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Preparation of lead (Pb) X-ray fluorescence reference materials for the EPA Pb monitoring program and the IMPROVE network using an aerosol deposition method

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ABSTRACT

X-ray fluorescence (XRF) is a commonly used analytical method to quantify lead (Pb), a toxic element, in atmospheric aerosol. The commercially available reference materials used for calibrating XRF do not mimic the concentrations and filter materials of particulate matter (PM) monitoring networks. In this study, we described an aerosol deposition method to generate Pb reference materials (RMs) over a range of concentrations to serve several purposes for the US Environmental Protection Agency (EPA) and Interagency Monitoring of PROtected Visual Environments (IMPROVE) monitoring networks including laboratory auditing, federal equivalency method evaluation, and calibration and quality control of XRF instruments. The RMs were generated using a laboratory-built aerosol chamber equipped with a federal reference sampler at concentration levels ranging from 0.0125 to 0.70 μg/m^3. XRF analysis at UC Davis was demonstrated to be equivalent to a US and EU reference method, inductively coupled plasma—mass spectrometry (ICP-MS), for measuring Pb on RMs following a methodology described in the United States and international standards. The Pb concentrations on subsets of the RMs were verified by three other XRF laboratories with different analyzers and/or quantification methods and were shown to be equivalent to the UC Davis XRF analysis. The generated RMs were demonstrated to have short and long-term stability, satisfying an additional requirement of reference materials.

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Introduction

Lead (Pb) in ambient particulate matter (PM) is monitored around the world because it is toxic to humans and the environment (EPA report, 2013). The major atmospheric Pb sources are mining and smelting (Cheng and Hu 2010; Csavina et al. 2011; Goix et al. 2013), smelting of scrap materials and recovery of batteries (Yatkin and Bayram 2008), industry (Cheng and Hu 2010), incinerator (Font et al. 2015), traffic, and coal burning (Xu et al. 2012). In the United States, atmospheric Pb is monitored for compliance with the US National Ambient Air Quality Standard (NAAQS) in the EPA Pb Monitoring Network. In addition, two US $PM_{2.5}$ speciation networks, Chemical Speciation Network (CSN; see http://www.epa.gov/ttn/amtic/speciepg.html) and the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network measure atmospheric PM-bound Pb concentrations collected on polytetrafluoroethylene (PTFE, also known as Teflon) filters by energy dispersive X-ray fluorescence (EDXRF). These networks monitor Pb, along with other elements, inorganic ions, and organic and elemental carbon to identify emission sources and evaluate trends in ambient air quality and in the case of IMPROVE, to monitor visibility impairment. In the European Union (EU), monitoring of atmospheric Pb concentrations is regulated together with As, Cd, and Ni (Directive 2004/107/EC of the European Parliament, 2004 and Directive 2008/50/EC of the European Parliament, 2008, hereafter EU Directives). European Environmental Agency reports air pollutants concentrations including Pb from 33 member countries in the Airbase database (European Environmental Agency Airbase Database).

The European Union's limit value for Pb in atmospheric aerosol is 0.5 μg/m^3 and the US NAAQS is 0.15 μg/m^3. The reference methods to measure atmospheric Pb are inductively coupled plasma mass spectroscopy (ICP-MS) and graphite furnace atomic absorption spectrometer in the EU and ICP-MS for Pb in total suspended particles (TSP) (40 CFR Parts 50, Appendix G)

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and EDXRF for Pb in PM_{10} (40 CFR Parts 50, Appendix Q) in the United States.

ICP-MS is a more sensitive method to measure Pb than XRF and commercially available calibration standards, quality check solutions and reference materials simulating atmospheric aerosol are available. However, ICP-MS requires labor intensive and expensive sample preparation and analysis, is subject to contamination and is destructive to the samples.

XRF analysis is faster, has low risk for sample contamination, is usually cheaper than ICP-MS and is not destructive to the samples. Typically, quantification by XRF involves establishing a linear relationship between X-ray intensities of a set of standards with known loadings. These standards are generally single element/compound thin films produced by Micromatter (Vancouver, Canada). However, these standards do not mimic the filter material used for air sampling or the PM matrix. Furthermore, the certified loadings of these standards (i.e., 12.9 and 54 $\mu g/cm^2$ Pb equal to 6.4 and 26.7 $\mu g/m^3$, respectively, with assuming 11.86 cm^2 deposition area and 24 m^3 sampled air volume) are higher than ambient air levels by orders of magnitude. XRF laboratories generally check their calibration with the NIST SRM 2783 ($PM_{2.5}$ on polycarbonate filter), which is a multielement standard reference material with loadings that attempt to represent ambient levels to address the shortcoming of thin film standards. However, the certified Pb loading of SRM 2783 (0.032 $\mu g/cm^2$ or 0.015 $\mu g/m^3$) is order of magnitude lower than NAAQS. Researchers have generated XRF standards for PM-bound elemental measurements using the same filters as used in the sampling and with mass loading ranges that span ambient levels. Vanhoff et al. (2000) generated standards from multielement solutions and assigned reference loadings by analyzing these standards by ICP-OES (optical emission spectrometer). Good agreement was observed between wavelength dispersive (WD) XRF and ICP-OES measurements of the generated standards. In Indresand et al. (2013), we reported on single compound standards generated for calibrating XRF analyzers for the IMPROVE network. We aerosolized dissolved high purity salts (ammonium sulfate and sodium chloride), dried them and collected on PTFE filters using an IMPROVE sampler. The loadings were certified by gravimetric analysis, and confirmed by ion chromatography.

The lack of reliable standards/reference materials close to NAAQS is problematic for PM network operations, laboratory auditing, and EPA Federal Equivalency Method (FEM) testing. EPA guidelines require filters with Pb concentrations of 0.10 $\mu g/m^3$ and 0.32 $\mu g/m^3$ for FEM testing and filters at 30%, 100%, and 250% of NAAQS for audit of the laboratories that measure Pb for the EPA Pb Monitoring Network (40 CFR Part 58). The decrease in Pb NAAQS from 1.5 to 0.15 $\mu g/m^3$ (40 CFR 58) triggered the need for audit and FEM reference materials at concentrations based on the lower NAAQS value.

The objectives of this study were to generate and accurately quantify Pb reference materials (RMs) on PTFE filters for laboratory auditing in the EPA Pb Monitoring Network, for EPA FEM testing and for calibration and quality checks in the IMPROVE network. We used a method similar to that used in Indresand et al. (2013) generate RMs for Pb. However, the PM masses on the Pb-RMs were not high enough to certify by gravimetric measurements. Instead, a methodology including measurement of Pb by ICP-MS and XRF at UC Davis were evaluated for equivalency using US (40 CFR Part 53), European and international standards (Guide to the Demonstration of Equivalence of Ambient Air Monitoring Method, 2010, hereafter called Guide; ISO 17043, 2010). Based on this equivalency, UC Davis XRF was established as the reference method for all RMs generated for quantification methods for use by EPA and IMPROVE. Three different XRF laboratories with different instruments and/or calibration methods were used to verify the RMs for EPA and IMPROVE and were shown to be equivalent to UC Davis XRF.

Methods

Aerosol generation, drying, and sampling system

Figure 1 shows the aerosol generation, drying and sampling system used for producing Pb -RMs. Lead acetate trihydrate salt (99.999% purity, Sigma-Aldrich, St. Louis, MO, USA) was dissolved in ultrapure water (Type 1 water, Milli-Q, Billercia, MA, USA) to obtain lead acetate solutions of 0.04 (for lower Pb mass RMs) or 0.4 mmol L^{-1} (for higher mass RMs). These molar concentrations were chosen based on the required Pb mass loadings, sampler flowrate and to minimize sampling times. The solution is aerosolized using a TSI Atomizer (Model 3076, TSI Inc., Shoreview, MN, USA) and particle-free air from a TSI Filter Air Supply (Model 3074B). The aerosolized wet Pb particles were pulled through a laboratory-built, 2 ft long stainless steel diffusion dryer to remove water from the particles. The Pb particles then flowed into a custom-built 0.23 m^3 (8 ft^3) air-tight stainless steel mixing chamber. Dry make up air was introduced into the chamber with a diffuser, which provided additional drying and sufficient volume for operation of the Thermo Scientific 2025i Partisol sampler (Franklin, MA, USA), a federal reference method sampler. A fan

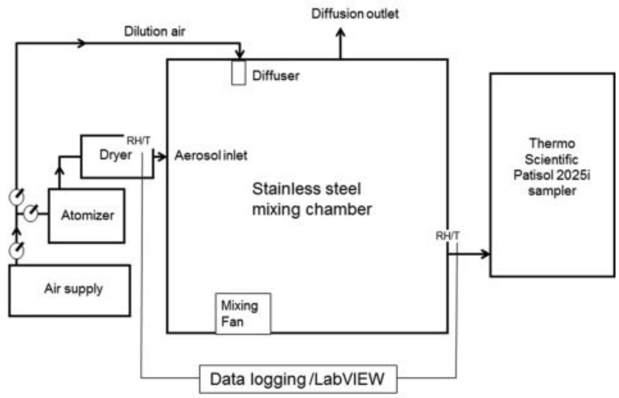

Figure 1. Schematic of the particle generation, mixing, and sampling system used to make Pb reference materials. Lead acetate solution is atomized, and the resulting particles are dried and mixed with particle-free, dry air in mixing chamber. The suspended particles are drawn through a Thermo Scientific Partisol 2025i sampler and collected on 47-mm polytetrafluoroethylene membrane filters. Relative humidity (RH) and temperature (T) are measured in two locations. The entire set-up is located in a fume hood.

inside the chamber aids in mixing the particle stream and the make-up air. The mixing chamber was slightly overpressurized so that laboratory air did not enter the chamber. Pressure was released from the chamber through a diffusion outlet located at the top of the chamber. The Pb aerosols moved from the chamber to the sampler via a stainless steel tubing with 1.5 inch (3.81 cm) internal diameter. No size-cut inlet was used on the sampler. The Partisol sampler was operated at the manufacturers stated flow rate of 16.67 L/min. Sampling durations of 6–24 min were used to obtain Pb masses on the filters equivalent to the concentration ranges needed for both EPA and IMPROVE. The atomizer, chamber and sampler were located in a fume hood so that no particulate Pb was introduced into the laboratory. The set-up and procedures are similar to that used by Indresand et al. (2013).

Production of Pb reference materials

Reference materials produced for the EPA Pb Monitoring Network were collected on 47 mm PTFE filters manufactured by Measurement Technology Laboratories (0.2 μm pore size, Minneapolis, MN, USA, hereafter MTL-RMs), which are used in the EPA Pb Monitoring Network. RMs for the IMPROVE network were collected on 47 mm on Teflo PTFE filters manufactured by Pall, Inc. (Teflo, 2 μm pore size), similar to those used by IMPROVE, hereafter Teflo-RMs. To be consistent with most air monitoring procedures, 47 mm filters were used instead of the 25 mm filters (3 μm pore size) used by IMPROVE.

MTL-RMs were produced at five Pb concentrations, two for audit purposes (0.10 and 0.32 μg/m^3, 12 RMs each) and three for FEM evaluation (0.045, 0.15, and 0.375 μg/m^3, 10 RMs each). For the IMPROVE network, 40 RMs from the XRF Pb method detection limit (0.008 μg/m^3) to slightly higher than IMPROVE observations (0.70 μg/m^3) were produced. The Pb mass loadings measured by XRF on the RMs were converted from μg/cm^2 to μg/m^3 by using the ambient sampling protocol values of 24 m^3 air volume and 11.86 cm^2 sample deposition area.

Prior to collecting the RMs, the aerosol generation and sampling system was cleaned three times with ultrapure water and three times with isopropyl alcohol. Chamber filter blanks, which were produced like RMs except only ultrapure water was used, were then collected and analyzed to ensure that there was no contamination in the system. Sampling times for chamber blanks ranged from 10 to 120 min. Laboratory blanks were not installed into the sampler but were handled, stored, and processed in the same manner as chamber blanks and RMs.

Pb measurements on RMs

Gravimetric analysis could not be used as a reference method for Pb on the RMs because the total PM on the lower range of RMs (range 2–14 μg) was near or below the uncertainty of the gravimetric analysis (3 μg, based on standard deviation of multiple analysis of an MTL filter using an ultrabalance with 0.1 μg sensitivity, Mettler Toledo, Model XP2U, USA). In this work, EDXRF at UC Davis, hereafter XRF-UCD, was used as the reference method for Pb on RMs by establishing its equivalence to ICP-MS, a US and European reference method for measuring atmospheric Pb. To verify the XRF-UCD reference concentrations on RMs, the measurements were compared to XRF analysis by three other laboratories. Given the PM mass loadings of the RMs (ranged from 0.2 to 2.2 μg/cm^2 for MTL-RMs and from 0.04 to 2.3 μg/cm^2 for IMPROVE RMs), all RMs can be considered thin samples as is needed for a linear response by XRF. Nonlinear responses such secondary absorption or enhancement of fluorescent X-ray is negligible for the RMs. Details of the analytical methods used to measure Pb are described below. The EDXRF analytical methods including excitation conditions, analysis time, and quantification techniques are those used routinely by XRF laboratories in this study to analyze ambient air samples; the methods have not been modified for this study to get the best accuracy and precision of Pb on RMs.

XRF analysis at UC Davis

All RMs and blanks were analyzed by XRF-UCD. UC Davis operates a fully integrated EDXRF instrument (Epsilon 5, PANalytical, Almelo, The Netherlands). The system incorporates 3-D polarizing optical geometry with a 600 Watts side-window dual anode (Sc/W) X-ray tube and 100 kV generator, up to 15 secondary and polarizing targets and a high-resolution liquid nitrogen cooled solid state Ge detector (PAN-32). Each RM was analyzed for 300s with 100 kV and 6 mA, using Molybdenum as secondary target in vacuum analytical atmosphere while spinning. Pb was detected by its Lβ line and quantified by linear calibration using the NIST SRM 2783 (Pb = 0.015 μg/m^3) and four Micromatter standards (Pb = 1.6, 1.7, 6.4 μg/m^3 and 26.7 μg/m^3). The intercept is set to zero for the calibration regression function. The intensity of one laboratory blank was subtracted from the intensities of RMs as to calculate the Pb loadings. Most RMs were analyzed by XRF once. However, selected RMs were analyzed multiple times for evaluating precision and performing stability tests as discussed below. The analytical conditions, details of calibration and quality control measures are available online (SOP 2014).

The mass loading of Pb for XRF-UCD (μg/cm^2), $c_{\text{XRF-UCD}}$, is quantified using Equation (1).

$$c_{XRF-UCD} = \frac{(I_{\text{net}} - I_{\text{blk}})}{b_{\text{cal}}} \qquad [1]$$

where, I_{net} is the net intensity of X-rays emitted by the sample (cps/mA) and I_{blk} is the net intensity of a blank filter (cps/mA) and b_{cal} is the calibration factor [(cps/mA)/(μg/cm^2)] calculated as the slope of the linear regression between elemental loadings of calibration standards and their blank subtracted (net) intensities.

The combined analytical uncertainty of XRF-UCD ($u_{\text{CXRF-UCD}}$) was estimated applying GUM (Guide to Express the Uncertainty of Measurement 2008) methodology to Equation (1), as shown in Equation (2):

$$u = \sqrt{\sum \left(\frac{\partial}{\partial x}\right)^2 u_x^2}$$

$$= \sqrt{\frac{u^2(I_{\text{net}})}{(b_{\text{cal}})^2} + \frac{u^2(I_{\text{blk}})}{(b_{\text{cal}})^2} + \left(\frac{(I_{\text{net}} - I_{\text{blk}})}{(b_{\text{cal}})^2}\right)^2 u^2(b_{\text{cal}})}, \qquad [2]$$

where, x is the components of Equation (1) and u_x is the uncertainty of each component. The uncertainties of I_{net} and I_{blk} were estimated as standard deviation of replicated sample and blank filter analysis, respectively. The uncertainty of b_{cal} was estimated from the deviation from linear fit of the calibration function and the uncertainty of the Micromatter calibration standards. The combined uncertainty is converted into expanded uncertainty (GUM 2008) by using a coverage factor, k (Equation (3)).

$$U_{C_{\text{XRF-UCD}}} = k * u_{C_{\text{XRF-UCD}}} \qquad [3]$$

The coverage factor takes into account the distribution of uncertainties possible for a given measurement and in this work, a coverage factor of 2 is used to give approximately the 95% confidence interval on the uncertainty value ($k = 1.96$ at 95% confidence level for a normal distribution).

It should be noted that the air volume and sampling were not included in the uncertainty calculations for any of the analytical methods because these were not parallel filters analyzed by two methods but the same filter analyzed by two methods so the air volume and sampling errors are the same for both.

ICP-MS analysis in UC Davis

Seven MTL-RMs at concentrations ranging from 0.06 to 0.75 μg/m^3 were analyzed by ICP-MS to test for equivalency between XRF-UCD and ICP-MS. This broad range of concentrations was used to meet the requirement in the Guide that at least 20% of the test samples for equivalency evaluation exceed the European limit value. Two of these 7 MTL-RMs (29%) were above European limit value (0.5 μg/m^3) and more were above NAAQS (0.15 μg/m^3), thereby meeting the requirement for both the European and EPA values. The filters were extracted with a mixture of acetone and 1N nitric acid following the method by Herner et al. (2006). The MTL-RMs were spiked with Bismuth (Bi) to determine the recovery of the analytical extraction method. A 30 mL of extraction solution, 75% acetone (Fisher, Inc., Optima grade, Pittsburgh, PA, USA), and 25% 1 N nitric acid (Fisher, Trace Metal Grade) were added, and the tubes were sonicated for 30 min at room temperature and transferred into precleaned test tubes. To remove the acetone from the extract, the samples were heated to 45°C and pure nitrogen (99.998%) was bubbled into the solution using a Reacti-Vap Evaporator (Pierce Corp, Rockford, IL, USA) equipped with Teflon coated needles. The sample volumes were reduced to 4 mL using the evaporator. The final volume was adjusted using 1 N nitric acid to be 10 mL.

Pb isotopes 204, 206, 207, and 208 m/z, along with Bi isotope 209 m/z, were quantified by ICP-MS (Agilent

7500ce, Santa Clara, CA, USA). Yttrium (89 m/z), lutetium (175 m/z), tantalum (181 m/z), and thorium (232 m/z) were continuously injected inline using a pump as the internal standards. Each sample and ICP-MS calibration standard was analyzed in triplicate. The instrument was calibrated using nine Pb standards prepared in concentration range of 0.5 ppb to 2000 ppb with correlation coefficient (r) higher than 0.999. A quality control solution with 100 ppb Bi and Pb was analyzed after calibration and after every 10 samples to monitor the instrumental drift. The drift was found to be less than 1%. The Bi recoveries were between 93% and 116%. Laboratory, chamber and reagent blanks were prepared and analyzed along with MTL-RMs. The average Pb concentration of laboratory blanks, 0.003 μg/m^3, is an order of magnitude lower than the lowest MTL-RM measured by ICP-MS, was subtracted from the measured Pb for each MTL-RMs.

The mass loading of Pb (μg/cm^2), $c_{\text{ICP-MS}}$, for ICP-MS is quantified using Equation (4).

$$c_{ICP-MS} = \frac{c_i v}{A}, \qquad [4]$$

where, c_i is the Pb concentration by ICP-MS (μg/mL, ranged from 150 to 1500 μg/mL), v is the sample liquid volume (mL), and A is the PM deposition area (cm^2). The combined analytical uncertainty of ICP-MS was estimated applying GUM methodology to Equation (4) as shown in Equation (5),

$$u_{C_{ICP}} = \sqrt{\left(\frac{v}{A}\right)^2 u^2(c_i) + \left(\frac{c_i}{A}\right)^2 u^2(v) + \left(\frac{c_i v}{A^2}\right) u^2(A)}. \qquad [5]$$

The uncertainty of c_i was estimated using the deviation from linear fit of calibration function of ICP-MS (uncertainty of standards is ignored) and standard deviation of triplicate measurements of the RMs. The uncertainties of liquid volume and PM deposition area were assumed to be 5% each. The combined uncertainty is converted into expanded uncertainty by a coverage factor 2 using Equation (3).

EDXRF analysis at Research Triangle Institute (RTI)

All 54 MTL-RMs were analyzed at RTI using an ARL Quant'X EDXRF (Thermo Scientific Inc., Franklin, MA, USA), here after XRF-RTI. The Quant'X is equipped with an Rh X-ray tube and a peltier cooled Si(Li) drifted detector. A thick Palladium filter is used to narrow the excitation bandwidth and a collimator is used to focus the X-ray beam. The samples are analyzed under vacuum with 200 s analysis time using 50 kV voltage and 1.0 mA current. The Pb Lβ line is used for quantification, and instrument is calibrated using certified standards from Micromatter. SRM 2783 is used to monitor analytical drift. The filters were analyzed four times, rotating the filter by 45° between each analysis. The concentration of Pb reported by RTI is the mean of the four measurements.

The mass loading of Pb (μg/cm^2), $c_{\text{XRF-RTI}}$, for XRF-RTI is quantified using Equation (1). The combined uncertainty was estimated applying GUM methodology shown in Equation (2). The uncertainty of the intensity is the standard deviation of four replicate measurements. The uncertainty of calibration was assumed to be 5% while uncertainty due to the deviation from linear fit of calibration function was not included. The combined uncertainty is converted into expanded uncertainty by using a coverage factor 2 (Equation (3)).

EDXRF analysis at the Desert Research Institute (DRI)

A subset of six Teflo-RMs with Pb concentrations of approximately 0.0125, 0.025, 0.05, 0.15, 0.30, and 0.50 μg/m^3 was analyzed at DRI (Reno, NV), using PANalytical Epsilon 5 EDXRF (Almelo, the Netherlands), hereafter XRF-DRI. The Epsilon 5 instrument at DRI uses a side window X-ray tube with a Gadolinium (Gd) anode as the X-ray source, and Zirconium is used as the secondary target. Samples are analyzed one time under vacuum for 200 s with 100 kV voltage, and 6.0 mA current. The Pb Lα is used for quantification and the instrument is calibrated using standards from Micromatter and SRM 2783.

The mass loading of Pb (μg/cm^2), $c_{\text{XRF-DRI}}$, for XRF-DRI is quantified using Equation (1) and the combined uncertainty was estimated applying GUM methodology (Equation (2)). The uncertainties of intensities are propagated from the counting statistics of the sample and background spectra. The uncertainty of calibration was assumed to be 5% but the uncertainty of the deviation from linear fit of calibration function is ignored. The combined uncertainty is converted into expanded uncertainty by using a coverage factor 2 (Equation (3)).

EDXRF analysis at the Joint Research Centre-European Reference Laboratory for Air Pollution (JRC-ERLAP)

Another subset of six Teflo-RMs with Pb concentrations of approximately 0.02, 0.04, 0.08, 0.15, 0.32, and 0.70 μg/m^3 was analyzed by JRC-ERLAP. The ARL Quant'X spectrometer (Thermo Scientific Inc., Franklin, MA, USA) at JRC-ERLAP is equipped with an air cooled X-ray tube (Rh anode, 50 W maximum power, 4–50 kV voltage, 0.02–1.98 mA current), a peltier cooled Si (Li) drifted crystal detector (15 mm^2 crystal area, 3.5 mm crystal depth, and 155 eV resolution), and a pulse processor (32 bit digital type, 20 eV channels, 1–40 ms adjustable shaping time, up to 100,000 cps live count rate and 400–40,960 eV energy range). Primary X-ray beam filters were placed in front of the X-ray beam in order to optimize the X-ray excitation conditions and background. All samples are analyzed twice without spinning using Pb Lβ. The JRC-ERLAP quantifies Pb in μg/filter using a standardless method (Yatkin et al. 2012), hereafter XRF-JRC. In the standardless method, the loadings are calculated as a function of sample intensities, modeled background using the filter type used for sampling, mass absorption coefficient, instrumental sensitivity determined by analyzing of thin film samples, excitation area, sum of interferences and total PM on filter. The results from JRC are the average of two replicates.

The combined analytical uncertainty of XRF-JRC by GUM has been previously published (Yatkin et al. 2012). It was demonstrated by Yatkin et al. (2012) that the XRF-JRC is equivalent to ICP-MS to measure Pb in PM$_{10}$ at the European limit value.

Data evaluation

In order for XRF-UCD to be a candidate for a reference method to measure Pb on RMs, XRF-UCD metrics were compared to method detection limit (MDL) and precision performance criteria (40 CFR Part 50, Appendix Q). The criterion for MDL is that the MDL must be equal to or less than 5% of NAAQS (40 CFR Part 53, subchapter 53.33). The MDL of XRF-UCD was calculated following three approaches: counting statistical error, analyzing of seven laboratory blanks from the same lot, and analyzing one blank ten times. The precision criterion is that the ratio of the difference between the maximum and minimum measurement to average measurement of samples measured three times on different days is less than 15%. One sample at each MTL-RM level was analyzed by XRF-UCD as required. The EU criterion is that the MDL must be less than or equal to 10% of EU Pb limit value.

After XRF-UCD had been shown to meet with MDL and precision criteria, it was demonstrated that XRF-UCD is equivalent to ICP-MS and therefore can be considered a reference method using the following methodologies: (1) the US method given in 40 CFR Part 58 Appendix A, (2) the EU method given in the Guide (2010), and (3) the international requirement given in ISO 17043 (2010).

The US methodology requires analysis of collocated samples by the reference and candidate method and that the precision and bias between the two methods as given in Equations (6)–(10), be less than or equal to 20 and 15%, respectively. Throughout this work, when collocated samples are required, the same samples are used for the two methods. The coefficient of variation (CV) is shown in Equation (6),

$$CV = \sqrt{\frac{n\sum_{i=1}^{n} d_i^2 - \left(\sum_{i=1}^{d} d_i\right)^2}{2n(n-1)}}\sqrt{\frac{n-1}{X^2_{0.1,n-1}}}, \quad [6]$$

where, n is number of the samples, d_i is the percent difference between the candidate and reference method as given in Equation (7), and $X^2_{0.1,n\text{-}1}$ is the 10th percentile of a chi-squared distribution with n–1 degrees of freedom.

$$d_i = \frac{c_x - c_y}{\mathrm{mean}(c_x, c_y)}100, \quad [7]$$

where, c_x and c_y are the results from reference and candidate method, respectively. The bias is calculated from a set of equations (Equations (8)–(10)):

$$|AB| = AB + t_{0.95,n-1}\frac{AS}{\sqrt{n}}, \quad [8]$$

$$AB = \frac{1}{n}\sum_{i=1}^{n} |d_i|, \quad [9]$$

$$AS = \sqrt{\frac{n\sum_{i=1}^{n} |d_i|^2 - \left(\sum_{i=1}^{d} |d_i|\right)^2}{2n(n-1)}}, \quad [10]$$

where, $t_{0.95,n-1}$ is the 95th quantile of a t-distribution with n–1 degrees of freedom. The bias estimator is an upper bound of the mean absolute value of the percent differences (AB).

The EU method (Guide 2010) relies on the differences between collocated pairs of samples analyzed by the reference method (ICP-MS) and the candidate method (XRF-UCD) and the expanded uncertainty of candidate method with respect to the reference method. The first step in determining the expanded uncertainty of XRF-UCD according to the Guide is to create a linear relationship between the measurements by XRF-UCD(y) and ICP-MS(x) (Equation (11)).

$$c_{XRF-UCD} = b_0 + b_1 c_{ICP-MS}, \quad [11]$$

where, b_o and b_1 are the intercept and slope, respectively. The XRF-UCD expanded uncertainty ($U_{GUIDE,}$ Equation (12)) is calculated using a coverage factor (k = 2), the sum of the square of residuals (RSS, Equation (13)), the number of samples analyzed by both XRF-UCD and ICP-MS (n), the random uncertainty of the ICP-MS measurements ($u_{ran(ICP\text{-}MS)}$) and the XRF-UCD bias from ICP-MS result (the last term in the Equation (12)).

$$U_{GUIDE}(c_{XRF-UCD}) = ku_{C_{XRF-UCD}} = k\sqrt{RSS/(n-2) - u_{ran}{}^2(c_{ICP-MS}) + [b_0 + (b_1 - 1)c_{ICP-MS}]^2}, \qquad [12]$$

$$RSS = \sum^{n} (c_{XRF-UCD} - b_0 - b_1 c_{ICP-MS})^2. \qquad [13]$$

For the two methods to be considered equivalent, the relative expanded uncertainty of XRF-UCD ($U_{GUIDE}/c_{XRF\text{-}UCD}$, hereafter $U_{r,GUIDE}$) must be less than or equal to a specified value at a specified ambient air Pb concentration. Based on EU directives, the XRF-UCD $U_{r,GUIDE}$ must be equal to or below 25% at a Pb concentration of 0.5 μg/m^3. No such uncertainty requirements in the US exist to show equivalency, however, Appendix Q of 40 CFR Part 50 includes a section to estimate the EDXRF uncertainty combining fitting uncertainty (varies between 2 and 100%), calibration uncertainty (assumed to be 5%), sampling/deposition area uncertainty (assumed to be 5%) and attenuation uncertainty (negligible for Pb). Although there is no limit defined in Appendix Q for uncertainty, it is reasonable to assume a relative expanded uncertainty (U_r) of 15% (5% from calibration and 5% fitting, gives $U_r = k\sqrt{50\%^2 + 5\%^2} = 15\%$ with $k = 2$) for Pb measurements at the Pb-NAAQS level. In our work, we demonstrate the equivalency of XRF-UCD to ICP-MS by showing that both $U_{r,GUIDE}$ and the relative expanded uncertainties by GUM ($Uc_{XRF\text{-}UCD}/c_{XRF\text{-}UCD}$, hereafter $U_{r,GUM}$) are below the estimated US EPA value of 15% at 0.15 μg/m^3 and the EU standard of 25% at 0.5 μg/m^3. Additionally, if $U_{r,GUIDE}$ is similar to or lower than $U_{r,GUM}$, $U_{r,GUM}$ can be used as the XRF-UCD expanded uncertainty for Pb at concentrations without need of further testing against ICP-MS. Conversely, if $U_{r,GUM}$ is lower than $U_{r,GUIDE}$, then $U_{r,GUM}$ does not include all the sources of measurement uncertainties of XRF-UCD, and hence underestimates the uncertainty compared to the ICP-MS. Thus, we used the Guide to demonstrate the XRF-UCD equivalency to ICP-MS at NAAQS and EU limit value and as the validity of GUM uncertainty for XRF-UCD measurements when $U_{r,GUM}$ is higher than $U_{r,GUIDE}$.

The Guide also requires performing an equivalency field test with at least 20 ambient air samples. However, we were not testing the methods for equivalency of field samples, but of laboratory RMs, which are much less complex than ambient air samples, so only seven samples were analyzed. Increasing the number of samples with the same matrix (single compound samples) will not serve to simulate the large variation in ambient air aerosol profile, which is the intent of analyzing at least 20 samples.

The ISO 17043 methodology is shown in Equation (14). E_n is a ratio of the absolute difference between candidate method and reference method of paired measurement to root-mean-square of the expanded uncertainties of two methods.

$$E_n = \frac{|c_{Lab,i} - c_{Lab,j}|}{\sqrt{U_{C_{Lab,i}}{}^2 + U_{C_{Lab,j}}{}^2}}, \qquad [14]$$

where, $c_{Lab,i}$ and $c_{Lab,j}$ are the measured Pb concentrations by Lab i and j, respectively, and $U_{CLab,i}$ and $U_{CLab,j}$ are the expanded uncertainties of $c_{Lab,i}$ and $c_{Lab,j}$, respectively. When the E_n number is lower than 1, the difference between two analytical methods is within the expanded uncertainty, and can be considered equivalent. The E_n value was calculated for XRF-UCD and ICP-MS paired measurements to demonstrate equivalency of XRF-UCD to ICP-MS throughout the range of RMs in comparison.

To validate XRF-UCD measurements on filters prepared for EPA and IMPROVE, three other nondestructive XRF measurements by XRF-RTI (for EPA RMs), and XRF-JRC and XRF-DRI (for Teflo-RMs) were used and shown to be equivalent to XRF-UCD using the US methodology and E_n only. When E_n numbers are calculated between XRF laboratories, the lowest uncertainty of XRF-UCD among $U_{r,GUIDE}$ and $U_{r,GUM}$ was utilized to minimize the denominator of Equation (14), as conservative approach.

Two more methods are used to evaluate comparability of Pb measurements on the same RMs. One method is linear regression and its associated slope, intercept and coefficient of determination (R^2). Although a slope near unity and a high R^2 can be a good indicator of agreement between the methods, the method has some limitations, because regression is affected by outliers and the highest point of the regression. The other method calculates the relative difference between the results from any method and reference method sample by sample. Hence, the agreement between the method and reference can be assessed throughout the Pb range in comparison. Relative difference was calculated using Equation (15).

$$\text{Relative difference} = \frac{(c_{\text{Lab}} - c_{\text{Ref}})}{c_{\text{Ref}}}. \qquad [15]$$

Relative difference is a good tool to compare the results from a candidate method laboratory to the reference one; however, there is no standardized criterion on the acceptance. Generally a relative difference below 10% is a reasonable limit as it is the same as the quality check criterion of ICP-MS in 40 CFR Parts 50, Appendix G.

A final consideration for comparing methods is that the particle deposit may not be uniform across the filter as shown by Brown et al. (2009) for the Partisol 2000 which could potentially lead to difference in the measurement if the whole filter is not analyzed. In XRF measurements only the center of the filter is interrogated by the X-ray beam. Since the instruments have similar beam size, we can assume that the XRF laboratories measured very similar portions of the samples such that the resulting measurements such that have little to no additional error is added due to sample inhomogeneity. However, ICP-MS analysis uses the whole filter, so it is possible that some of measurement differences between XRF and ICP-MS are due to filter inhomogeneity.

Other ISO requirements are long-term and short-term stability and homogeneity of reference materials (ISO 35 2006). The long-term stability is associated with the effect of storage conditions during the shelf-life of the RMs. Short-term stability is associated with short time effects such as transport, temperature differences between storage and transport and repeated measurements. Pb is expected not to be influenced by temperature during transportation because it is a nonvolatile element. The same subset of RMs analyzed by XRF-DRI except for one RM damaged during handling was analyzed by XRF-UCD again to test the effect of transport. To test if repeated XRF analysis affects the stability of RMs, a subset of MTL-RMs with Pb concentrations of 0.1, 0.15, 0.32, and 0.50 μg/m^3 (7 RMs each) were analyzed three times on two different XRF analyzers at UCD (for a total of 6 analyses per filter). The RMs stored in the refrigerator were analyzed two years after generation to evaluate the long-term stability. A relative difference of ±5% was used as criterion of good short-term and long-term stability.

Results

Establishing XRF-UCD as a reference method

The MDL of XRF-UCD was calculated and ranged from 2 to 5% of NAAQS for the counting statistical error approach. The MDL by the second approach (standard deviation of seven laboratory blanks) was 1% of NAAQS. The MDL by the third approach (standard deviation of 10 replicates of a laboratory blank) was 5% of NAAQS. The MDLs are also lower than 10% of EU Pb limit value. The XRF-UCD precision calculated from triplicate analysis of a subset of filters ranges from 0 to 8%, which is significantly lower than the criterion (15%). Thus, XRF-UCD meets the MDL and precision requirements to be a reference method to measure Pb on PTFE RMs. As a point of reference, the MDL of ICP-MS was estimated as the three times the standard deviation of multiple readings of the blank (EPA 40 CFR Appendix B to Part 136), and found to be 0.001 μg/m^3, which is well below the US and EU requirements.

The US method to show equivalence was evaluated by calculating the precision and bias between XRF-UCD and ICP-MS. The precision was 6% and the bias was 8% both of which are lower than the criteria (20% and 15%, respectively). Thus, XRF-UCD and ICP-MS are equivalent according the US methodology and XRF-UCD is

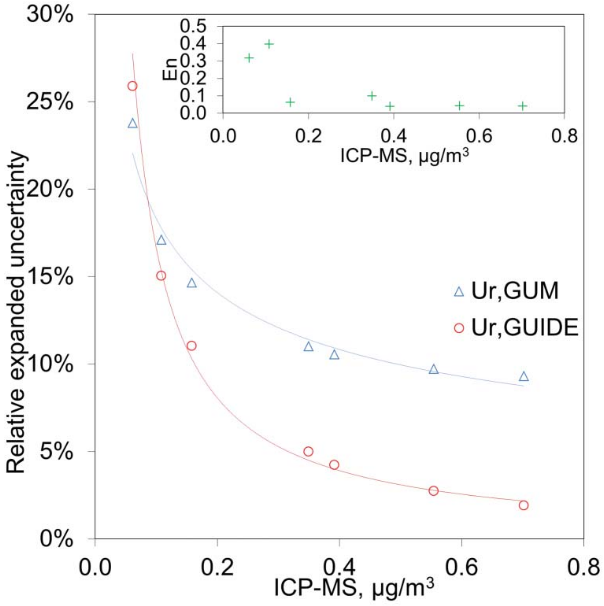

Figure 2. The relative expanded uncertainty of XRF-UCD estimated using the methodology of Guide ($U_{r,GUIDE}$) and using GUM ($U_{r,GUM}$). The inner graph shows the E_n values (Equation (14)). The range of samples is 0.124–1.420 μg/cm^2 (x-axis). These were converted to μg/m^3 using 11.86 cm^2 deposition area and 24 m^3 air volume.

established as a reference method for measuring Pb on RMs.

Applying the EU method to show equivalency, Figure 2 shows $U_{r,GUIDE}$ and $U_{r,GUM}$ for XRF-UCD as a function of ICP-MS concentrations. The $U_{r,GUM}$ is 14.7% at 0.16 μg/m^3, which is the closest RM to NAAQS. By interpolation, $U_{r,GUM}$ is found to be 15.7%, at NAAQS, which is slightly higher than the value of 15% estimated for the US method. $U_{r,GUIDE}$ is less than 15% at NAAQS. $U_{r,GUM}$ and $U_{r,GUIDE}$ are well below 25% at 0.5 μg/m^3. Thus XRF-UCD is equivalent to ICP-MS for measuring Pb based on the EU directives and can be accepted as equivalent based on our estimated and assumed criteria from the US document. The inner graph of Figure 2 shows the E_n number (the ISO17043 equivalency method) calculated using U_{GUM} (Equation (3)). E_n is lower than 1 throughout the range indicating equivalence of the methods for all RMs. These three equivalency tests together indicate that XRF-UCD can be considered equivalent to ICP-MS on MTL-RMs.

Figure 2 also compares $U_{r,GUIDE}$ and $U_{r,GUM}$ throughout the concentration range of RMs. $U_{r,GUIDE}$ becomes equal to $U_{r,GUM}$ at about 0.08 μg/m^3. Thus, the $U_{r,GUM}$ can be used to estimate uncertainty at Pb concentration higher than 0.08 μg/m^3. Both $U_{r,GUM}$ and $U_{r,GUIDE}$ showed a decreasing trend with Pb concentrations with a significant power correlation ($R^2 > 0.97$), showing that extrapolation and interpolation can be used to estimate the uncertainty within or beyond the range. Furthermore, the strong correlations also showed that the random variation in uncertainty is negligible due to constant matrix on RMs.

The linear regression between ICP-MS and XRF-UCD is shown in Figure 3. The error bars are U_{GUM}. The two methods agreed well with a slope of 0.999 and R^2 of 0.999. The inner plot in Figure 3 shows the relative difference as function of RM concentrations. The relative difference is lower than 10% at Pb concentrations higher than 0.1 μg/m^3. Only at the lowest Pb concentrations (0.06 μg/m^3) does the relative difference slightly exceed 10% (13%). The relative difference approaches zero as Pb loadings increase. The variation of relative difference also showed that the homogeneity of PM deposition on RMs is not an important factor affecting comparability between two methods. Both of these analysis show good agreement between the ICP-MS and XRF-UCD as confirmed by the equivalency tests.

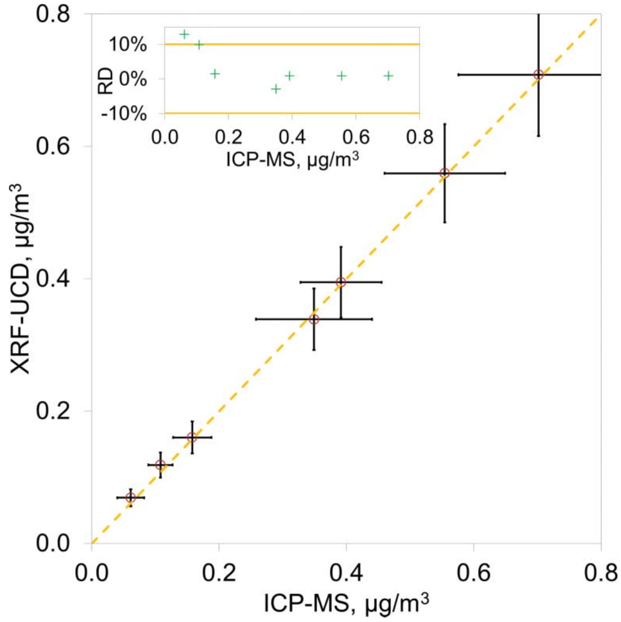

Figure 3. Comparison of XRF-UCD and ICP-MS measurements over the full range concentrations of the Pb RMs produced. Error bars indicate the measurement uncertainties estimated by GUM. The linear regression (with 95% confidence levels for the slope and intercept) is $y = (0.999 \pm 0.01)\ x + (0.0034 \pm 0.0038)$ with an R^2 of 0.999. The inner graph shows the XRF-UCD relative difference (RD). The range of mass loadings for these RMs is 0.124–1.420 μg/cm^2 (x-axis). These were converted to μg/m^3 using 11.86 cm^2 deposition area and 24 m^3 air volume.

MTL-RMs generated for EPA

Figure 4 shows the comparison of the Pb measurements between XRF-UCD and XRF-RTI for 54 MTL-RMs. Two methods agreed well with a regression slope of 1.009 (R^2 of 0.997). The relative difference was less than or equal to 10% with exception of only 2 RMs out of 54 as shown in the inner graph in Figure 4. The precision and bias between XRF-UCD and XRF-RTI calculated following the US methodology were 3% and 4%, respectively, which are well below the criteria. The E_n numbers, also shown in the inner graph in Figure 4, were well below 1 for all samples, meaning that the absolute differences between XRF-RTI and XRF-UCD are within their uncertainty. Both relative difference and E_n decrease with increasing Pb concentrations indicating that the differences between two methods are close to zero at high Pb concentrations. These analyses show that XRF-RTI and XRF-UCD measured Pb loadings on RMs equivalently and that XRF-RTI verifies the XRF-UCD measurements and the MTL-RMs.

Teflo-RMs generated for use by IMPROVE

The equivalency of XRF-UCD to ICP-MS at the low mass loadings required for this project was established in "Establishing XRF-UDC as a reference method" and indicates that XRF calibrated with

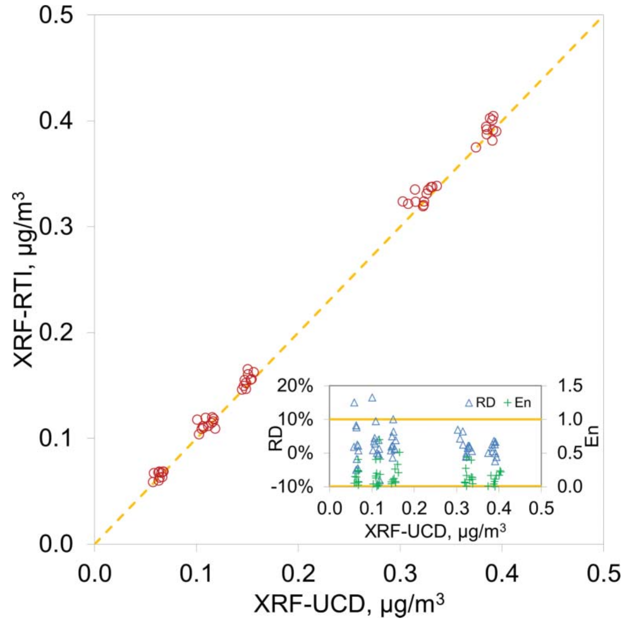

Figure 4. Comparison of XRF-UCD and XRF-RTI on 30 MTL-RMs generated for FEM testing and 24 MTL-RMs generated for laboratory performance testing. The linear regression (with 95% confidence levels for the slope and intercept) is $y = (1.009 \pm 0.006)\ x + (0.002 \pm 0.002)$ with an R^2 of 0.997. Error bars (uncertainties by GUM) on the figure are not shown for visual clarity. The XRF-UCD relative expanded uncertainties vary between 14 and 33% while the XRF-RTI ones are between 14 and 15%. The inner graph shows relative difference (RD) of XRF-RTI and XRF-UCD and the E_n values. The range of samples is 0.116–0.798 μg/cm^2 (x-axis). These were converted to μg/m^3 using 11.86 cm^2 deposition area and 24 m^3 air volume.

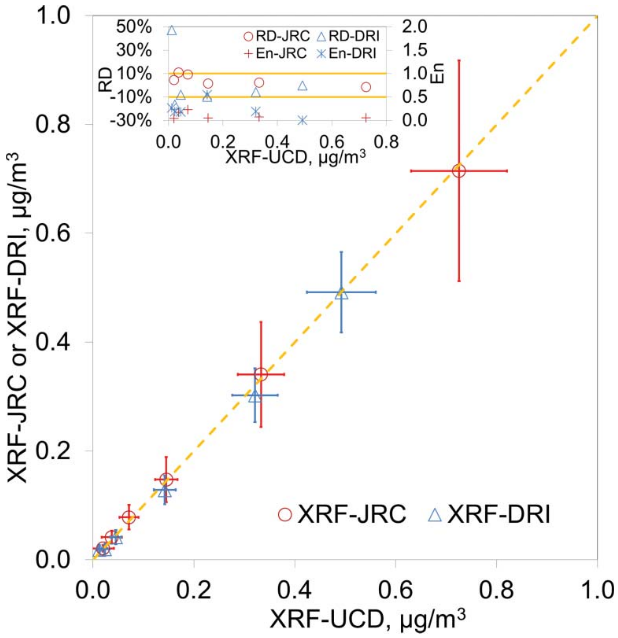

Figure 5. Comparison of XRF-UCD to XRF-DRI and XRF-JRC. Error bars represent expanded uncertainty estimated by GUM. The linear regressions (with 95% confidence levels for the slope and intercept) between XRF-UCD and XRF-JRC and between XRF-UCD and XRF-DRI are $y = (0.98 \pm 0.01)\ x + (0.006 \pm 0.003)$, $R^2 = 0.999$, and $y = (0.99 \pm 0.02)\ x - (0.004 \pm 0.006)$, $R^2 = 0.998$, respectively. The inner graph shows the relative difference (RD) and E_n for both methods. The range of samples is 0.026–1.116 μg/cm^2 (x-axis). These were converted to μg/m^3 using 11.86 cm^2 deposition area and 24 m^3 air volume.

Micromatter standards which are much higher than the measured mass loadings and are dissimilar in filter materials and sample matrix, never the less provide excellent measurement of low loadings of particulate Pb collected on Teflon filters. However, as part of this study, we generate multiple RMs in the mass loading range that spans the IMPROVE sample Pb loading to be used as calibration standards to provide precise Pb measurements, improve credibility of the Pb measurements and document the traceability of the RMs for the IMPROVE program, similar to our the work done for IMPROVE sulfur standards (Indresand et al. 2013). The linear regressions between XRF-UCD and XRF-JRC and between XRF-UCD and XRF-DRI are shown in Figure 5. The inner graph shows the relative difference and E_n number of the measurements. Nevertheless, the relative difference of XRF-JRC was equal to or below 10% except one RM (11%, XRF-UCD Pb = 0.0374 μg/m^3). The relative difference of XRF-DRI was equal to or below 10% except the two lowest Teflo-RMs (XRF-UCD Pb = 0.0126 and 0.0239 μg/m^3). The between XRF-JRC and XRF-UCD precision and bias calculated following the US methodology were 6 and 9%, respectively, which are lower than criteria. The precision and bias calculated between XRF-DRI and XRF-UCD were 25% and 30%, respectively. However, when the lowest RM is excluded, the precision and bias became 9% and 15%, respectively, which meet the criteria. All the XRF-JRC and XRF-DRI E_n numbers are well below 1. Both relative difference and E_n showed random variations at Pb lower than 0.05 μg/m^3. At Pb concentrations higher than that, relative difference and E_n decrease with increasing Pb concentrations indicating that the differences between methods are close to zero at high Pb loadings.

The results show that Pb-RMs can be generated on Teflon filters and accurately measured by XRF-UCD as verified by XRF-DRI and XRF-JRC above 0.05 μg/m^3. The precision, bias and E_n showed that XRF-JRC and XRF-DRI are both equivalent to XRF-UCD at Pb concentrations higher than 0.05 μg/m^3. XRF-UCD and XRF-JRC agreed well at Pb lower than 0.05 μg/m^3, but not XRF-UCD and XRF-DRI, and none of RMs analyzed by XRF-UCD and ICP-MS was below 0.05 μg/m^3 to

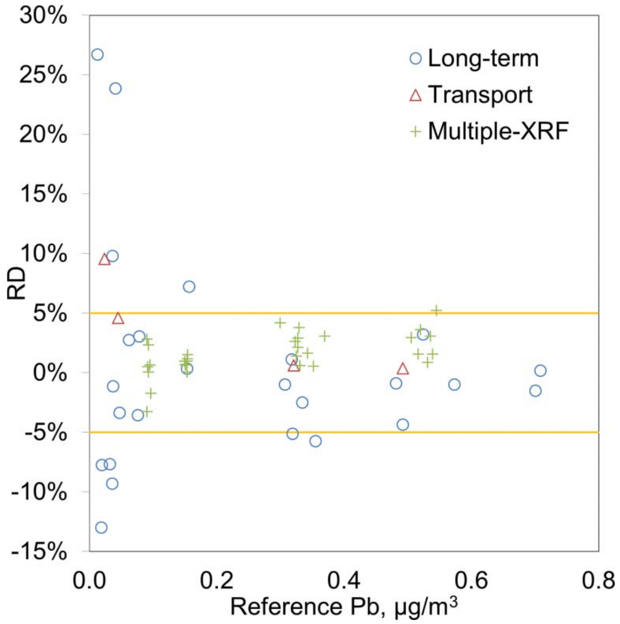

Figure 6. The RD [(Reanalysis-Reference)/Reference] of RMs tested for long-term stability (Long-term), short-term stability after transport (Transport) and short-term stability after multiple times XRF analysis (Multiple-XRF). The long-term RD of the lowest RM (0.013 μg/m^3, 96%) was excluded for better resolution on the graph. The range of samples is 0.026–1.434 μg/cm^2 (x-axis). These were converted to μg/m^3 using 11.86 cm^2 deposition area and 24 m^3 air volume.

check the agreement between two methods. Therefore, more tests are needed with RMs below 0.05 μg/m^3 to check the equivalency between ICP-MS and XRF-UCD as well as between XRF laboratories at these very low levels.

Stability of the RMs

Figure 6 shows the results of long-term and short-term (transport and multiple XRF analyses) stability tests. For the short-term stability due to transport, the relative difference is less than ±5% except for lowest RMs which have Pb concentrations at approximately 0.0125 and 0.025 μg/m^3. The relative difference of the lowest two RMs (96 and 10%, respectively) are still lower than the relative expanded uncertainties of XRF-UCD, which are 177 and 88%, respectively, indicating that the variations in XRF-UCD of the lowest two RMs are within measurement uncertainty. The relative difference of MTL-RM subset analyzed using two XRF analyzers with three replicates was below 5% for all RMs.

The mean and standard deviation of the absolute relative differences of RMs analyzed for long-term stability was found to be 5 ± 6%, ranging between 0 and 27% (Figure 6). For Pb higher than 0.05 μg/m^3, the relative difference are less than or equal to 5% with only two exceptions, which are close to 5% (6 and 7%). For Pb concentrations less than 0.05 μg/m^3, the relative difference is still considerably smaller than the relative expanded uncertainty of XRF-UCD.

Thus, the stability of the RMs, particularly Pb higher than 0.05 μg/m^3, is established.

Conclusion

We have developed a method for generating Pb reference materials at targeted concentrations for multiple purposes including the evaluation of Federal Equivalency Method by the US EPA, laboratory audits for Pb Monitoring Network by EPA, and calibration/quality check of EDXRF analysis used by IMPROVE. Low mass level reference materials are needed by EPA due to the revised NAAQS level for Pb and by IMPROVE due to the low levels of Pb found in atmospheric particulate matter in rural and pristine areas. The reference materials generated ranged in concentrations (using volumes equivalent to 24-hour sampling) between 0.0125 and 0.70 μg/m^3. The methodologies described in the US, EU and international documents were followed to show the equivalency of the XRF analysis at UC Davis to ICP-MS and establish XRF analysis at UC Davis as a reference method for analyzing Pb reference materials. Three other XRF laboratories verified the Pb reference masses over 0.05 μg/m^3 by showing equivalency to the XRF method at UC Davis. The generated reference materials were also demonstrated to be stable over the short-term and long-term, indicating that storage in refrigerator, transport between laboratories and analyzing multiple times in EDXRF instruments do not alter the Pb concentrations. We were therefore able to produce stable and accurately quantified low concentration Pb reference materials for use by EPA and IMPROVE.

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