elemental measurements of PM, particularly for checking the stability of ED-XRF instruments, and development work on them continues.

## Funding

The authors gratefully acknowledge financial support from the National Park Service and Environmental Protection Agency under Cooperative Agreement Number H8C07080001.

## References

- Brown, R. J. C., K. E. Jarvis, B. A. Disch, S. L. Goddard, E. Adriaenssens, and N. Claeys. 2010. Comparison of ED-XRF and LA-ICP-MS with the European reference method of acid digestion-ICP-MS for the measurement of metals in ambient particulate matter. *Accred. Qual. Assur.* 15 (9):493–502. doi:10.1007/s00769-010-0668-7.
- Canepari, S., C. Perrino, M. L. Astolfi, M. Catrambone, and D. Perret. 2009. Determination of soluble ions and elements in ambient air suspended particulate matter: Inter-technique comparison of XRF, IC and ICP for sample-by-sample quality control. *Talanta* 77 (5):1821–1829. doi:10.1016/j.talanta.2008.10.029.
- Dabek-Zlotorzynska, E., T. F. Dann, P. K. Martinelango, V. Celo, J. R. Brook, D. Mathieu, L. Ding, and C. C. Austin. 2011. Canadian national air pollution surveillance (NAPS) PM<sub>2.5</sub> speciation program: Methodology and PM<sub>2.5</sub> chemical composition for the years 2003–2008. *Atmos. Environ.* 45 (3):673–686. doi:10.1016/j.atmosenv.2010.10.024.
- Foster, R. D. 2000. Sputnik-generated multi-element aerosol-on-filter standards for XRF measurement of harmful elements in workplace air. *X-Ray Spectrom.* 29 (6):467–474. doi:10.1002/1097-4539(200011/12)29:6<467::AID-XRS455>3.0.CO;2-M.
- Hand, J. L., B. A. Schichtel, M. Pitchford, W. C. Malm, and N. H. Frank. 2012. Seasonal composition of remote and urban fine particulate matter in the United States. *J. Geophys. Res. Atmos.* 117:22.
- Hansen, D. A., E. S. Edgerton, B. E. Hartsell, J. J. Jansen, N. Kandasamy, G. M. Hidy, and C. L. Blanchard. 2003. The southeastern aerosol research and characterization study: Part 1 – overview. *J. Air Waste Mgmt. Assoc.* 53 (12):1460–1471. doi:10.1080/10473289.2003.10466318.
- Hyslop, N. P., K. T. Trzepla, and W. H. White. 2015. Assessing the suitability of historical PM<sub>2.5</sub> element measurements for trend analysis. *Environ. Sci. Technol.* 49 (15):9247–9255. doi:10.1021/acs.est.5b01572.
- Indresand, H., W. H. White, K. Trzepla, and A. M. Dillner. 2013. Preparation of sulfur reference materials that reproduce atmospheric particulate matter sample characteristics for XRF calibration. *X-Ray Spectrom.* 42 (5):359–367. doi:10.1002/xrs.2456.
- ISO Guide 33. 2000. Uses of certified reference materials 33: 2000. Geneva, Switzerland: International Organization for Standardization (ISO).
- Kane, J. S. 2000. The use of reference materials: A tutorial. *Geostandards Newslett.* 25 (1):7–22. doi:10.1111/j.1751-908X.2001.tb00784.x.
- Kang, C. M., S. Achilleos, J. Lawrence, J. M. Wolfson, and P. Koutrakis. 2014. Interlab comparison of elemental analysis for low ambient urban PM<sub>2.5</sub> levels. *Environ. Sci. Technol.* 48 (20):12150–12156. doi:10.1021/es502989j.
- Oster, C., G. Labarraque, and P. Fiscaro. 2015. Certification of a reference material of metal content in atmospheric particles deposited on filters. *Anal. Bioanal. Chem.* 407 (11):3035–3043. doi:10.1007/s00216-014-8194-9.
- Oztürk, F., A. Zararsiz, R. Kirmaz, and G. Tuncel. 2011. An approach to measure trace elements in particles collected on fiber filters using EDXRF. *Talanta* 83:823–831. doi:10.1016/j.talanta.2010.10.038.
- Solomon, P. A., D. Crumpler, J. B. Flanagan, R. K. M. Jayanty, E. E. Rickman, and C. E. McDade. 2014. US national PM<sub>2.5</sub> chemical speciation monitoring Networks-CSN and IMPROVE: Description of networks. *J. Air Waste Manage. Assoc.* 64 (12):1410–1438. doi:10.1080/10962247.2014.956904.
- Stacey, P., and O. Butler. 2008. Performance of laboratories analysing welding fume on filter samples: Results from the WASP proficiency testing scheme. *Ann. Occup. Hyg.* 52 (4):287–295. doi:10.1093/annhyg/men016.
- Szilagyi, V., and Z. Hartanyi. 2005. Development of an X-ray fluorescence spectrometric method for the analysis of atmospheric aerosol samples. *Microchem. J.* 79:37–41.
- Taylor, J. K. 1985. In *Standard reference materials: Handbook for SRM users*, ed. Commerce USDo, 120. 1985 ed. Gaithersburg, MD. <https://archive.org/details/standardreferenc2601tayl>
- Vanhoof, C., V. Corthouts, and N. De Brucker. 2000. An improved aerosol generation system for the preparation of XRF calibration filters. *Adv. X-Ray Anal.* 43:449–455.
- Wise, S. A., and R. L. Watters. 2002. *Certificate of analysis standard reference material 2783*. Gaithersburg, MD: National Institute of Standards and Technology (NIST).
- Yatkin, S., H. S. Amin, K. Trzepla, and A. M. Dillner. 2016. Preparation of lead (Pb) X-ray fluorescence reference materials for the EPA Pb monitoring program and the IMPROVE network using an aerosol deposition method. *Aerosol Sci. Technol.* 50 (4):309–320. doi:10.1080/02786826.2016.1150956.
- Yatkin, S., M. Gerboles, and A. Borowiak. 2012. Evaluation of standardless EDXRF analysis for the determination of elements on PM<sub>10</sub> loaded filters. *Atmos. Environ.* 54:568–582. doi:10.1016/j.atmosenv.2012.02.062.
- Yatkin, S., K. T. Trzepla, W. H. White, and N. P. Hyslop. 2018. Generation of multi-elemental reference materials on PTFE filters mimicking ambient aerosol characteristics. *Atmos. Environ.* 189:41–49. doi:10.1016/j.atmosenv.2018.06.034.