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Airborne particulate matter (PM) filter analysis and modeling by total reflection X-ray fluorescence (TXRF) and X-ray standing wave (XSW)

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To Marta and Danielle, for their birth.

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ABSTRACT

This work is presented as an improvement of a recently introduced method for airborne particulate matter (PM) filter analysis [1]. X-ray standing wave (XSW) and total reflection X-ray fluorescence (TXRF) were performed with a new dedicated laboratory instrumentation. The main advantage of performing both XSW and TXRF, is the possibility to distinguish the nature of the sample: if it is a small droplet dry residue, a thin film like or a bulk sample. Another advantage is related to the possibility to select the angle of total reflection to make TXRF measurements. Finally, the possibility to switch the X-ray source allows to measure with more accuracy lighter and heavier elements (with a change in X-ray anode, for example from Mo to Cu). The aim of the present study is to lay the theoretical foundation of the new proposed method for airborne PM filters quantitative analysis improving the accuracy and efficiency of quantification by means of an external standard. The theoretical model presented and discussed demonstrated that airborne PM filters can be considered as thin layers. A set of reference samples is prepared in laboratory and used to obtain a calibration curve. Our results demonstrate that the proposed method for quantitative analysis of air PM filters is affordable and reliable without the necessity to digest filters to obtain quantitative chemical analysis, and that the use of XSW improve the accuracy of TXRF analysis.

1. Introduction

In recent years epidemiological studies have shown that the exposure to elevated levels of airbone particulate matter (PM) creates several health effects [2]. These studies demonstrated that to understand aerosol effects on human health it is mandatory not only to study atmospheric particles sources, transport media and fate but also their chemical composition and physical properties. In most cases aerosol analysis provides information only about the mass concentration and perhaps also particle size. However, these primary indicators of PM pollutants (mass concentrations of PM2.5 and PM10) are inherently imperfect measures of PM toxicity, and identification of the more toxic components of ambient air PM and their various health effects would provide a basis for more targeted airborne concentration limits and efficient control strategies. Therefore, speciation monitoring is fundamental to identify the most toxic PM components and their specific health effects for epidemiological research and exposure-response relationships [3].

Furthermore, it might be helpful, or even necessary, to get information about the chemical state of a specific element of interest present in the particles [4].

Airborne PM samples are generally collected on thin membrane filters [5]. The use of conventional spectroscopic analysis techniques (such as inductively coupled plasma-ICP [6] and atomic absorption spectroscopy-AAS [7]) for filter analysis has many disadvantages. The necessary acid digestion methods involve the use of potentially hazardous reagents; moreover there are problems of contamination by reagent impurities, the loss of volatile elements is often observed and analyte dilution below the instrumental detection limit may occur. In addition, sample digestion is very labor-intensive and time-consuming work.

The use of direct analytical methods avoids the difficulties mentioned above. Filters can be directly analyzed by analytical methods such as X-ray fluorescence (XRF) or instrumental neutron activation analysis (INAA) [8]. XRF has been considered a particularly useful technique for elemental analysis of airborne particulate matter [9]. It is a non-destructive technique, allowing for samples archiving. However for XRF some analytical problems may occur: the sensitivity to many elements is still limited and quantitative

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measurement of filter samples can be difficult without an appropriate calibration method and reference standards.

Total reflection X-ray fluorescence analysis (TXRF) [10] is based on the principle that, when an exciting X-ray beam impinges on a thin sample positioned on a very flat support below the critical angle of total reflection on the support, this radiation is totally reflected. In this way, matrix effects can be neglected and TXRF allows the detection of extremely small amounts of elements [11].

Generally, techniques with excitation at small glancing angles, such as X-ray reflectivity [12] and glancing incidence X-ray diffraction [13] are summarized in a group called grazing incidence X-ray spectrometry. TXRF belongs to this group and it is considered a static method from the excitation point of view. The continuous variation of the glancing incident angle with very small step size allows a new dimension in the TXRF response. The fluorescence radiation collected during the step-scan can be also plotted against the glancing angle leading to an X-ray standing wave (XSW) profile [14]. Elements of interest peak intensities are extracted from each spectrum and plotted against the corresponding incident angle to give the intensity profile.

Variable beam geometry in TXRF instrumentation allows the determination of angular dependent signal intensities and evaluation of the sample preparation method on a factual basis, instead of a merely empirical one. Indeed, from XSW analysis it is possible to distinguish the nature of the sample: if it is a small droplet dry residue, a thin film like or a bulk sample [15]. XSW for a dry residue of a small droplet (or particulate) shows a fluorescence intensity that is nearly constant below the critical angle of the carrier and in condition of total reflection, but it decreases, just after the incident angle, to reach the constant value of a half. A very thin film or a monolayer on top of a carrier such as an air filter has a fluorescence intensity that is zero at an angle of 0°. Raising the angle, the intensity increases until just less than the critical angle, leading to the fourfold intensity, compared to the drop in value after the critical angle region. In the condition of a bulk sample, as for example a substrate (or blanck carrier) with no deposited material, the background intensity has very small values below the critical angle. Above this angle, the primary beam penetrates into the bulk sample deeper and deeper, and the fluorescence intensity continuously increases [15].

Recently we demonstrated that TXRF analysis is also suitable for the investigation of air PM filters because it allows nondestructive multi-element analysis of trace and ultratrace amounts of most elements [16]. Summarizing the procedure consists of sandwiching the filter between two thin sheets of polypropylene [17]. To perform TXRF measurements the prepared filter is then placed onto a quartz glass sample carrier to maintain its flatness. The advantages of this procedure are several: filters prepared in this way can be directly inserted into the measurement chamber, without any chemical treatment and dilution; the fluorescence signal is maximized at the critical angle; the sample remains unaltered and thus can be archived. So, in principle, it is possible to perform other analyses on the same sample, as for example colorimetric investigations and structural analysis by means of diffraction techniques.

TXRF quantitative analysis is usually performed by addition of an internal standard to the sample; however it is very difficult to perform this method with solid samples, because the standard should be equally distributed in the dried residue [18]. Moreover, in many cases, calibration by standard addition is feasible, but it requires additional sample preparation, especially in the case of multi-element determination. Nonetheless the use of an internal standard requires that the sample amount is small (nanogram (ng) range) so that the thin film approximation can be applied, hence absorption effects of both exciting and detected radiation can be neglected [19] and the relationship between fluorescence intensity and sample amount is linear. Deviations from the linear relation (saturation effects) can be observed in the case of higher sample masses (depending on the elements present in sample and matrix). Saturation effects are due to differences in the absorption of primary radiation and self absorption of fluorescence radiation leading to high statistical errors.

Very recently we demonstrated that direct analysis of airborne PM filters by means of TXRF with the use of an external standard for quantification is possible [1].

The aim of the present study is to lay the theoretical foundation of the proposed method for airborne PM filters analysis and to improve the accuracy and efficiency of the quantification by means of an external standard.

A set of standard, reference and experimental samples were analyzed by means of a new dedicated laboratory instrument, presented herewith for the first time [20], very suitable to analyze airborne PM filters.

2. Experimental

2.1. Samples of study

Three different kinds of PM10 filter samples were used for the purposes of this study: a certified standard sample (NIST-SRM 2783), laboratory prepared reference samples (by Atomic Layer Deposition – ALD), and experimental samples with collected airborne PM (collected in a EU-funded project – the 6th frame of PHIME [21] and NIH project Award Number R01ES019222).

The reference standard sample used is the air particulate standard filter produced by the U.S. National Institute of Standards and Technology (NIST-SRM 2783). The material deposited on this filter is representative of that collected in a typical urban industrial area [22].

ALD technique was chosen to deposit reference samples. Indeed this technique allows the deposition of thin films having very low thicknesses (from a few atomic layers) on complex geometry substrates. A major advantage of laboratory prepared samples by ALD is that the thin film thickness (directly proportional to the mass by material density and surface area) is directly related to the number of cycles, a process parameter that can be determined in advance. Because of the experience of Chem4Tech research group depositing titania at low temperature by means of ALD [23], it was chosen as the reference material.

A set of Teflon filter membranes (37 mm diameter, PTFE-Teflon) with a given amount of Ti was prepared in the laboratory by means of ALD, performed in a Cambridge Nanotech Inc Savannah 100 system. The reactor is a stainless steel cylinder (18.1 cm diameter and 3.6 cm height) with a bottom heated plate of 179 cm^2. Titanium oxide is deposited starting from tetrakis(dimethylamido)titanium(IV) (TDMAT) as the titanium source and milliQ water (H_2O) as the oxygen source. TDMAT (99,999%) (Sigma–Aldrich Chemical Co., Germany) was used without any further purification. MilliQ water was produced in the laboratory with a Millipore DirectQ-5 purification system starting from tap water. The precursors are injected into the reactor directly from 25 g stainless steel reservoirs held respectively at 90 °C for the TDMAT and at room temperature for the water to develop enough vapor pressure. Nitrogen gas with 99,999% purity was used as the carrier gas to feed the precursor vapors alternatively to the reaction chamber. The deposition temperature was 90 °C and the base pressure of the reactor was 0.5 Torr. The carrier gas with unreacted precursors and reaction products was evacuated from the reactor through the exhaust by the rotary vane vacuum pump that also maintains the base pressure in the system. The processing cycle consists of a 0.1 s TDMAT pulse, 10 s purging time, a 0.1 s H_2O pulse,

Table 1
Reference samples prepared in laboratory by means of ALD.

Sample name	Cycles number	TiO_2 thickness (nm)
F1	1	0.1
F6	8	0.5
F7	20	1.3
F8	30	2.0
F9	50	3.4
F10	60	4.0
F11	150	10.1
F12	210	14.1

and 10 of purging time. A TiO_2 thickness of 0.068 nm is deposited each cycle.

Eight samples of increasing thickness were prepared with different cycles number from 1 to 210 (Table 1).

Finally, atmospheric aerosols (environmental samples) were collected on commercial filters (37 mm diameter, PTFE-Teflon) for PM10 in selected municipal districts of Bagnolo Mella (Brescia) in the frame of PHIME and NIH project. Next section describes the procedure for collection of these samples.

2.2. Samples collection

Atmospheric aerosols samples (environmental samples), were collected with personal samplers on volunteer student adolescents. The samplers used were 10 μm particle diameter cut-point Personal Environmental Monitors (PEM) (SKC, Inc., Eighty-Four, PA) each of which was attached to a student's backpack strap, located near the breathing zone. Each PEM was connected to a Leland Legacy pump (SKC, Inc., Eighty-Four, PA) which was carried in the backpack. The pumps were pre-calibrated to a 10 l/min flow rate with a soapless piston primary calibrator (Defender, BIOS, Butler, NJ) with post-sampling flow rate confirmed as well. The pumps were run for 24 consecutive hours with the child's school backpack either carried by the child or placed near the child during school or in the room while they were sleeping. Each child was asked to complete a personal diary with complete records of their activities and locations during the sampling period.

The study site was chosen because in a previous study [24] an increased prevalence of parkinsonism was observed in the vicinities of Mn–Fe-alloy plants located in the Brescia province.

2.3. Sample preparation for TXRF and XSW analysis

All samples are treated according to the procedure proposed in [17] to be measured. In particular the procedure consists of sandwiching each filter between two thin sheets of polypropylene, each with a thickness of 125 μm. To perform TXRF and XSW measurements the prepared filter is then placed onto a quartz glass sample carrier to maintain its flatness.

As it was already shown [1], this method has many advantages: it is simple and fast, samples treated in this way can be simply handled and directly measured by any TXRF instrumental configuration, without additional chemical treatment. Finally samples can be archived for further analysis.

2.4. Instrumentation

Very different TXRF set-ups have been presented in the last forty years for XSW analysis. In this work measurements were performed with a GNR Explorer diffractometer [20] equipped with a Silicon Drift Energy Dispersive detector to collect fluorescence spectra in total reflection mode (Fig. 1). The direct drive torque motors motion in θ–θ geometry, the 230 mm goniometer radius and the motorized (z, χ, ϕ) axes (Fig. 1) sample stage provided high accuracy and flexibility in sample positioning and fluorescence signal enhancement. The accuracy achievable for incidence angle was around 10–5° thanks to optical encoders, while the sample height minimum adjustment was less than 1 μm. Each specimen was fixed with silicone paste (high purity vacuum grease) on a quartz reflector, which in turn was glued onto an aluminum cylindrical sample holder mounted on the sample stage. The sample was then aligned following thin film alignment procedures for X-ray reflectivity measurements with the aid of a NaI(Tl) Scintillation Detector. Moreover a parabolic mirror (Max-Flux Optic) was placed in front of the Mo-anode X-ray tube in order to achieve a monochromatic K-alpha ($\lambda = 0.07107$ nm) quasi-parallel beam (divergence less than 0.05°) and a remarkable intensity gain. The length of the parabolic mirror used in both XSW and TXRF was 40 ± 0.2 mm.

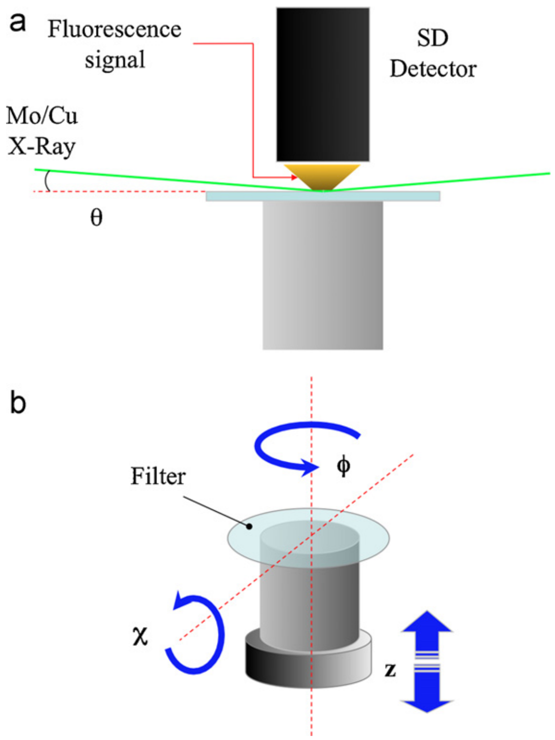

Fig. 1. New instrument experimental setup: (a) measurement set-up and (b) motorized axes available on the sample stage.

The voltage and current were set at 30 kV and 20 mA, respectively, for all measurements. The X-ray tube was properly conditioned before starting the measurement session.

The fluorescence signal from the sample was acquired by an XGLab Silicon Drift Detector [20], whose active area is 30 mm^2 with an energy resolution of approximately 126 eV at Mn K_α and a shaping time of 1 μs; the detector was fixed at a few mm distance above the sample.

The X-ray source was changed to Cu as an alternative anode to better excite low Z elements by means of its lower energy K-alpha emission line ($\lambda = 0.15418$ nm).

2.5. Quantitative analysis

One of the main advantages of TXRF with respect to other XRF techniques is the easy method of quantification, because if the matrix effect can be neglected a linear calibration is possible.

Quantitative analysis is based on the integrated area of each element TXRF peak. This area is proportional to the mass of the element in the sample. A linear calibration can be made using external standards, with a certified amount of elements.

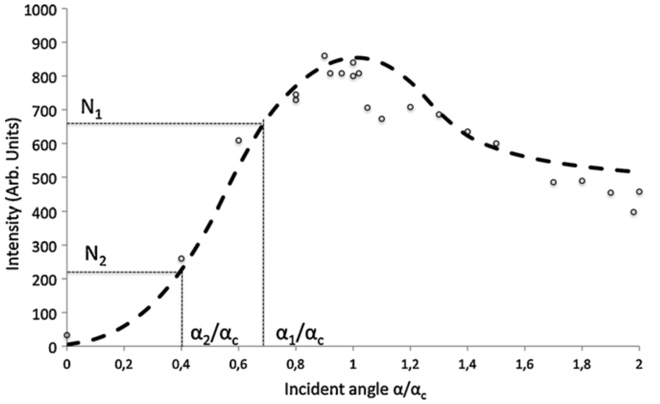

Fig. 2. Experimental XSW data (dots) obtained considering the Fe (K-alpha) peaks area of the standard NIST-SRM 2783 sample; the simulation of XSW is also reported (dotted line).

In this work we show that, for air particulate matters filters, standard samples can be produced by ALD, to make external quantification.

Manganese content in all environmental samples, collected in Bagnolo Mella, was quantified by means of the external standard procedure, i.e. associating Mn peak area of NIST-SRM 2783 TXRF pattern with the certified reported Mn amount.

3. Results and discussion

Fig. 2 shows the experimental XSW profile obtained on the NIST-SRM 2783 Standard Reference filter measured with a Cu tube as the X-ray source. The iron K-alpha peak intensity was chosen to be plotted in the XSW profile because it was the most intense signal in the fluorescence spectrum of this sample (see TXRF pattern shown in Fig. 3).

One of the main conditions to perform quantitative analysis by TXRF is the thin film like nature of the sample, otherwise the principle of X-ray total reflection may be lost. Experimental XSW profile reported in Fig. 2 shows a behavior very similar to the one expected for a thin film like sample. Considering that in the present case the air particulate matter filter is sandwiched between two organic foils, it may be modeled as a sum of particulate type and layer type contribution. As a consequence the XSW profile of this sample may be modeled as the sum of the contribution of particulate and thin film profiles, with an evident thin film contribution prevalence.

It is possible to determine two significant angles in the XSW profile of thin films: alpha1 and alpha2 [25]. Their respective intensities N1 and N2 lead to the evaluation of layer (thin film) type and particulate type contribution to the XSW. Alpha1 and alpha2 can be calculated by Eqs. (1) and (2):

$$\alpha_1 = \frac{\alpha_{crit}}{\sqrt{2}} \tag{1}$$

$$\alpha_2 = \frac{\alpha_{crit}}{\sqrt{6}} \tag{2}$$

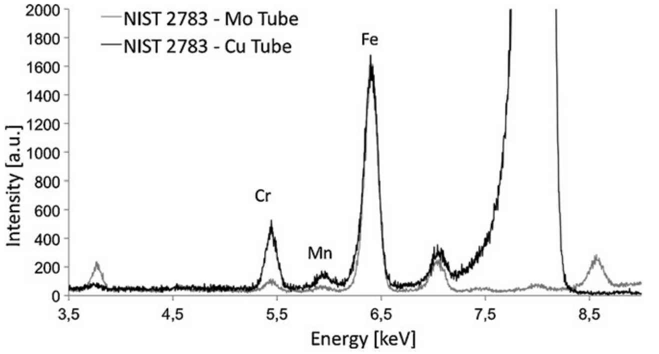

Fig. 3. TXRF patterns collected on the NIST-SRM 2783 standard filter, by using two different X-ray sources: Mo and Cu. Spectra are normalized with respect to Fe peak intensity.

It was reported [26] that the percentage of layer (thin film) type (cL) is given by Eq. (3).

$$C_L = \frac{3}{2}\left(1 - \frac{N_2}{N_1}\right) 100\% \tag{3}$$

The corresponding percentage of particulate type (cP) is given by Eq. (4):

$$C_P = \frac{3}{2}\left(\frac{N_2}{N_1} - \frac{1}{3}\right) 100\% \tag{4}$$

Both these values sum up to 100%.

Alpha1, alpha2 and the corresponding N1 and N2 values are shown in Fig. 2.

To evaluate the proposed thin film model for air particulate matter filters a simulation of the XSW experimental profile was performed and reported in Fig. 2 (dotted line). The simulation was performed considering a thin layer of Fe and a divergence of the primary beam, due to the sample dimension [27,28]. The corresponding values of N1 and N2 were extracted and the relative contribution of particle type and layer type were calculated. Thin film type percentage is about 99,5%. This result is very important, because it confirms that we can model our samples as thin films with a good approximation neglecting the particulate type contribution (0.5%).

In the last presented work [1] we operated with a fixed instrumental geometry (fixed incidence angle). In that case the total reflection condition may not be satisfied for all samples, and the corresponding spectra can have lower element intensities. Since the quantitative analysis, by means of the external standard method [1], started from the net area of an element peak, errors in peak area evaluation imply errors in the elemental quantification. The observation of Fig. 2 highlights that differences about 20% in the determination of the critical angle (this may be due to an incorrect positioning of sample in the sample holder) lead to an error about 20% in the intensity. As already reported [1] to overcome this problem we performed several TXRF measurements of each sample (usually 10) rotating the sample on itself. In this way we can be almost statistically confident that it was inserted in the right position to satisfy total reflection conditions, at least once. Among all the collected TXRF spectra on each sample, that with the highest

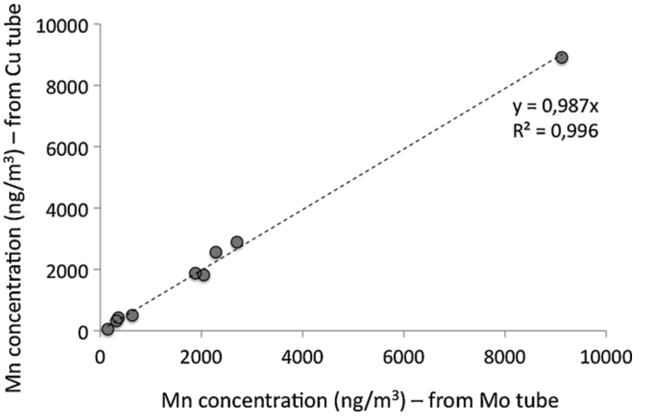

Fig. 4. Comparison of Mn concentration data obtained on the same environmental samples measured with two different instruments (see Ref. [1]) experimental configurations and X-ray sources (Mo and Cu).

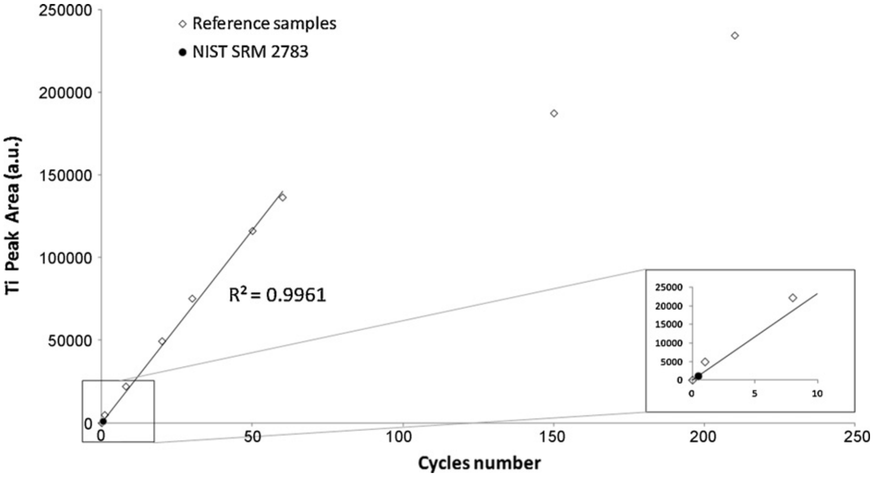

Fig. 5. Calibration line for quantitative analysis of Ti. Ti K-alpha peak area is reported versus ALD cycles number (directly related to the mass).

intensity was used to perform quantitative analysis, assuming that it was collected in total reflection conditions.

XSW measurements allow the identification of the best conditions to perform TXRF analysis: that is the incident angle value where the fluorescence signal of a chosen element (i.e. Fe in our case, see Fig. 2) is the highest. This represents a major improvement both for the speed and the reliability of TXRF measurements on such samples. Indeed it can give the confidence that the measurement is performed in total reflection condition.

Once these two conditions have been satisfied, thin film nature of samples and total reflection condition, the proposed external standard method can be used to perform quantitative analysis of any air particulate matter filter sample, treated by the proposed procedure [17].

As another proof of both the reliability of the proposed TXRF analysis method and the advantages of sample preparation procedure [17] we repeated the analysis of the NIST-SRM 2783 Standard Reference filter with a Mo X-ray source to compare the sensitivity obtained with the Cu X-ray source. Measurements were made with the same instruments, changing X-ray source. Fig. 3 shows the two TXRF patterns (normalized with respect to Fe) collected on a NIST-SRM 2783 standard filter using the two different X-ray sources. This comparison highlights another advantage of the new instrumentation proposed by GNR: the possibility to change the anode material which is the X-ray source (i.e. Cu instead of Mo). Indeed the characteristic radiation originating from the secondary target can be selected to have the best excitation for the elements of interest, avoiding analyte peak overlap [29]. For example, using Cu as a secondary target for X-ray excitation, it is possible to improve detection limits of elements with atomic numbers in the range of 19–25. It is evident that the Mn (atomic number 25) peak is higher in the spectrum collected with the Cu tube compared to the one collected with Mo tube (Fig. 3). In particular Mn area is about 2.5 times larger. Considering that the target of both PHIME and NIH projects is Mn, from these results it is possible to conclude that the use of Cu as X-ray source for Mn detection improves both the time for measurement as well as Mn detection limit and therefore is more suitable for its investigation. However this result is important for any investigation of elements in the atomic weight range of 19–25.

Environmental samples collected in the frame of PHIME and NIH project were measured with the new instrument [20], having glancing incidence configuration and Cu as the X-ray source, and with the instrument described in Ref. [1], having fixed angle instrumental configuration and Mo anode. Fig. 4 shows the comparison of Mn concentration, Mn was chosen as the element of interest [30], obtained with the two experimental sets. Despite differences concerning X-ray sources and instrumental configurations the data correlation is very good, so we can conclude that the proposed method of external standard based analysis is reliable. In addition XSW measurements give a major improvement to select the best measuring condition, speeding up the analysis time.

The quantification accuracy of the proposed method can be improved building up a calibration line instead of using one point calibration. Reference samples for calibration in the case of airborne PM filters analysis require a very low amount of deposited material (ng/cm^2), uniformly deposited on the filter. Since it is very hard to satisfy these conditions with conventional deposition techniques, reference samples were prepared in laboratory depositing different amounts of titania on filters by means of ALD (Table 1). The Ti K-alpha peak was used to determine XSW profiles of each reference sample, to find the total reflection conditions from the maximum of each curve. TXRF measurements of reference samples are performed in the settled total reflection condition and then used to construct a calibration line. In Fig. 5 Ti K-alpha peak area is plotted against the number of ALD cycles.

The first six points of the plot lay on a straight line, with a very good linear correlation ($R^2 = 0.9961$), as it would be expected from thin film samples with increasing Ti mass. However at higher cycle numbers there is a deviation from the linearity probably because the critical mass for this system is reached [31]. The Ti K-alpha peak area is extracted also from the TXRF spectrum of the NIST-SRM 2783 filter measured in the same experimental configuration of reference samples, and it has the lowest intensity value reported. This result supports the use of this method assuring that the critical mass is much greater than the usual experimental sample mass range.

Considering all the presented results this analysis technique appears very promising for airborne PM filter investigation.

4. Conclusions

In this work XSW and TXRF measurements were performed to demonstrate that air particulate matter filters can be modeled as thin film samples and that is possible to perform their direct chemical quantitative analysis.

These measurements were performed with a new instrument, that is very suitable for airborne PM filter investigation: it allows to collect TXRF and XSW spectra on the same experimental setup and as well and the X-ray tube can be changed, to improve the response signal of lighter elements.

XSW can be used to find the right incident angle, to perform fluorescence spectrometry in total reflection condition of X-rays.

Indeed this condition is necessary to perform an accurate quantification of element masses by means of an external standard.

To improve the accuracy of quantitative analysis, a set of reference samples to construct a calibration line was prepared in laboratory by means of ALD and analyzed. The obtained results demonstrated that the critical mass condition is far from the mass usually involved in the analysis of air particulate matter filters.

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