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Comparison of multiple X-ray fluorescence techniques for elemental analysis of particulate matter collected on air filters

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Abstract

This work reports on qualitative and semi-quantitative elemental analysis of particulate matter (PM) collected on PTFE membrane filters, for a source apportionment study conducted in Brescia (Italy). Sampling was undertaken in a residential area where an increase in Mn emissions has been highlighted by previous studies. Filters are measured by means of X-ray Fluorescence (XRF) based techniques such as micro-XRF and grazing incidence XRF using synchrotron radiation, Mo or W excitation sources, after applying an automatized sample preparation method. A heterogeneous distribution in PM shape, size and composition was observed, with features typical of anthropogenic sources. XRF measurements performed at various incidence angle, on large areas and different experimental setup were reproducible. The results demonstrate a successful comparison of the various XRF instrumentation, and the decrease in Mn content with the distance away from the identified emission source. This work highlights the potentialities of the presented approach to provide a full quantitative analysis, and ascertain its suitability for providing a direct, fast, simple and sensitive elemental analysis of filters in source apportionment studies and screening purposes.

Keywords

Particulate matter; Membrane filters; X-ray Fluorescence techniques; Manganese; Air pollution; Direct analysis

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1. Introduction

Air pollution monitoring and control is one of the major concerns in European and fast developing countries (Fenger, 2009) due to related severe health effects that may affect the population, especially the weaker part. On this purpose, reference methods were established by European Directives (Directive, /107/EC of the European Parliament & of the Council of 15 December 2004, relating to arsenic, cadmium, mercury, nickel & polycyclic aromatic hydrocarbons in ambient air, n.d; Directive, /50/EC of the European Parliament & the Council of 21 May 2008, on ambient air quality & cleaner air for Europe, n.d) and several international standards (EN 1234, 1998; <http://ec.europa.eu/environment/air/quality/legislation/pdf/equivalence.pdf>, n.d.; ISO 12103–1:2016: - Road vehicles - Test contaminants for filter evaluation - Part 1: Arizona test dust, n.d; ISO 9855:1993 - Ambient air - Determination of the particulate lead content of aerosols collected on filters - Atomic absorption spectrometric method, n.d).

Particulate matter (PM) is one of the prominent primary and secondary pollutants in the air. It is made of solid and liquid materials suspended in the atmosphere. PM composition varies from inert carbonaceous to mixtures containing metals, organic vapours (Spurny, 1996), acid salts and biological elements such as endotoxins, allergens, and pollen fragments (Fuzzi et al., 2015; Schäppi, Monn, & Wüthrich, 1996; Womiloju, Miller, Mayer, & Brook, 2003). PM may cause adverse health effects at the respiratory, cardiovascular and neurological levels (Lee, Kim, & Lee, 2014), depending on particle size and composition (Höhr, Steinfartz, Schins, & Knaapen, 2002). Although the specific toxicological mechanisms are still not well-assessed, several studies have demonstrated that exposure to various air pollutants is associated with reductions in lung function and growth, asthma, allergic rhinitis and respiratory infections in children (Janssen, Brunekreef, & Vliet, 2003). In particular, small particles of diameter less than 10 µm, pose the greatest problems, as they can penetrate deeper into the smaller airways, and be integrated into the bloodstream (“<http://www.epa.gov/pm/>,” n.d.).

It has been clearly demonstrated that the PM composition may directly be linked to specific health effects (Kampa & Castanas, 2008; Pöschl, 2005; Valavanidis, Fiotakis, & Vlachogianni, 2008), and for this reason it is important to develop efficient, sensitive and continuous means of assessing their composition. A wide range of elements can be found in PM. The major elements are Al, Ca, Fe, Mg, K and Si, usually present in their oxidized forms. In addition, a heterogeneous distribution of heavy metals may be observed within particles of diverse origins. Elements such as Cd, As, Cr, Pb and Ni are emitted in the form of gases during coal and oil combustion, and processing of Pb-Zn ores (Tian, Zhu, Gao, & Cheng, 2015), but many others, including Mn and radionuclides, may be trapped in PMs.

PM sampling is routinely performed on membrane filters. Several types of commercial filters are suitable for the determination of specific properties of atmospheric particles, in particular their mass, size and chemical composition. Among those, borosilicate, quartz and polyvinyl chloride (PVC) filters are widely used for determining the mass deposition and the concentrations. However, the most used materials for determining the PM composition are

cellulose acetate, polytetrafluoroethylene or Teflon™ (PTFE) and polycarbonate, selected based on its properties and the needs of the experimental protocol.

Elemental chemical analysis of PM is performed using sensitive analytical techniques such as Atomic Absorption Spectroscopy (AAS) (ISO 9855:1993- Ambient air - Determination of the particulate lead content of aerosols collected on filters - Atomic absorption spectrometric method, n.d) or inductively coupled plasma (ICP) optical emission spectroscopy. In recent years, ICP atomic emission spectrometry and ICP Mass Spectroscopy (MS) (Yang, Wan, & Foley, 2012) have replaced the traditional AAS methods for the analysis of a wide range of trace elements in PM. However, the use of these techniques presents many drawbacks related to potentially complex sample preparation procedures, mainly based on wet chemistry methods to achieve the most complete sample solubilisation possible. These types of procedures are quite expensive and time-consuming, and may present some limitations for PM analysis, as it has been shown for the microwave digestion method (Wang, Yang, & Ke, 1996).

Alternative techniques, such as energy dispersive X-ray fluorescence (XRF), offer the possibility of direct analysis and may overcome the above-mentioned disadvantages. In particular, XRF is considered suitable for PM analysis, and it yields to results comparable to ICP-MS (Yatkin, Gerboles, Borowiak, & Tanet, 2011). Total Reflection XRF (TXRF) is a highly sensitive surface elemental analysis based on a particular geometrical setup of XRF, that allows the detection of ultra-trace elemental levels in or below the ppb range. In this condition, an enhancement of the fluorescence signal of the sample occurs when a properly prepared sample is placed onto the surface of an X-ray reflector which is impinged with an X-ray beam at extremely grazing incidence angle, typically below the critical angle of the reflector, which minimizes the background, and its fluorescence signal is then efficiently collected by a detector placed at 90° a few millimetres above the reflector surface (Klockenkämper & von Bohlen, 2014). TXRF has recently emerged as a good alternative analytical technique in the environmental field (Borgese et al., 2009), and it has been applied so far to assess pollution levels in air (Bontempi et al., 2010; Borgese et al., 2012; Borgese, Zacco, Pal, Bontempi, & Lucchini, 2011), water (Borgese, Bilo, Tsuji, & Fernández-Ruiz, 2014; Marguí, Tapias, Casas, Hidalgo, & Queralt, 2010), soil (Bilo et al., 2014; Gallardo, Queralt, Tapias, Candela, & Margui, 2016; Margui, Iglesias, Camps, Sala, & Hidalgo, 2016), and bio-indicators (F Bilo et al., 2017; Bilo, Borgese, Zacco, Lazo, & Zoani, 2015; Bilo, Moscoso et al., 2015; Borgese et al., 2009). Literature reports the use of TXRF to analyse PM composition following different sample preparation procedures (De La Calle, Cabaleiro, Romero, Lavilla, & Bendicho, 2013), most of which include a solubilisation step to obtain the conventional liquid residue which is then deposited onto the sample carrier. Most of commercial TXRF spectrometers do not allow performing direct filter measurements due to a high risk of detector damage (contamination on the entrance windows, saturation, etc.). Recently, we have proposed an alternative procedure to prepare filter samples for their measurement in TXRF spectrometers, and demonstrated its suitability to analyse PM collected on PTFE membrane filters (Borgese et al., 2011, 2012). This procedure has been implemented automatically in a new device, that has been proposed for environmental pollution screening, using tree leaves as bio-monitors (F Bilo et al., 2017). This sample preparation method allowing for direct analysis leads to easier handling and storage of

delicate and thin samples including membranes. The key advantages are simplicity and rapidity of use. In addition, the samples remain unaltered and thus can be archived, allowing complementary investigations such as colorimetric measurements, 3D optical microscopy and additional non-destructive XRF analysis to be performed.

The present study is conducted in an area of the Brescia (Italy) province, where anthropogenic pollution has contaminated the air, soil and deposited dust with several elements including manganese. Moreover, an increased prevalence of Parkinsonism was observed in the vicinities of an industrial source, which was associated higher levels of Mn detected (Lucchini et al., 2007). Mn is a recognized neurotoxic agent and an element many times linked to neurotoxic effects (Spurny, 1996). Environmental monitoring may therefore play a relevant role in terms of preventive intervention and health risk assessment. The aim of this work is to validate elemental analysis of PM collected on membrane filters prepared to allow them to be analysed directly, by the complementary means of benchtop micro-XRF (μ -XRF) and TXRF instrumentation, and synchrotron radiation (SR) XRF at glancing incidence, in the context of a source apportionment study specifically following the relationship of airborne Mn concentration to distance from an industrial source.

2. Material and methods

2.1. Sample preparation

Airborne PM sampling was conducted within a larger study on the neurotoxic impact of metal exposure in children, workers and elderly (<http://ec.europa.eu/environment/air/quality/legislation/pdf/equivalence.pdf>, n.d.; Wang et al., 1996). Airborne PM₁₀ samples were collected on commercial 37 mm diameter PTFE membrane filters with low background for interference-free chemical determinations (SKC, Pennsylvania, USA), near an active ferroalloy plant located in Bagnolo Mella, a town in the province of Brescia, Italy. In this study, sampling was performed for 24 consecutive hours using 10 pm Personal Environmental Monitors (PEM) connected to Leland Legacy pumps (SKC, Pennsylvania, USA) (Borgese et al., 2011). Aerosol particles are sampled through a single-stage impactor to remove particles above the 50% cut-point of 10 pm in aerodynamic diameter. These larger particles are collected on a greased ring and are discarded after sampling. Particles smaller than the 50% cut-point pass through the impactor and are collected on the filter. Pre-calibration of pumps was performed at 10 l/min flow rate by using a soap-less piston primary calibrator with controlled post-sampling flow rate (Defender, BIOS, Butler, NJ).

Three sampling locations were set, respectively numbered #1, #2, and #3, at increasing distance from the plant, as shown in Fig. 1. Sampling site #1 is in the garden of a resident participant, where the pump was placed under a small shed, at about 2.5 m above the ground. Sampling site #2 is the Bagnolo Mella City-Hall, where the pump was located on a ledge on the second floor of the municipal building. Sampling site #3 is the primary school of Bagnolo Mella, where the pump was connected to a window with outwards flap opening at the second floor of a building, protected only by the upper side of the window. The sampling was performed simultaneously at the three locations, collecting one filter per location. At the end of the sampling period, the filters were transferred to the laboratory in clean plastic envelopes.

A standard filter produced by the U.S. National Institute of Standards and Technology (NIST-SRM 2783) was used as a multi-elemental standard reference material (SRM). The amount of PM_{2.5} deposited onto the reference filter is in the range of concentrations regularly found in a urban industrial site.

Each filter was processed with the SMART STORE™ (Xear Pro S.r.l, Italy), a new automatic device for sample preparation, classification and storage. This system includes a sample inlet, packaging, and cutting system, coupled with a QR code printer for sample labelling and classification in a database accessible by remote connection to personal computers and mobile devices. Filters were sandwiched between two thin adhesive sheets of polypropylene (Xear Pro S.r.l, Italy) with possible impurities of S and Hf, and cut in a circle of 30 mm diameter. The obtained disc was placed onto a quartz reflector carrier for TXRF measurements (Borgese, Zacco, Pal, Bontempi, Lucchini et al., 2011; Borgese et al., 2012) and fixed with re-positioning spray glue (Spray Mount, 3M, USA).

2.2. Experimental setups

2.2.1. 3D optical profiler—A non-contact 3D optical profiler (S-neox, Senssofar, Barcelona) was used to investigate the particle distribution on filter #1 surface. The instrument sensor head combines confocal, interferometry and focus variation techniques for depth resolution. The confocal scanning has no moving parts, but uses a micro-display technology based on ferroelectric liquid crystal on silicon, that allows a rapid and stable scanning of the confocal images. The optical core mounts different LED light sources: red (630 nm), green (530 nm), blue (460 nm) and white. The result is colour-coded depth information determined from the chromatic depth distortion of the microscope objective, leading to a pseudo-colour qualitative topography map. Confocal RGB images are collected with a bright field objective (20 x, NA 0.45, working distance 4.5 mm, epi-illumination setup). The spatial sampling is 0.69 μm (pixel size on the surface) and the optical resolution is 0.31 μm (line and space, half of the diffraction limit according to the Rayleigh criterion. Values for blue LED).

2.2.2. μ - XRF spectrometer— μ -XRF was used to map the elemental distribution of PM deposited on the filter #1. Measurements were performed at the laboratory of Osaka City University (Japan). The instrument is equipped with a metal-ceramic X-ray tube with a Mo anode (MCBM 50–0.6B, rtw, Germany) operating at 50 kV and 0.35 mA. The focal spot size at the anode was $50 \times 50 \mu\text{m}^2$. Irradiation time was 100 s per pixel. Near the X-ray tube was attached a full poly-capillary X-ray lens, which focused the primary X-rays to a diameter of 10 μm at the sample position. The working distance was about 2 mm and the X-ray energy was 17.4 keV. Fluorescence radiation was measured by a Silicon-Drift Detector (SDD) with a sensitive area 10 mm^2 , energy resolution < 150 eV at 5.9 keV (Liu, Imashuku, & Kawai, 2013). X-Y-Z motor stage was used to determine the position of the sample to be analysed. The scanned area was $500 \times 500 \mu\text{m}^2$.

2.2.3. Benchtop TXRF spectrometers—TXRF measurements were performed with two benchtop TXRF spectrometers, the S2 PICOFOX (Bruker AXS Microanalysis GmbH, Berlin, DE) and the 200TX (Oursstex, Japan), by irradiating the samples 600 s live time. The

S2 Picofox is equipped with a Mo tube, operating at 50 kV and 750 μ A, a multilayer monochromator (17.5 keV), FWHM 139.43 eV and a 10 mm² SDD. The incident X-ray beam is 7 mm wide with an incidence angle lower than 0.1°. The spectral fitting and deconvolution was performed by the SPECTRA instrument software after manual identification of the elements. The net peak area of Mn K_{alpha} fluorescence line is calculated after background subtraction.

The non-monochromatic 200TX portable spectrometer is equipped with a W tube operating at 50 kV and 0.175 mA and air cooled SDD with 10 mm² active area. The maximum excitation energy is 9.5 keV (Liu et al., 2013). The incident rays were restricted to 10 mm width using by a waveguide slit at a grazing angle of 0.07° and a sampling area of 10 mm length by 8 mm width. Manual calibration and element identification is provided. Spectra are processed with Origin software to extract the net peak area of Mn K_{alpha} line.

2.2.4. SR-XRF—The measurements were performed at the X-ray Fluorescence beamline at Elettra - Sincrotrone Trieste[†] (Italy)(Jark, Eichert, Luehl, & Gambitta, 2014), in a seven-axis diffractometer setup, operated under vacuum (Lubeck et al., 2013). The reflected intensity was registered by a photodiode detector (Si-photodiode, Hamamatsu) and the fluorescence radiation was collected by a SDD detector of 30 mm² active area (X Flash, Bruker), equipped with an API3.3 window and an electron trap, placed at 10 mm from the sample surface. Each sample was positioned at precisely 1° with respect to the incident x-ray beam. The beam was monochromatized by the use of a Si(111) set of crystals, to an excitation energy up to 14keV. Even though this study is mainly focused on Mn, the whole available energy range was used, to compare with benchtop instrumentation. In the sample plan normal to the beam, the beam size was about 200 by 100 μ m (horizontal $\times$ vertical). The beam spectral purity was ensured by the use of a higher order suppressor. Three consecutive areas (without any superposition) with height equal to the beam height (100 μ m) were measured for each three samples and for the SRM, with an acquisition time set to 600 s live time. PyMca 4.7.3 software was used to analyse the spectra (Solé, Papillon, Cotte, Walter, & Susini, 2007). The identification of all elements in presence inside the spectrum was performed manually and the net peak area of Mn K_{alpha} was determined by spectra fitting.

3. Results and discussion

Previous studies on soil, vegetables (Bontempi et al., 2010) and indoor deposited dust (ISO 9855:1993 - Ambient air - Determination of the particulate lead content of aerosols collected on filters - Atomic absorption spectrometric method, n.d) revealed that the concentration of heavy metals in the neighbourhood around the active ferroalloy plant is higher with respect to other areas in the Brescia province. This fact may be related to several other anthropogenic industrial activities of the area(Borgese et al., 2013; Borgese, Zacco, Pal, Bontempi, Lucchini et al., 2011; Lucas et al., 2015; Zacco et al., 2009), and for the sake of clarification a dedicated source apportionment study is currently undergoing.

Several characteristic features of PM can be used to evaluate the causal effect between air pollution and potential emission sources, such as their morphology and chemical

composition. As it was shown by Götschi (Götschi et al., 2005)(Götschi et al., 2005) in a study on PM level in 21 cities within the European Community Respiratory Health Survey, anthropogenic pollution and crustal element sources are the two key factors responsible for the chemical composition of PM in air.

A first morphological assessment was undertaken. Fig. 2 shows the 3D optical profile image of sample #1, highlighting a heterogeneous distribution of particles size, recognizable as the metallic-looking cylinders, ranging approximately from 1 to 50 μm . Our data are in a good agreement with those reported by Marris, Deboudt, Flament, Grobety, & Gieré (2013).

The μ -XRF maps in Fig. 3 show the fluorescence distribution of Fe, Ca, Mn, and Si in a $500 \times 500 \mu\text{m}^2$ area for sample 1. These elements were selected as they are the fingerprints of industrial and natural sources. At a first sight, it can be noted that Si is present only in a few aggregates or spots within the surface probed. Fe instead is not homogeneously distributed all over the scanned area of the filter, with small round shape spots with higher concentration mostly jointly with Mn. Generally speaking, the larger spots may be related to the presence of smaller/finer particles widespread more uniformly on the filter surface. A deeper analysis shows distinct distribution patterns of the elements with nodules of high concentration in the same position, highlighted with coloured circles. The coexistence of Fe, Ca and Si entails the common origin of these particles. Both natural and anthropogenic sources may affect the presence of Ca, Fe and Si in the PM. The presence of these elements may be related to vehicular emissions and suspended road dust (Cesari, Donateo, Conte, & Contini, 2016), likely confirmed by the geographical and urban conformation of the area. In addition, construction and demolition activities can increase the Ca concentration (Gugamsetty et al., 2012). However, a study on source apportionment using positive matrix factorization analysis in central Italy reported that crustal element such as Fe, Ca and Si may also be transported by wind-blown dust. It is interesting to note the presence of the highest amount of Fe and Mn at the same position, most probably due to their coexistence in a bigger particle. Indeed, in a previous study, we found high concentrations of Fe and Mn in air PM filters collected in the environment surrounding a similar industrial plant (Borgese, Zacco, Pal, Bontempi, Lucchini et al., 2011). Another study performed in France reported the presence of Mn and Fe with different oxidation states and Mn/Fe elemental proportion as measured at incremental distances from the chimney source of a metallurgic plant, as these particles evolved during their atmospheric transport (Marris et al., 2013). Therefore, this strongly support the hypothesis of the causal effect relation with the emissions from the ferroalloy plant of this area.

If μ -XRF analysis revealed the chemical composition of PM deposited on the filters, it did not bring any information about the total elemental mass loaded on the filter. Therefore, the samples were analysed with XRF in grazing incidence configuration with SR (SR-XRF) and benchtop TXRF instrumentations. TXRF is preferred due to the improved sensitivity and low background noise with respect to the conventional XRF geometry (Borgese, Bilo, Tsuji, Fernandez-Ruiz et al., 2014), but the features of filter samples do not allow to achieve total reflection conditions (total sample flatness, infinitively thin homogeneous deposition, highly reflective substrate, etc.). Indeed, no difference in the resulting spectrum was observed positioning the sample on the quartz glass or as stand-alone in the sample holder. In this

condition, we were not in the total reflection regime but in a grazing incident regime, where some of the main advantages of TXRF remains due to the geometry of the setup, with its incident angle spraying the beam over a wide area and its detector position close to the sample which improves the solid angle of fluorescence emission collection. However, for simplicity, we will always refer to “TXRF measurements” when dealing with benchtop instrumentation in the following text. Measurements of one central circular segment, and three adjacent circular segments are performed with TXRF and SR-XRF respectively.

Fig. 4 shows, as an example, the spectra obtained by SR-XRF at three different positions on sample 1. The same elements are identified in all the three collected samples: Al, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Pb; while in the SRM Al and V are absent. Different peak heights corresponding to different elemental mass loaded on the three analysed areas are observed. The comparison of Mn K_{α} peaks obtained in three positions of the same filter surface are reported in Table 1 with the average value and the relative standard deviation (RSD) calculated for each dataset. It is clear that the inhomogeneity increases with mass deposition, as it can be expected considering the morphology of PM, the composition of the bigger particles, and the width of circular segments, equal to 100 μm . The limit of detection for Mn, calculated from the measurements of the SRM, is 46 ± 6 ng, higher than the corresponding value reported in (Borgese, Zacco, Pal, Bontempi, Lucchini et al., 2011). This is most probably related to the very low intensity of the peak, due to the small excited area. The better homogeneity is observed for the SRM, which may be also due to the lower aerodynamic equivalent diameter of the collected particles, 2.5 instead of 10. Indeed, great dispersion in the particles size also impacts the XRF spectrum as the emission is more anisotropic. Notwithstanding this, the total mass deposited of Mn on the whole filter surface was calculated and was found to decrease with the distance from the ferro-alloy plant, confirming the high causal effect relation between this emission source and content of Mn in the surrounding environment and highlighting the suitability of the proposed approach.

From a quantitative point of view, to achieve a higher precision and a more realistic representation of the mass deposition on the filter, a wider filter area must be irradiated. Two different benchtop TXRF spectrometers were used to analyse the same sets of filters. Fig. 5 shows the spectra collected by the Mo X-ray tube spectrometer. The following elements K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb, are identified in all the three samples. The highest peak heights are found for sample 1, which has, as expected, the highest mass deposition. However, not all the elements present a decreasing trend from sample 1 to sample 2 and 3. In particular, Zn and Pb are higher in sample 3 than in sample 2. The same set of elements, except Cu and Pb, are identified in the measurements collected with the W X-ray tube spectrometer, with significantly lower intensity, three orders of magnitude lower net areas values, as reported in Table 2. The Mo TXRF has a better resolution of the Mn K_{α} peak equal to 144 eV and constant with respect to the W TXRF presenting increasing values from 192, 196, and 348 eV for samples #1, #2 and #3 respectively. In both cases, the fluorescence signal of Mn (see Fig. 5b and Fig. 6b) shows the already observed trend, maintaining the respective relative ratio, as it is clear from the normalized values reported in Table 2. This confirms again the previous causal effect relationship with the identified emission source. The good replicability of measurements obtained between the two TXRF spectrometers

datasets is an indication of the better representativeness of this kind of measurements with respect to elemental mass depositions. The correspondence between the data sets obtained by different XRF techniques is noteworthy, and strongly supports the relevance of the proposed method for sample preparation and direct XRF analysis.

Particles shape and size are heterogeneously distributed on the filter surface. Samples as prepared are easily measured with different XRF configurations such as μ -XRF, SR-XRF, and benchtop commercial TXRF spectrometers. Although with some differences, mainly due to the spectrometers' configurations, results are consistent and reproducible. Obviously, the presence of the polymeric foil increases the overall sample thickness, and may introduce absorption effects, affecting detection limits, but it has no influence on the outcome of the experiment, especially when a larger beam is used. Spectrometers with a larger X-ray beam irradiated area provide a better representativeness of elemental determination of particles deposited on filter. For this reason, these are used for semi-quantitative analysis. In this context, further studies will be devoted to develop appropriate external calibration algorithm to improve the accuracy of the quantitative elemental analysis, and comparison with reference techniques like ICP.

4. Conclusions

This study shows the suitability of the sample preparation with SMART STORE™ followed by direct XRF measurements for elemental analysis of PM collected on PTFE membrane filters. The potentialities of this novel approach for screening purposes as well as qualitative and semi-quantitative analysis are demonstrated considering different XRF configuration spectrometers such as μ -XRF, SR-XRF, and benchtop TXRF spectrometers equipped with Mo and W excitation sources.

PM shows a heterogeneous distribution on the filter surface, as anticipated. The source apportionment study, though limited to a few samples and sampling sites, reveals distinctive trend on the element repartition, compatible with causal effect relationship between the metallurgic plant emission source and vehicular suspended road dust. Results of SR-XRF confirm the inhomogeneity of PM distribution and the need of a wider irradiated area for a better representativeness of the total elemental mass deposition. The benchtop spectrometers show highly consistent results, notwithstanding the different experimental setups. The good agreement among the results obtained with the different geometry of XRF setups strongly highlights the suitability of the proposed sample preparation method.

Although the proposed approach presents some limitation, the direct XRF analysis of the filters prepared with SMART STORE™ present appreciable advantage: it is non destructive, and allows a fast and easy surface analysis. These features make it suitable and the only presently available method to perform direct analysis of PM collected on filter membranes for screening purposes of environmental pollution assessment with commercial TXRF spectrometers. Further studies will be dedicated to improve the accuracy of quantitative analysis. A dedicated calibration procedure will be further developed to obtain accurate and precise results.

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Fig. 1.
Map of sampling area: residential garden (#1), city-hall (#2), primary school (#3), point source (circled).

Fig. 2. Surface morphology of sample 1 analysed with 3D optical profiler in an area of $877.2 \times 660.5 \mu\text{m}^2$.

Fig. 3.

Chemical maps showing the Fluorescence intensity distribution of a) Fe, b) Mn, c) Ca and d) Si on the surface of sample 1. The scanned surface is $500 \times 500 \mu\text{m}^2$. Based on the relation between fluorescence intensity and mass, red and blue colours represent the highest and lowest element mass, respectively. Coloured circles highlight the different elemental combination observed in the same area of the filter: black: Fe, Mn and Si; white: Fe spots; yellow: Mn and Ca; red: Ca and Si; green: Mn, Ca, and Si. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Fig. 4.
SR-XRF spectra collected on a) Sample 1, 2 and 3, and b) SRM.

Fig. 5.

a) Spectra of samples 1 (black), sample 2 (red), and sample 3 (blue) obtained by the Mo X-ray tube TXRF spectrometer; b) enlargement of the energy region comprising Mn Kaipha line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6.

a) Spectra of samples 1 (black), sample 2 (red), and sample 3 (blue) obtained by the W X-ray tube TXRF spectrometer; b) enlargement of the energy region comprising Mn K α line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Results obtained from SR-XRF measurements at three different positions (a, b and c) on the SRM, sample 1, sample 2 and sample 3. Net areas of Mn K_{alpha} line, the calculated average values, RSD and the corresponding mass deposited with standard deviation are reported in the 3rd, 4th and 5th columns.

Sample	Net area	Average	RSD %	Mass (µg)
SRM-a	3.7	3.3	10	0.32 ± 0.01 ^a
SRM-b	3.0			
SRM-c	3.3			
1-a	377	272	52	27 ± 14
1-b	329			
1-c	109			
2-a	141	129	53	10 ± 5
2-b	56			
2-c	191			
3-a	15.7	12.9	27	1.1 ± 0.3
3-b	13.8			
3-c	9.1			

^a certified value.

Table 2

Results obtained from benchtop TXRF spectrometers measurements of sample 1, sample 2 and sample 3. Net areas of Mn K_{alpha} line and the corresponding normalized value for Mo- and W-X-ray tube are reported.

Sample	Mo X-ray tube		W X-ray tube	
	Net area	Normalized area	Net area	Normalized area
Sample 1	5,118,334	100	2313	100
Sample 2	942,330	18	528	23
Sample 3	65,745	1	52	2