An interlaboratory comparison study on the measurement of elements in PM$_{10}$

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**Highlights**

- Interlab comparison of XRF and ICP-MS labs was conducted to measure elements in PM$_{10}$.
- XRF labs are comparable for S, K, Ti, Mn, Fe, Cu, Br, Sr and Pb.
- ICP-MS confirmed XRF-interlab comparability of Al, K, Ca, Ti, V, Fe, Cu, Sr and Pb.
- ICP-MS results are inconsistent with the XRF laboratories for Fe and Zn.

**Abstract**

An inter-laboratory comparison study was conducted to measure elemental loadings on PM$_{10}$ samples, collected in Ispra, a regional background/rural site in Italy, using three different XRF (X-ray Fluorescence) methods, namely Epsilon 5 by linear calibration, Quant’X by the standardless analysis, and PIXE (Particle Induced X-ray Emission) with linear calibration. A subset of samples was also analyzed by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). Several metrics including method detection limits (MDLs), precision, bias from a NIST standard reference material (SRM 2783) quoted values, relative absolute difference, orthogonal regression and the ratio of the absolute difference between the methods to claimed uncertainty were used to compare the laboratories. The MDLs were found to be comparable for many elements. Precision estimates were less than 10% for the majority of the elements. Absolute biases from SRM 2783 remained less than 20% for the majority of certified elements. The regression results of PM$_{10}$ samples showed that the three XRF laboratories measured very similar mass loadings for S, K, Ti, Mn, Fe, Cu, Br, Sr and Pb with slopes within 20% of unity. The ICP-MS results confirmed the agreement and discrepancies between XRF laboratories for Al, K, Ca, Ti, V, Fe, Cu, Sr and Pb. The ICP-MS results are inconsistent with the XRF laboratories for Fe and Zn. The absolute differences between the XRF laboratories generally remained within their claimed uncertainties, showing a pattern generally consistent with the orthogonal regression results.

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1. Introduction

X-ray based analytical techniques (e.g., Energy Dispersive X-ray Fluorescence Spectroscopy, EDXRF and Particle Induced X-ray Emission, PIXE) have been employed for many years to determine the concentration of elements in particulate matter (PM) (IMPROVE program, CSN program). X-ray analysis is faster, cleaner (with no or low sample contamination) and usually cheaper than wet analytical techniques because it does not require any sample pretreatment for air filters. Unlike wet analytical techniques, X-ray analysis does not involve destruction of the samples being analyzed. This is one of its major advantages allowing the further determination of additional components in the same sample. Typically, the measurement of elemental mass loadings on PM samples...
using X-ray analyzers involves establishing a linear relationship between X-ray intensities and a set of calibration standards at a range of loadings (linear calibration). These standards are generally single element/compound thin films produced by Micromatter (Vancouver, Canada). XRF laboratories generally check their calibration with the NIST SRM 2783 (PM2.5 on polycarbonate filter), which is a multi-element standard reference material with loadings representative of ambient air levels.

As an alternative to repeated linear calibrations using these standards, EDXRF can also be operated in standardless mode, which is expected to be sample matrix and loading independent. The standardless EDXRF analysis is based on the initial calibration with pure element standards and further deconvolution of spectra that allows the determination of all elements in any sample matrix. It was demonstrated that standardless EDXRF analysis, namely UniQuant (v. 6.09), is comparable to inductively coupled plasma-mass spectrometry (ICP-MS) for the determination of many PM-bound elements (Yatkin et al., 2012). Hurst et al. (2011) compared EDXRF (PANalytical, The Netherlands) results of elements in welding fumes by linear calibration using custom made single element standards produced using dust generator to results obtained by standardless analysis software (UniQuant, v. 4.54). They found comparable results (relative difference between two methods being lower than 15%) for Ni, Mn, Cr and Fe. Okuda et al. (2015) compared the magnetic sector ICP-MS and EDXRF (EDXL300 by Rigaku, Japan) with the standardless quantification method on the analysis of elements in PM2.5, collected from diesel exhaust. They reported good agreement on the measurements of Mg, Si, Ca, Fe, Ni, Cu, Zn, Ce and Pt; mean ratios of the results of these methods remained between 80 and 120%.

Several inter-laboratory comparisons have been carried out to check the reproducibility of different analytical methods to measure elements in PM samples. Nejedly et al. (1998) performed PIXE and EDXRF measurements of PM-loaded polytetrafluoroethylene (PTFE or Teflon®) filters. They reported good comparability (absolute mean difference between two methods being lower than 10%) for K, Ca, Mn, Fe and Zn, but relatively poor comparability for Si and S. Calzolai et al. (2008) compared PIXE and EDXRF on the reported loadings (linear calibration). These standards are generally simple of ambient air levels.

The objective of the present study is to compare the XRF results of lightly-loaded PM10 samples on PTFE filters from three laboratories: 1) Crocker Nuclear Laboratory (CNL) at the University of California, Davis operating PANalytical Epsilon 5 analyzers (Almelo, Netherlands) with linear calibration (hereafter referred to as ES), 2) The European Reference Laboratory for Air Pollution of the European Commission Joint Research Centre operating ARL QuanT'X with the standardless quantification method (hereafter referred to as UQ) and 3) Istituto Nazionale di Fisica Nucleare -Laboratorio BEni Culturali (INFN-LABEC) operating PIXE with linear calibration (hereafter referred to as PIXE). Method detection limits (MDLs), precision, bias from SRM 2783, orthogonal regression and the ratio of the absolute difference between the methods to claimed uncertainty were utilized to compare the results from the three XRF laboratories. A randomly selected subset of samples was also analyzed by an ICP-MS laboratory, known to be a reliable analytical technique for high Z elements.

2. Materials and methods

2.1. Sampling and weighing

The samples used for this test were collected in the regional background-rural site of Ispra in Italy (Belis et al., 2012). A total of 60 PM10 samples were included in the study. The PM10 samples were collected every 6 days from January to December of 2012 for 24 h on PTFE filters ( Pall Corporation, USA, model: Teflo R2PJ047) using a Hydra double line PM sampler (FAI-Instruments, Italy) according to EN 12341, European Standard (1998), which prescribes a 2.3 m3/h sampling flow.

As prescribed in EN 12341 and EN 14907, European Standard (2005), the PM10 samples and blank filters were conditioned for at least 2 days prior to weighing under stable environmental conditions, at 50% relative humidity and 20°C. The filters were weighed using a microbalance with 1-μg resolution (Mettler Toledo, Switzerland) following the procedure of EN 14907. The balance was calibrated yearly using mass standards (class-E1, from Mettler Toledo, Switzerland) and drift checks were performed with standard weights (class-E2 from Mettler Toledo, Switzerland) before any weighing.

The diameter of the deposition area on the 47 mm filter was measured with a caliper, and an average deposition area of 11.64 cm2 was calculated.

The PM10 concentrations varied from 2.3 to 113.5 μg/m3 (mean ± s = 22.6 ± 19.7 μg/m3, s: standard deviation, median = 14.6 μg/m3). Only 8% of the samples exceeded the EU limit value (50 μg/m3) while 63% and 20% of the samples were lower than 20 and 10 μg/m3, respectively. The samples were first analyzed by JRC (UQ), followed by CNL (ES) and LABEC (PIXE). The randomly selected subset (n = 30) to be analyzed by ICP-MS represents well the entire data set with the same range (mean ± s = 28.8 ± 28.2 μg/m3, median = 15.8 μg/m3). 57% and 22% of the samples were lower than 20 and 10 μg/m3, respectively, while 22% were higher than 50 μg/m3.

2.2. Epsilon 5 setup and calibration

The E5 analyzer incorporates a 3-dimensional polarizing optical geometry, together with a side-window 600 Watt dual anode (Sc/W) X-ray tube and 1000 kV generator, up to 15 secondary and polarizing targets and a high-resolution liquid nitrogen cooled solid state Ge detector (PAN-32). The samples were analyzed under vacuum with spinning. All the elements were detected and quantified by their Kα lines except Pb which was analyzed by its Lβ line. The system is calibrated annually using Micromatter thin film reference materials, NIST SRM 2873 certified reference material and custom made certified reference materials for Na, Cl and S. The analytical conditions, details of calibration and quality control measures are given elsewhere (CNL-SOP, 2014; Supplementary Information 1-SI1). The elemental mass, cE5 (μg/filter), of any given element on each filter was calculated using Eq. (1).
where, $b_{cal}$ is the calibration factor \((\text{cps/mA})/(\mu g/cm^2))\) calculated as the slope of the linear regression between elemental loadings of calibration standards and their blank subtracted (net) intensities \(\text{INT}_{\text{net}}\) \((\text{counts/s})\). $I_{0}$ is the net intensity of XRF X-rays emitted by the sample \((\text{cps/mA})\), $b_{lb}$ is the net intensity of a blank filter \((\text{cps/mA})\), and $A_{d}$ is the PM deposition area on the filter \((cm^2)\). The same blank intensity was used to correct all the sample intensities. Since the calibration intercepts were found to be insignificant, they were not included in the calculations of loadings.

2.3. Quant’X setup and standardless analysis

The ARL Quant’X spectrometer 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 \((15 \text{mm}^2 \text{ crystal area, 3.5 mm crystal depth and 155 eV resolution})\), and a pulse processor \((32 \text{ bit digital type, 20 eV channels, 1–40 ms adjustable shaping time, up to 10,000 cps live count rate and 400–40,960 eV energy range})\). 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. Each sample was analyzed two times under vacuum. The analytical conditions, details of calibration and quality control measures are given in SI1.

UniQuant software (version 6.09) was used to interpret the ARL Quant’X XRF spectra. The concept of “standardless” analysis was applied. The instrumental sensitivities were derived as a function of net intensity to elemental mass ratio \((\text{intensity/mass, cps/0.1 mg element})\) and elemental mass fraction \((\text{elemental mass/total mass, % or ppm})\), and they are constant and sample independent (see http://www.uniquant.com/pdf/UQSHandbook.pdf). In this method, matrix effect calculation using a fundamental parameters algorithm to solve the Sherman equation \((\text{intensities})\) (Sherman, 1955) and instrumental sensitivity determined by measuring one set of single elements standards from Micromatter \((\text{relationship between intensity and elemental mass})\) are combined to analyze any sample. The details of the standardless analysis methodology are given in Yatkin et al., 2012 and SI1. Elemental masses on each filter, $c_{UQ}$ \((\mu g/\text{filter})\), are calculated using Eq. (2), where $I$ is the drift corrected fluorescence intensity \((\text{counts/s, cps})\) and $b_{lb}$ is the interference and drift corrected background modeled by UniQuant utilizing filter type for sampling \((\text{cps})\). $\mu$ is the mass absorption coefficient of any measured element \((cm^2/\mu g)\). $W$ is the weight factor of oxides assuming that all elements exist at the highest oxidation states \((\text{calculated from stoichiometry})\). $K$ is the instrumental sensitivity \((\text{ratio of counts to mass of element i, cps/\mu g})\) determined using thin film standards of pure elements from Micromatter \((\text{Initial calibration})\). $A_{d}$ is the excited area \((cm^2)\) of the filter to which the sample was deposited. The ARL Quant’X spectrometer 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 \((15 \text{mm}^2 \text{ crystal area, 3.5 mm crystal depth and 155 eV resolution})\), and a pulse processor \((32 \text{ bit digital type, 20 eV channels, 1–40 ms adjustable shaping time, up to 10,000 cps live count rate and 400–40,960 eV energy range})\). 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. Each sample was analyzed two times under vacuum. The analytical conditions, details of calibration and quality control measures are given in SI1.

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The first part in the square brackets is the standard equation of the software used to calculate the elemental mass ratio \((\text{mass of element in the excited area}/\text{total mass in the excited area})\) of any given sample. For ambient PM samples, the elemental mass ratios are multiplied by $A_{d}/A$ and $m_{PM}$ to be converted to the total mass of each element loaded on each filter, assuming even distribution of the PM on the filter and the absence of PM evaporation in the measuring chamber.

2.4. PIXE

At the INFN-LABEC laboratory in Florence, equipped with a 3 MV Tandetron accelerator, an external beam line is fully dedicated to the analysis of aerosol samples. A comprehensive description of the set-up is reported in Lucarelli et al. (2014). Briefly, samples were bombarded by a 2 mm² 3 MeV proton beam that is extracted in air through a thin \((500 \text{ nm})\) Si$_{3}$N$_{4}$ window. Three different detectors are used to detect the elements with $Z > 10$. Low-energy X-rays \((\text{from 1 keV up to 8 keV})\) are detected by a SDD (Silicon Drift Detector) with 10 mm² sensitive area and 300 $\mu m$ thickness equipped with a magnetic proton deflector. X-rays of very low energies, down to 1 keV \((\text{Na Kα line})\) are used to detect the lighter elements through an ultra-thin entrance window \((8 \mu m \text{ beryllium})\) purged with helium gas. An array of two KETEK GmbH SDDs, with 113 mm² area and 450 $\mu m$ thickness, shielded by 450 $\mu m$ Mylar foils, detect X-rays in the range \(3–20 \text{ keV}\). With currents on the order of 100 nA, measurements lasted only 120 s for each sample, \((\text{which is one order of magnitude shorter than the other two XRF analyzers})\).

The acquired spectra are fitted by means of the GUPIX software (Campbell et al., 2010) and elemental mass \((\mu g/\text{filter})\) is calculated using Eq. (3):

\[
c_{\text{PIXE}} = \frac{Y}{b_{cal} \cdot Q} \cdot A_{d}
\]

where $Y$ is the number of the collected X-rays emitted by the element of interest \((\text{counts})\), $Q$ is the integrated beam charge \((\mu C)\), $A_{d}$ is the sample deposition area and $b_{cal}$ is a linear calibration factor \((\text{counts}/(\mu C \cdot \mu g/cm^2))\) obtained by measuring a set of thin film standards \((\text{Micromatter Inc.})\).

2.5. ICP-MS

Filters were extracted using 8 ml ultrapure HNO$_3$ \((69\%, \text{Romil-UpA, UK})\), 2 ml ultrapure H$_2$O$_2$ \((30\%, \text{Romil-UpA, UK})\) and 0.5 ml ultrapure HF \((51\%, \text{Romil-UpA, UK})\) in a microwave oven \((\text{Milestone Labstation Ethos 900, Italy})\) to be analyzed by ICP-MS \((\text{Agilent 7500ce, Japan})\). The details of the ICP-MS method are given in SI1.

2.6. Data evaluation

The method detection limits \((\text{MDLs})\) were initially computed and compared among the three laboratories. The E5 MDLs were calculated as three times the standard deviation of the unused laboratory blanks \((n = 6)\). The MDLs for UQ and PIXE were calculated as three times the standard deviation of the underlying background of each analyzed sample, and then they were converted to loadings using Eqs. (2) and (3), respectively. Then, they were averaged to calculate the MDLs of UQ and PIXE. The precision \((\text{relative standard deviation of multiple analysis, RSD})\) of the E5 and UQ was determined by analyzing three times each a low \((\text{PM mass less than 0.5 mg})\), a medium \((\text{PM between 1 and 2 mg})\) and a high \((\text{PM higher than 4 mg})\) loaded filter. The precision of PIXE was checked by measuring the NIST SRM 2783 more than once during every measurement.

All XRF laboratories analyzed NIST SRM 2783 on a routine basis. The bias from the NIST SRM 2783 were calculated and compared. The laboratory blanks and field blanks were also analyzed. No contamination was measured on the field blanks.

Three methods were used to evaluate comparability of laboratories. One method is linear regression and its associated slope,
measurement of As, Cd, Ni and Pb in PM10 and PM2.5 samples) in a data method to a reference one (GF-AAS and ICP-MS for measurement uncertainty of a candidate method properly and then to confirm the uncertainty with a set of measurements against a reference method. The relative expanded uncertainty of UQ was pre-}

\[ E_n = \frac{|C_{ES} - C_{lab}|}{\sqrt{U_{C_{ES}}^2 + U_{C_{lab}}^2}} \]  

where, \( C_{lab} \) is the loading from UQ or PIXE; \( U_{C_{ES}} \) and \( U_{C_{lab}} \) are the expanded uncertainties of E5 and other laboratories. Although the \( E_n \) value represents a method to compare a candidate method to a reference one (GF-AAS and ICP-MS for measurement of As, Cd, Ni and Pb in PM10 and PM2.5 samples) in European directives (Directive, 2004/107/EC of the European Parliament, 2004; and Directive, 2008/50/EC of the European Parliament, 2008), the methodology can still be used to compare two measurement methods. When the criterion (\( E_n \leq 1 \)) is met, the differences between the laboratories are within the measurement uncertainties.

The relative expanded uncertainties (\( U_r = U_{lab}/C_{lab} \)) of the E5 and UQ measurements were estimated following the GUM method (Evaluation of measurement data-Guide to the expression of uncertainty in measurement, 2008). The details are described in the Supplementary Information 2. The expanded uncertainty of PIXE was estimated including the statistical counting and peak fitting errors of GUPIX software as well as the uncertainty of the calibration standards. In this study, the \( U_r \) from three XRF laboratories was also reported to compare between them.

The critical step of the \( E_n \) methodology is to estimate the measurement uncertainty of a candidate method properly and then to confirm the uncertainty with a set of measurements against a reference method. The relative expanded uncertainty of UQ was previously confirmed against ICP-MS (Yatkin et al., 2012). E5 measure-

The comparison of MDLs with the mean of loadings from three XRF laboratories for samples with concentrations higher than their MDLs is shown in Fig. 1. The E5 MDL for S was computed to be 0, since the intensities of S on blanks were all 0. The general variations in MDLs of the three XRF laboratories are similar, being higher for low Z elements and Ba. The PIXE MDLs for low Z elements are lower than those for the EDXRF laboratories. The PIXE MDLs for elements between K and V are higher than EDXRFs while they are lower between Mn and Zn. The mean loadings of each element are well above than the MDLs except for Ba.

The biases from certified values of SRM 2783 (mean ± s) are illustrated in Fig. 2. The mean biases of the three XRF laboratories are lower than 20% for Al, Si, S (not for E5), K, Ca, Ti, Cr (not for PIXE), Mn, Fe, Ni (not for UQ), Cu and Pb. For Zn and Mg, the absolute bias for PIXE and E5 exceeded 20%. PIXE and UQ were positively biased and E5 was negatively biased for V, with the bias exceeding 20%.

The precision of the three XRF laboratories was lower than 10% with the exception of lightly loaded PM_{2.5} samples (for E5 and UQ). The precision improves with increasing loadings.

3.2. Comparison of results

The basic statistics of the results with the relative expanded uncertainties (\( U_r \)) at the mean loadings measured by the three XRF laboratories are given in Table 1. Three XRF laboratories met the ARD criterion (<20%) at least for 2/3 of samples for S, K, Fe, Zn, Br and Sr, which can be assessed in good agreement. In addition to those elements, E5 and PIXE met criterion for Cr, Mn, Cu and Pb, which two laboratories are most likely in good agreement. Cl, Ti, Ca and V were only met by E5 or PIXE, which the laboratories is most likely not in good agreement.

The \( U_r \) of three laboratories varied between 11 and 152%, which \( U_r \) decreased with loadings. The \( U_r \)-UQs are generally higher than the others except Ni and Pb that can be attributed to the higher
number of factors contributing to uncertainty for UQ than for the others.

The slopes of orthogonal regression between E5 and UQ and E5 and PIXE for the samples with loadings higher than the MDLs are plotted in Fig. 3, along with the uncertainty of the slopes (for equations, see European Commission, Jan 2010, Annex B). The individual regression plots of other elements are given in SI, Fig. S1. The slopes between UQ and PIXE are given in SI, Fig. S3.

The three XRF laboratories were in good agreement for S, K, Fe, Zn, Br, Sr, Ti, Mn, Cu, and Pb, which the first six are consistent with the ARD results. Good agreement was also reported between XRF laboratories for S, K, Fe and Zn (Nejedly et al., 1998; Calzolai et al., 2008; Kang et al., 2014). For Mn, Cu and Pb, ARD of UQ did not meet the criterion, but slope and R² did, thus UQ can be assessed in good agreement with E5 and PIXE. In addition to those elements, E5 and PIXE agreed well for Si and Ca, E5 and UQ agreed well for Cr and UQ and PIXE agreed well for Al.

Very strong association (R² > 0.97) with relatively poor agreement for Al and Si (slopes around 0.65) between E5 and UQ indicates that one of the two laboratories is biased. The Al and Si intercepts are significant, 2343 and −3108 ng/filter corresponding to 38% and −25% of the median of E5 and UQ, respectively (See Fig. S2). As seen in Fig. 2, the absolute differences between the SRM biases of the UQ and E5 for Al and Si were about 25% and 15%, respectively. The Al and Si differences between the two laboratories are higher for PM10 samples than for the SRM 2783. The Al and Si associations between E5 and PIXE are excellent (R² = 1.0) with slopes of 0.71 and 0.87, respectively, and with very low intercepts (203 and 948 ng/filter corresponding to 4% and 8% of the median of E5 and PIXE, respectively). The absolute differences between the SRM biases of the E5 and PIXE for Al and Si are about 20% and 5%, respectively, which were higher than the difference in the slopes above.

A linear calibration was also applied to the Quant’X spectra to investigate the origin of the Al bias between the E5 and UQ. The details of this methodology are given in SI4. Quant’X with linear calibration (hereafter Quant’X-Linear) and E5 agreed very well (see Fig. 4A–Al), showing that the bias between Epsilon 5 and Quant’X was caused by the different calibration methods (linear and standardless). That is likely the case for Si, too. The researchers reported Si slopes between XRF laboratories remaining within 20% of unity with scattered plots at low loadings (Nejedly et al., 1998;
Calzolai et al., 2008; Kang et al., 2014). For Al, Calzolai et al. (2008) reported good agreement. Kang et al. (2014) reported mean Al values form three XRF laboratories being in significant agreement, but, plots are scattered with slopes higher than 20% of the unity. These results showed that agreement between XRF laboratories could be variable for Al and Si, most likely resulted from loadings and different set up.

E5 and UQ associated very well (\(R^2 = 0.98\)) but with relatively poor agreement for Ca (slope = 0.78, intercept = -2064 ng/filter). The relative difference between the two laboratories on the bias from the SRM is \(\sim 35\%\) (see Fig. 2), which is higher than the slope above. Quant’X-Linear and E5 were in good agreement for Ca (slope = 0.85, \(R^2 = 1.0\), see Fig. 4S–Ca), which is similar to the slopes between E5 and UQ and between Quant’X-linear and ICP-MS (see SI4). Hence, it can be concluded that the UQ quantification shows a bias of around \(-15\%\) compared to ICP-MS and around \(-25\%\) compared to the E5, the latter of which is similar to the ones for Al and Si. The agreement between E5 and PIXE on Ca is good. The absolute difference between the SRM Ca-bias for the E5 and PIXE was around 17% (see Fig. 2), which is very consistent with the slope between the two laboratories (0.86). The good agreement for Ca has been previously reported (Nejedly et al., 1998; Calzolai et al., 2008; Kang et al., 2014).

E5 vs. UQ are in good agreement for Ti with relatively poor association (\(R^2 = 0.80\)) and 0.79 (\(R^2 = 0.86\)). The scattering between the two laboratories likely indicates random variability. In the PM10 samples collected in 2011 in Isprva \(n = 38\), Ba, for which the L lines interfere with Ti K\(α\), was found to be at high concentrations measured by the ICP-MS (unpublished results). In these samples, Ti measured by UQ was around 20% higher than that measured by ICP-MS. These results suggest that the UQ may have overestimated Ti due to unaccounted for Ba L interference. In addition, the good agreement between E5 and PIXE (slope = 0.80) with excellent association (\(R^2 = 0.98\)) in samples and in the SRM 2783 supports the possibility of Ba interference to Ti. Similar to the SRM 2783 bias (see Fig. 2), the agreement between the three XRF laboratories on V is relatively poor, likely arising from the low loadings. The Cr slopes of E5 vs. UQ and E5 vs. PIXE for only 16 samples are 0.97 (\(R^2 = 0.91\)) and 1.28 (\(R^2 = 0.92\)) with significant intercepts (See Fig. S2), the latter of which is consistent with the SRM-biases. It is likely that better agreement could be observed with samples at high loadings of Cr and V.

The Ni slopes of E5 vs. UQ and E5 vs. PIXE are 1.23 (\(R^2 = 0.90\)) and 1.01 (\(R^2 = 0.67\)), which are consistent with the SRM-biases. In fact, when two samples with Ni over 240 ng/filter are excluded, the E5 vs PIXE slope becomes 0.77 (\(R^2 = 0.94\)). It is likely that the samples at high loadings could yield better agreement between the XRF laboratories.

The Cl slopes of E5 vs. UQ and E5 vs. PIXE are 1.32 (\(R^2 = 0.94\)) and 0.40 (\(R^2 = 0.74\)), respectively. In fact, when the samples with Cl over 10,000 ng/filter \(n = 6\) are excluded, the slope between E5 and PIXE becomes 0.89 (\(R^2 = 0.95\)). Relatively scattered patterns over the identity line also indicate the presence of random variability between the three XRF laboratories (see Cl plot in

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**Fig. 3.** The slopes of orthogonal regression between E5 and UQ and between E5 and PIXE. The colors of the marker borders indicate the \(R^2\) values given by the color scale at the up-right corner. Error bars represent uncertainty of slopes. Mg-slope of E5 vs UQ (1.82) and Cl of E5 vs PIXE (0.40) were replaced by 1.4 and 0.6, respectively, to achieve better resolution on the plot. Ba-slope of E5 vs UQ is not significant. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 4.** The slopes of orthogonal regression between ICP-MS and three XRF laboratories. The colors of the marker borders indicate the \(R^2\) values given by the color scale at the up-right corner. It should be noted that Cr slopes higher than 2 were replaced by 2 to achieve better resolution on the plot. Error bars represent uncertainty of slopes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
The Pb slopes of ICP-MS vs. E5, vs. UQ and vs. PIXE are 0.64 between XRF laboratories as well as bias in the ICP-MS quantification. Poor association between ICP-MS and XRF laboratories confirmed the majority of the above elements except Pb for E5 and Sr for UQ. Good Fe and Zn agreements between the XRF laboratories but disagreement with ICP-MS suggest a bias in the ICP-MS method. Quant’X with standardless analysis is biased from the other XRF laboratories for Al, Si, Ti and Ca. The disagreement between ICP-MS and the XRF laboratories’ slopes. The Cr and Ni slopes are above 2.3 and lower than 0.5, respectively, except Ni for ICP-MS vs. UQ (0.77) with poor association (R^2 = 0.52). The Fe slopes are higher than 1 with high R^2 and relatively high intercept (~2500 ng/filter) corresponding to ~20% of the median. Exclusion two samples with the highest Fe loadings yielded better correlations with slopes within 20% of unity, high R^2 and relatively high intercept (~1300 ng/filter corresponding to ~10% of the median). Similar to Zn, three XRF laboratories were in good agreement for this subset with excellent association (R^2 > 0.99). These results show good Fe agreement between XRF laboratories as well as bias in the ICP-MS quantification. The Pb slopes of ICP-MS vs. E5, vs. UQ and vs. PIXE are 0.64 (R^2 = 0.81), 0.96 (R^2 = 0.90) and 0.84 (R^2 = 0.91), respectively, which are somewhat consistent between XRF laboratories’ slopes, except with the slope of E5 being too low. Excluding two samples yielded better agreement between ICP-MS and E5 (slope = 0.78, R^2 = 0.95). The Sr slopes of ICP-MS vs. PIXE and vs. E5 are within 20% of unity whereas the UQ slope (1.21) slightly exceeds this range.

In the literature, there are few studies reporting comparison between XRF and ICP-MS on the atmospheric aerosol samples. Niu et al. (2010) reported comparable results from EDXRF and ICP-MS for Fe, Mn, Cu, Zn and Pb, which are similar with the findings of this study except Zn. Okuda et al. (2015) reported comparable EDXRF and ICP-MS results on the diesel exhaust samples for Mg, S, Ca, Fe, Ni, Cu, and Zn. Interlaboratory comparison between ICP-MS and XRF may vary depending on the loadings and level of contamination during sample preparation for ICP-MS.

The mean E_n numbers for E5 vs. UQ and E5 vs. PIXE for the elements quantified by the three XRF laboratories are given in Fig. 5 (See Fig. S6 for mean E_n of UQ vs. PIXE). The mean E_n numbers remained below the acceptability threshold (E_n ≤ 1) for all elements with the exception of Mg for E5 vs. UQ and E5 vs. PIXE, and Si, Ca and Ni for only E5 vs. UQ. The samples with E_n exceeding the threshold are less than 30% for the above elements, and for Al and Zn for E5 vs. UQ. The low numbers of samples exceeding the threshold for V, Cr and Ba are mainly associated with the low loadings and high uncertainty of these elements on the studied samples. For all elements, E_n increased with the decreasing loadings, which is likely due to the higher uncertainties for concentrations near the MDLs.

4. Summary and conclusion

Elemental determinations from three X-ray laboratories were compared for NIST SRM 2783 reference material and PM_{10} samples. A subset of PM_{10} samples were also analyzed by an ICP-MS laboratory. The comparison of between-laboratories for SRM 2783 and PM_{10} samples is summarized in Table 2.

The precisions of the three XRF laboratories are good, being lower than 10% for the majority of the elements. The XRF laboratories are in good agreement when measuring S, K, Ti, Mn, Fe, Cu, Br, Sr and Pb in PM_{10} (Table 2). The three XRF laboratories are also in good agreement for Cl with few exceptions, most likely due to evaporation. The comparison between ICP-MS and the XRF laboratories confirmed the majority of the above elements except Pb for E5 and Sr for UQ. Good Fe and Zn agreements between the XRF laboratories but disagreement with ICP-MS suggest a bias in the ICP-MS method. Quant’X with standardless analysis is biased from the other XRF laboratories for Al, Si, Ti and Ca. The disagreements in trace elements (e.g. V, Cr and Ni) resulted from low loadings; higher loadings are likely to yield good agreement. The absolute differences between three XRF laboratories mainly remained...
within their claimed uncertainties for the majority of the quantified elements. As the overall result of this study, X-ray laboratories with different analyzers, setups, and quantification methods could measure comparable loadings in low loaded PM10 samples collected on PTFE filters.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.10.084.

References


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