

Contents lists available at ScienceDirect

# Atmospheric Environment



journal homepage: www.elsevier.com/locate/atmosenv

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



Sinan Yatkin<sup>a,\*</sup>, Claudio A. Belis<sup>b</sup>, Michel Gerboles<sup>b</sup>, Giulia Calzolai<sup>c</sup>, Franco Lucarelli<sup>c</sup>, Fabrizia Cavalli<sup>b</sup>, Krystyna Trzepla<sup>a</sup>

<sup>a</sup> Crocker Nuclear Laboratory, University of California, Davis, CA 95616, USA

<sup>b</sup> European Commission, Joint Research Centre, Institute for Environment and Sustainability, Via Enrico Fermi 2749, 21027 Ispra (VA), Italy <sup>c</sup> Dept. of Physics and Astronomy, University of Florence and National Institute of Nuclear Physics (INFN)- Florence, V. G. Sansone 1, 50019 Sesto Fiorentino

(FI), Italy

# HIGHLIGHTS

• Interlab comparison of XRF and ICP-MS labs was conducted to measure elements in PM<sub>10</sub>.

• 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.

# ARTICLE INFO

Article history: Received 24 June 2015 Received in revised form 26 October 2015 Accepted 28 October 2015 Available online 2 November 2015

Keywords: Inter-laboratory comparison XRF ICP-MS Standardless PM<sub>10</sub>

# ABSTRACT

An inter-laboratory comparison study was conducted to measure elemental loadings on PM<sub>10</sub> 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<sub>10</sub> 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, 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.

© 2015 Elsevier Ltd. All rights reserved.

# 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

E-mail address: syatkin@ucdavis.edu (S. Yatkin).

http://dx.doi.org/10.1016/j.atmosenv.2015.10.084 1352-2310/© 2015 Elsevier Ltd. All rights reserved. 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

<sup>\*</sup> Corresponding author. Crocker Nuclear Laboratory, UC Davis, Jungerman Hall, One Shields Avenue, Davis, CA 95616, USA.

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 (PM<sub>2.5</sub> 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 only 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 PM<sub>2.5</sub> collected from diesel exhaust. They reported good agreement on the measurements of Mg, S, 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 measurement of loadings in PM<sub>10</sub> and PM<sub>2.5</sub> samples. They reported good comparability (PIXE vs. XRF slopes being 10% different from unity) for Al, Si, S, K, Ca, Fe, Cu and Zn. Gerboles et al. (2011) reported the results of collocated 17 PM<sub>10</sub> samples analyzed by several techniques including EDXRF, ICP-MS and graphite furnace - atomic absorption spectrometry (GF-AAS). They reported that EDXRF measured Cd, Ni, As and Pb comparable to the other techniques. Kang et al. (2014) compared three commercial EDXRF laboratories on low-concentration PM<sub>2.5</sub> samples. They found that the three laboratories measured S, Cl, K, Ca, V, Fe, Ni and Zn comparable with each other, but they did not compare well for Na, Pb, Al, Si, Ti and Cu. Traversi et al. (2014) compared the results obtained on the same PM<sub>10</sub> samples from ICP-AES (Atomic emission spectrometer) and from PIXE. They reported comparable results for Fe, Cu, Pb, Mn, Ni and As from two methods, but they did not compare well for Al, V and Cr.

None of the exercises described above compared XRF results by linear calibration with the ones by the standardless analysis. The objective of the present study is to compare the XRF results of lightly-loaded PM<sub>10</sub> 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 E5), 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 PM<sub>10</sub> samples were included in the study. The PM<sub>10</sub> 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 m<sup>3</sup>/h sampling flow.

As prescribed in EN 12341 and EN 14907, European Standard (2005), the  $PM_{10}$  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, Model AX26) 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  $11.64 \text{ cm}^2$  was calculated.

The PM<sub>10</sub> concentrations varied from 2.3 to 113.5  $\mu$ g/m<sup>3</sup> (mean  $\pm$  s = 22.6  $\pm$  19.7  $\mu$ g/m<sup>3</sup>, s:standard deviation, median = 14.6  $\mu$ g/m<sup>3</sup>). Only 8% of the samples exceeded the EU limit value (50  $\mu$ g/m<sup>3</sup>) while 63% and 20% of the samples were lower than 20 and 10  $\mu$ g/m<sup>3</sup>, respectively. The samples were first analyzed by JRC (UQ), followed by CNL (E5) 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  $\pm$  s = 28.8  $\pm$  28.2  $\mu$ g/m<sup>3</sup>, median = 15.8  $\mu$ g/m<sup>3</sup>). 57% and 22% of the samples were lower than 20 and 10  $\mu$ g/m<sup>3</sup>.

#### 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 100 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 K<sub> $\alpha$ </sub> lines except Pb which was analyzed by its L<sub> $\beta$ </sub> 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, c<sub>E5</sub> (µg/filter), of any given element on each filter was calculated using Eq. (1).

$$c_{E5} = \frac{(I_{net} - I_{blk})}{b_{cal}} \cdot A_d \tag{1}$$

where,  $b_{cal}$  is the calibration factor [(cps/mA)/(µg/cm<sup>2</sup>)] calculated as the slope of the linear regression between elemental loadings of calibration standards and their blank subtracted (net) intensities (the intercept was set to zero), I<sub>net</sub> is the net intensity of XRF Xrays emitted by the sample (cps/mA), I<sub>blk</sub> is the net intensity of a blank filter (cps/mA), and A<sub>d</sub> is the PM deposition area on the filter (cm<sup>2</sup>). 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 mm<sup>2</sup> 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 1,00,000 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 "standarless" analysis was applied. The instrumental sensitivities were derived as a function of net intensity to elemental mass ratio (intensity/mass, cps/0.1 mg element) and elemental mass fraction (elemental mass/total mass, % or ppm), and they are constant and sample independent (see http://www.uniquant.com/pdf/UQ5brochure.pdf). In this method, matrix effect calculation using a fundamental parameters algorithm to solve the Sherman equation (intensities) (Sherman, 1955) and instrumental sensitivity determined by measuring one set of single elements standards from Micromatter (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<sub>110</sub> ( $\mu$ g/filter), are calculated using Eq. (2), where I is the drift corrected fluorescence intensity (counts/s, cps) and I<sub>0</sub> is the interference and drift corrected background modeled by UniQuant utilizing filter type for sampling (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 (calculated from stoichiometry). K is the instrumental sensitivity (ratio of counts to mass of element i,  $cps/\mu g$ ) determined using thin film standards of pure elements from Micromatter (Initial calibration). A is the excited area  $(cm^2)$  of the filter to which the X-ray excitation is applied (no collimator used) while A<sub>d</sub> is the PM deposition area on the filter ( $cm^2$ ).  $m_{PM}$  is the excited PM mass in μg. The software calculates the interference for each measured element, which is unknown to the authors, and the interferences are subtracted to compute the elemental mass as shown in Eq. (2):

$$c_{UQ} = \left[\frac{(I - I_{i0})\mu}{WAK} - \sum Interference\right] \frac{A_d}{A} m_{PM}$$
(2)

The first part in the square brackets is the standard equation of the software used to calculate the elemental mass ratio (mass of element in the excited area/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 mm<sup>2</sup> 3 MeV proton beam that is extracted in air through a thin (500 nm) Si<sub>3</sub>N<sub>4</sub> window. Three different detectors are used to detect the elements with Z > 10. Low-energy X-rays (from 1 keV up to 8 keV) are detected by a SDD (Silicon Drift Detector) with 10 mm<sup>2</sup> sensitive area and 300  $\mu$ m thickness equipped with a magnetic proton deflector. X-rays of very low energies, down to 1 keV (Na Ka line) are used to detect the lighter elements through an ultra-thin entrance window (8  $\mu$ m beryllium) purged with helium gas. An array of two KETEK GmbH SDDs, with 113 mm<sup>2</sup> area and 450  $\mu$ m thickness, shielded by 450  $\mu$ m Mylar foils, detect X-rays in the range 3–20 keV. With currents on the order of 100 nA, measurements lasted only 120 s for each sample, (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/filter) is calculated using Eq. (3):

$$c_{PIXE} = \left(\frac{Y}{b_{cal} \cdot Q}\right) \cdot A_d \tag{3}$$

where Y is the number of the collected X-rays emitted by the element of interest (counts), Q is the integrated beam charge ( $\mu$ C), A<sub>d</sub> is the sample deposition area and b<sub>cal</sub> is a linear calibration factor (counts/( $\mu$ C\* $\mu$ g/cm<sup>2</sup>)) obtained by measuring a set of thin film standards (Micromatter Inc.).

## 2.5. ICP-MS

Filters were extracted using 8 ml ultrapure  $HNO_3$  (69%, Romil-UpA, UK), 2 ml ultrapure  $H_2O_2$  (30%, Romil-UpA, UK) and 0.5 ml ultrapure HF (51%, Romil-UpA, UK) in a microwave oven (Milestone Labstation Ethos 900, Italy) to be analyzed by ICP-MS (Agilent 7500ce, Japan). The details of the ICP-MS method are given in SI1.

# 2.6. Data evaluation

The method detection limits (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 (relative standard deviation of multiple analysis, RSD) of the E5 and UQ was determined by analyzing three times each a low (PM mass less than 0.5 mg), a medium (PM between 1 and 2 mg) and a high (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 biases 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, intercept and coefficient of determination (R<sup>2</sup>). Although a slope near unity and a high  $R^2$  can be a good indicator of agreement between the laboratories, the method has some limitations, because regression is affected by outliers and the highest point of the regression. The other method, namely absolute relative difference (ARD, 100\* abs(lab/mean(lab1, lab2, lab3)-1), calculates the relative difference between the results from laboratories sample by sample. These methods are good tools to compare results from laboratories; however, there are no standardized criteria on the acceptance of good agreement. In this study, ARD less than 20% and slope less than 20% different from unity with R<sup>2</sup> higher than 0.8 were utilized as criteria to assess laboratories to be in "good agreement". The third method, namely E<sub>n</sub> number described in ISO 17043 (2010), checks if the absolute relative difference between two laboratories remains within their expanded uncertainties. En was calculated using Eq. (4) for paired results from E5 and UQ and from E5 and PIXE.

$$E_n = \frac{|c_{E5} - c_{lab}|}{\sqrt{Uc_{E5}^2 + Uc_{lab}^2}} \tag{4}$$

where,  $c_{lab}$  is the loading from UQ or PIXE;  $Uc_{E5}$  and  $Uc_{lab}$  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 PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>r</sub> 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 measurements on fifteen artificially loaded samples were compared to ICP-MS in a recent study (Unpublished results). The slope of the ICP-MS versus E5 results remained within 10% of unity for Al, K, Ti, Mn, Fe, Ni, Cu and Pb, and within 25% of unity for Na, Mg, Ca, Co, Zn, Br, Rb and Cd. These results revealed that the E5 and ICP-MS results are comparable.

#### 3. Results and discussion

#### 3.1. Comparison of MDLs, SRM bias and precision

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  $\pm$  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  $PM_{10}$  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<sub>r</sub>) 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



Fig. 1. Method detection limit estimates with the samples mean calculated from the three XRF laboratories. It should be noted that the mean values of Si, S, K, Ca and Fe are shown as mean/10 to achieve better resolution on the plot.



Fig. 2. The mean biases of the three XRF laboratories from certified loadings on SRM 2783. Error bars represent one standard deviation.

#### Table 1

The basic statistics of loadings (c, mean  $\pm$  s in ng/filter) from the three XRF laboratories with their relative expanded uncertainties (U<sub>r</sub>) at the mean of each laboratory and ARD (mean  $\pm$  s). The bold-italics show laboratories meeting ARD criterion (<20%) for at least 2/3 of the samples. n refers to the number of samples with measured loadings higher than the MDLs of the three XRF laboratories.

		E5			UQ			PIXE				
n		с	Ur	ARD	ARD c		ARD	с	Ur	ARD		
Mg	40	$2829~\pm~1997$	30%	$28~\pm~19\%$	$4398~\pm~3031$	34%	$49~\pm~22\%$	$2356~\pm~1897$	17%	$23~\pm~12\%$		
Al	59	$10389 \pm 11378$	12%	$17 \pm 12\%$	$9113 \pm 7682$	26%	$26~\pm~29\%$	$7505~\pm~8122$	13%	$22~\pm~14\%$		
Si	49	$21854 \pm 23122$	11%	$27~\pm~6\%$	$13822 \pm 15638$	28%	$44~\pm~15\%$	$19779 \pm 20093$	12%	$17~\pm~10\%$		
S	60	$30677 \pm 23406$	11%	$6 \pm 2\%$	$28593 \pm 22561$	19%	3 ± 2%	$28260 \ \pm \ 21675$	12%	$4 \pm 2\%$		
Cl	60	$3596~\pm~6637$	11%	11 ± 10%	$5332 \pm 8684$	22%	$32~\pm~23\%$	$2379~\pm~2921$	17%	$25~\pm~16\%$		
K	60	$15207 \pm 11795$	11%	$2 \pm 2\%$	$15413 \pm 12191$	24%	$2 \pm 2\%$	$16147 \pm 12814$	12%	$3 \pm 2\%$		
Ca	50	$12284 \pm 12114$	11%	$25~\pm~9\%$	$8945 \pm 9575$	26%	$35 \pm 18\%$	$10759~\pm~10458$	13%	11 ± 9%		
Ti	56	$753~\pm~704$	11%	$12 \pm 11\%$	$917~\pm~697$	30%	$30~\pm~27\%$	$582~\pm~567$	39%	$28~\pm~16\%$		
V	22	$79~\pm~72$	32%	$21~\pm~13\%$	$73 \pm 53$	58%	$23~\pm~18\%$	$114 \pm 59$	89%	20 ± 22%		
Cr	16	$129~\pm~143$	39%	$13 \pm 10\%$	$265~\pm~231$	27%	$23~\pm~14\%$	$135 \pm 173$	45%	13 ± 8%		
Mn	52	$345~\pm~246$	20%	13 ± 10%	$406~\pm~277$	27%	$23 \pm 8\%$	$305~\pm~217$	24%	$10 \pm 4\%$		
Fe	60	$24186 \pm 20661$	11%	$6 \pm 2\%$	$23398 \pm 19786$	24%	$2 \pm 2\%$	$21055 \pm 17909$	11%	8 ± 3%		
Ni	55	$81 \pm 54$	52%	$25~\pm~16\%$	$147 \pm 67$	23%	$60~\pm~20\%$	$70 \pm 54$	33%	$36 \pm 8\%$		
Cu	60	$846~\pm~714$	26%	$10 \pm 11\%$	$1026~\pm~734$	28%	$28~\pm~19\%$	$754~\pm~642$	14%	19 ± 10%		
Zn	60	$1137~\pm~888$	13%	10 ± 8%	$1278~\pm~986$	25%	$6 \pm 4\%$	$1172~\pm~756$	14%	$10 \pm 12\%$		
Br	54	$148~\pm~91$	33%	10 ± 8%	$143~\pm~96$	34%	$5 \pm 5\%$	$148~\pm~93$	30%	10 ± 8%		
Sr	48	$1336~\pm~1987$	36%	8 ± 12%	$1128~\pm~1784$	22%	7 ± 7%	$1206~\pm~1948$	19%	6 ± 6%		
Ba	15	$2151~\pm~1324$	51%	$33~\pm~24\%$	$2397~\pm~609$	152%	$69 \pm 36\%$	$1651~\pm~1433$	40%	$37~\pm~20\%$		
Pb	42	$374~\pm~253$	61%	15 ± 11%	$414~\pm~274$	31%	$25~\pm~12\%$	$318~\pm~250$	73%	$15 \pm 14\%$		

The bold-italics show laboratories meeting ARD criterion (<20%) for at least 2/3 of the samples.

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 R<sup>2</sup> 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 ( $R^2 > 0.97$ ) 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 PM<sub>10</sub> samples than for the SRM 2783. The Al and Si associations between E5 and PIXE are excellent ( $R^2 = 1.0$ ) 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. 4S–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;



**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<sup>2</sup> 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.)

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 is 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 about 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 ( $R^2 = 0.80$ ). The scattering between the two laboratories likely indicates random variability. In the PM<sub>10</sub> samples collected in 2011 in Ispra (n = 38), Ba, for which the L lines in-

terfere with Ti K $\alpha$ , 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<sup>2</sup> = 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<sup>2</sup> = 0.91) and 1.28 (R<sup>2</sup> = 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



**Fig. 5.** The mean  $E_n$  (the ratio of absolute difference to uncertainty) of E5 vs. UQ and E5 vs. PIXE. Error bars represent 1s. The numbers in the graph represents the percentages of  $E_n$  exceeding 1, where the green highlighted represent the percentages over 30%. The  $E_n$  of E5 vs. UQ for Si (3.23) and Ca (2.84) were replaced by 2 to achieve better resolution on the plot. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. S1). The possible reason for the random and systematic variability could be the volatility of Cl, which evaporates under vacuum and beam irradiation (Calzolai et al., 2008; Yatkin and Gerboles, 2013).

The slopes between XRF laboratories showed Zn quantification by order UQ > E5> PIXE whereas SRM 2783 quantifications were E5 = PIXE > UQ. ARD of three laboratories are well below 20%. The association between three laboratories are excellent ( $R^2$  > 0.99). In the literature, XRF laboratories reported variable Zn bias from SRM 2783, between -15% and 17% (Oztürk et al., 2011; Barrett et al., 2012; Shaltout et al., 2013; Okuda et al., 2013; Masiol et al., 2015). Hence, SRM 2783 biases of XRF laboratories may vary notably.

The slopes of orthogonal regression between ICP-MS and the three XRF laboratories are plotted in Fig. 4 for elements quantified by four techniques. The Al slopes of ICP-MS vs. E5, vs. UQ, and vs. PIXE are 0.85 ( $R^2 = 0.82$ ), 0.59 ( $R^2 = 0.77$ ) and 0.85 ( $R^2 = 0.85$ ), respectively, which are very consistent with the between-XRF laboratories' slopes. In addition, the intercept between ICP-MS vs. UQ (3279 ng/filter) is significant and similar to the one between E5 and UQ, which is another finding showing the systematic bias in UQ quantification. In addition to Al, the ICP-MS vs. XRF laboratories' slopes of K, Ca, Ti, Cu and Sr are very consistent with between-XRF laboratories' slopes. The Zn slopes of ICP-MS vs. E5, vs. UQ and vs. PIXE are 1.52 ( $R^2 = 0.74$ ), 1.75 ( $R^2 = 0.74$ ) and 1.24  $(R^2 = 0.77)$ , respectively. Good agreement between XRF laboratories but not with ICP-MS laboratory pointed out a bias in ICP-MS quantification. Poor association between ICP-MS and XRF laboratories but excellent between XRF laboratories ( $R^2 > 0.99$ , see Fig. S5) pointed out a random ICP-MS bias, too. Relatively poor agreement between EDXRF and ICP-MS was also reported by Niu et al. (2010), which was interpreted arising from high Zn contamination in PTFE blanks. Low sample to blank ratio (1.9  $\pm$  0.6, mean  $\pm$  s) likely contributed to the poor Zn agreement between ICP-MS and XRF laboratories. The V slopes of ICP-MS vs. E5, vs. UQ and vs. PIXE are 1.07 ( $R^2 = 0.90$ ), 0.42 ( $R^2 = 0.79$ ) and 0.58 ( $R^2 = 0.81$ ), respectively, which are somewhat consistent with between-XRF laboratories' slopes. The Cr and Ni slopes are over 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  $\sim -20\%$  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  $\sim -10\%$  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 ( $E_n \leq 1$ ) 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<sub>10</sub> (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

#### Table 2

The summary of between-laboratories comparisons for SRM-bias and  $PM_{10}$  samples. "Yes" refers to absolute SRM-bias less than 20% and slope being within 20% of unity with  $R^2 > 0.8$ . "n.a." refers to "not available".

Comparison	Mg	Al	Si	S	Cl	К	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Sr	Ва	Pb
E5 vs UQ	No	No	No	Yes	No	Yes	No	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	No	Yes
E5 vs PIXE	Yes	No	Yes	Yes	No	Yes	Yes	Yes	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
E5 vs ICP-MS	n.a.	Yes	n.a.	n.a.	n.a.	Yes	Yes	Yes	Yes	No	Yes	No	No	Yes	No	n.a.	Yes	n.a.	No
E5-SRM Bias	No	Yes	Yes	No	n.a.	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	No	n.a.	Yes	No	Yes
UQ vs PIXE	No	Yes	No	Yes	No	Yes	Yes	Yes	Yes	No	Yes	Yes	No	Yes	No	Yes	Yes	No	Yes
UQ vs ICP-MS	n.a.	No	n.a.	n.a.	n.a.	Yes	No	No	No	No	Yes	No	No	Yes	No	n.a.	No	n.a.	Yes
UQ-SRM Bias	Yes	Yes	Yes	Yes	n.a.	Yes	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	n.a.	Yes	No	Yes
PIXE vs ICP	n.a.	Yes	n.a.	n.a.	n.a.	Yes	Yes	Yes	No	No	Yes	Yes	No	Yes	No	n.a.	Yes	n.a.	Yes
PIXE-SRM Bias	No	Yes	Yes	Yes	n.a.	Yes	Yes	Yes	No	No	Yes	Yes	Yes	Yes	No	n.a.	Yes	No	Yes

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 PM<sub>10</sub> samples collected on PTFE filters.

# Acknowledgments

This study was supported by the National Park Service under cooperative agreement **#PIIAC91045** with the University of California at Davis. The authors are grateful to Valerio Pedroni and Jose Cancelinha from the Institute for Environment and Sustainability of the Joint Research Centre for the sampling of PM<sub>10</sub>, Margaret Cruz from UCDavis-CNL for the measurement of samples with the Epsilon 5, and Nicole P. Hyslop and Charles McDade from UCDavis-CNL for their comments and editing the manuscript.

## 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

- Barrett, P.M., Resing, J.A., Buck, N.J., Buck, C.S., Landing, W.M., Measures, C.I., 2012. The trace element composition of suspended particulate matter in the upper 1000 m of the eastern North Atlantic Ocean; a16N. Mar. Chem. 142, 41–53.
- Belis, C., Pedroni, V., Cancelinha, J., Borowiak, A., 2012. Determination of Particulate Matter According to CEN and EMEP Standards at the Atmosphere Biosphere and Climate-integrated Station (ABC-IS), Ispra (IT) JRC79144, EUR 25802 EN, ISBN 978-92-79-28424-3 (pdf), ISSN 1831-9424 (online) http://dx.doi.org/ 10.2788/8320.
- Calzolai, G., Chiari, M., Lucarelli, F., Mazzei, F., Nava, S., Prati, P., Valli, G., Vecchi, R., 2008. PIXE and XRF analysis of particulate matter samples: an inter-laboratory comparison. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 266, 2401–2404.
- Campbell, J.L., Boyd, N.I., Grassi, N., Bonnick, P., Maxwell, J.A., 2010. The Guelph PIXE software package IV. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 268, 3356–3363.
- CSN network. Available at http://www.epa.gov/ttn/amtic/speciepg.html.
- Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Official J. L 23, 26/01/2005. http://eur-lex.europa.eu
- Directive 2008/50/EC of the European Parliament and the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, Official Journal of the European Union L 152/1 of 11.6.2008. http://eur-lex.europa.eu.
- European Commission, Jan 2010. Demonstration of equivalence of ambient air monitoring methods. Rep. by EC Work. Group. Available at: http://ec.europa.eu/ environment/air/quality/legislation/pdf/equivalence.pdf.
- European Standard, 1998. Ambient Air Quality Determination of the PM<sub>10</sub> Fraction of Suspended Particulate Matter, Reference Method and Field Test Procedure to Demonstrate Reference Equivalence of Measurement Methods EN12341, Brussels, Belgium. Available at: http://www.CEN.eu.

European Standard, 2005. Ambient Air Quality – Standard Gravimetric Measurement Method for the Determination of the PM<sub>2.5</sub> Mass Fraction of Suspended Particulate Matter EN 14907. Brussels, Belgium. Available at: http://www.CEN.eu.

- European Standard, 2010. Conformity Assessment General Requirements for Proficiency Testing ISO/IEC 17043:2010. Brussels, Belgium. Available at: http://www. CEN.eu.
- Evaluation of measurement data-Guide to the expression of uncertainty in measurement, 2008. Joint Committee for Guides in Metrology JCGM 100:2008 www.bipm.org.
- Gerboles, M., Buzica, D., Brown, R.J.C., Yardley, R.E., Hanus-Illnar, A., Salfinger, M., Vallant, B., Adriaenssens, E., Claeys, N., Roekens, E., Sega, K., Jurasović, J., Rychlik, S., Rabinak, E., Tanet, G., Passarella, R., Pedroni, V., Karlsson, V., Alleman, L., Pfeffer, U., Gladtke, D., Olschewski, A., O'Leary, B., O'Dwyer, M., Pockeviciute, D., Biel-Ćwikowska, J., Turšič, J., 2011. Interlaboratory comparison exercise for the determination of As, Cd, Ni and Pb in PM<sub>10</sub> in Europe. Atmos. Environ. 45, 3488–3499.
- Hurst, J.A., Volpato, J.A., O'Donnel, G.E., 2011. The determination of elements in welding fume by X-ray spectrometry and UniQuant. X-Ray Spectrom. 40, 61– 68.
- IMPROVE program. Available at: http://vista.cira.colostate.edu/IMPROVE.
- Kang, C.-M., Achilleos, S., Lawrence, J., Wolfson, J.M., Koutrakis, P., 2014. Interlab comparison of elemental analysis for low ambient urban PM<sub>2.5</sub> levels. Environ. Sci. Technol. 48 (20), 12150–12156.
- Lucarelli, F., Calzolai, G., Chiari, M., Giannoni, M., Mochi, D., Nava, S., Carraresi, L., 2014. The upgraded external-beam PIXE/PIGE set-up at LABEC for very fast measurements on aerosol samples. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 318, 55–59.
- Masiol, M., Squizzato, S., Ceccato, D., Pavoni, B., 2015. The size distribution of chemical elements of atmospheric aerosol at a semi-rural coastal site in Venice (Italy). The role of atmospheric circulation. Chemosphere 119, 400–406.
- Nejedly, Z., Campbell, J.L., Teesdale, W.J., Dlouhy, J.F., Dann, T.F., Hoff, R.M., Brook, J.R., Wiebe, H.A., 1998. Inter-laboratory comparison of air particulate monitoring data. J. Air Waste Manag. Assoc. 48, 386–397.
- Niu, J., Rasmussen, P.E., Wheeler, A., Williams, R., Chénier, M., 2010. Evaluation of airborne particulate matter and metals data in personal, indoor and outdoor environments using ED-XRF and ICP-MS and co-located duplicate samples. Atmos. Environ. 44, 235–245.
- Okuda, T., Fujimori, E., Hatoya, K., Takada, H., Kumata, H., Nakajima, F., Hatakeyama, S., Uchida, M., Tanaka, S., He, K., Ma, Y., Haraguchi, H., 2013. Rapid and simple determination of multi-elements in aerosol samples collected on quartz fiber filters by using EDXRF coupled with fundamental parameter quantification technique. Aerosol Air Qual. Res. 13, 1864–1876.
- Okuda, T., Schauer, J.J., Shafer, M.M., 2015. Improved methods for elemental analysis of atmospheric aerosols for evaluating human health impacts of aerosols in East Asia. Atmos. Environ. 97, 552–555.
- Oztürk, F., Zararsiz, A., Kirmaz, R., Tuncel, G., 2011. An approach to measure trace elements in particles collected on fiber filters using EDXRF. Talanta 83, 823–831.
- Shaltout, A.A., Boman, J., Al-Malawi, D.A.R., Shehadeh, Z.F., 2013. Elemental composition of PM<sub>2.5</sub> particles Sampled in Industrial and Residential areas of Taif, Saudi Arabia. Aerosol Air Qual. Res. 13, 1356–1364.
- Sherman, J., 1955. The theoretical derivation of fluorescent X-ray intensities from mixtures. Spectrochim. Acta 7, 283–306.
- Software UniQuant, Version 6.09, 2008. Thermo Fisher Scientific The Netherlands. Available at : http://www.uniquant.com .
- Traversi, R., Becagli, S., Calzolai, G., Chiari, M., Giannoni, M., Lucarelli, F., Nava, S., Rugi, F., Severi, M., Udisti, R., 2014. A comparison between PIXE and ICP-AES measurements of metals in aerosol particulate collected in urban and marine sites in Italy. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 318, 130–134.
- UC Davis-CNL XRF SOP. Available at http://vista.cira.colostate.edu/IMPROVE/ Publications/SOPs/ucdavis\_sops/sop301\_XRF\_2014.pdf.
- Yatkin, S., Gerboles, M., 2013. Investigation of the mass loss of water soluble ionic compounds caused by EDXRF analysis of PM<sub>10</sub> loaded filters. Atmos. Environ. 73, 159–168.
- Yatkin, S., Gerboles, M., Borowiak, A., 2012. Evaluation of standardless EDXRF analysis for the determination of elements on PM<sub>10</sub> loaded filters. Atmos. Environ. 54, 568–582.