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A new non-destructive method for chemical analysis of particulate matter filters: The case of manganese air pollution in Vallecamonica (Italy)

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ABSTRACT

Total Reflection X-ray Fluorescence (TXRF) is a well-established technique for chemical analysis, but it is mainly employed for quality control in the electronics semiconductor industry. The capability to analyze liquid and uniformly thin solid samples makes this technique suitable for other applications, and especially in the very critical field of environmental analysis. Comparison with standard methods like inductively coupled plasma (ICP) and atomic absorption spectroscopy (AAS) shows that TXRF is a practical, accurate, and reliable technique in occupational settings. Due to the greater sensitivity necessary in trace heavy metal detection, TXRF is also suitable for environmental chemical analysis. In this paper we show that based on appropriate standards, TXRF can be considered for non-destructive routine quantitative analysis of environmental matrices such as air filters. This work has been developed in the frame of the EU-FP6 PHIME (Public Health Impact of long-term, low-level Mixed element Exposure in susceptible population strata) Integrated Project (www.phime.org). The aim of this work was to investigate Mn air pollution in the area of Vallecamonica (Italy).

1. Introduction

Particulate matter (PM) represents a hazardous air pollutant that is recognized to have negative health impacts such as increased mortality and morbidity from respiratory and cardiovascular diseases [1]. Although specific mechanisms are not known, a number of studies have demonstrated that exposures to various air pollutants are associated with reductions in lung function and growth, asthma, allergic rhinitis and respiratory infections in children [2].

PM can be composed of a variety of materials including inert carbonaceous cores with multiple layers of various adsorbed or mixtures of many materials including metals, organic vapors, acid salts and biological elements such as endotoxins, allergens, and pollen fragments [3].

Particle size and particle composition are the main properties responsible for the impacts on human health, with particle composition influencing its toxicity [4]. Burnett et al. [5] found that daily mortality in eight Canadian cities was more strongly associated with the constituents of fine PM than the fine mass alone.

Urban PM has been found to contain significant amounts of metals [6], which may mediate the health related effects of PM exposures, as demonstrated in a number of studies [7–9]. Bioavailable metals in airborne PM have been particularly associated with enhanced airway hyperresponsiveness, altered immune resistance and pulmonary inflammation [10].

Heavy metals such as Cd, Hg and Au have been shown to have immunotoxic effects and be potent inducers of autoimmunity [11,12], which may lead to the onset and/or exacerbation of autoimmune diseases such as Type 1 diabetes, multiple sclerosis, systemic lupus erythematosus, rheumatoid arthritis and Parkinson's disease [13,14].

The effects of PM exposures on certain vulnerable populations, such as the elderly, those with compromised cardiopulmonary health, and children, are of particular concern for public healthcare institutions.

PM is routinely collected on filters and subsequently analyzed gravimetrically and/or by chemical analysis. Several techniques are available for compositional analysis, including atomic absorption spectroscopy (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), ion chromatography [15] and voltammetry [16]. The analysis of PM filter samples requires involved digestion procedures, making routine analysis expensive and time-consuming.

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Moreover, this analytical preparation may alter the elemental composition of the sample, by increasing the content of some elements by contamination or decreasing the content of some elements by losses, for example due to chemical reaction or degradation.

Current European Directives concerning air pollutant sampling and analysis [17,18] have established reference methods for heavy metals, including graphite furnace atomic absorption spectroscopy (GFAAS) and ICP-MS methods [19]. Energy dispersive X-ray fluorescence (EDXRF) has been used for many years for the direct analysis of aerosol filter samples. Detection limits can be found in Refs. [20,21]. However, other methods may be used if they yield equivalent results to the reference methods. Due to continued research and development [22], Total Reflection X-ray Fluorescence (TXRF) analysis has become a well-accepted chemical technique for quality control in the semiconductor industry [23]. The reflection of X-rays close to the critical angle makes this technique extremely sensitive with improvements in limits of detection. The development of compact and more sensitive instruments offers new opportunities for further improvement of this technique. TXRF appears particularly promising for environmental analysis, especially when heavy metals must be detected at very low concentrations, in the range of ng/m^3 [24]. Several reviews are available, providing detailed information on the TXRF technique and its main applications [25–27] including its use in environmental analysis [28].

TXRF has been reported as an alternative technique to monitor air particulate composition. This technique requires only microgram amounts of sample, much less than that needed for ICP-MS analysis [29,30].

Recently, we have reported [31] that the direct analysis of PM filters without the delay and difficulty posed by digestion needs much shorter preparation time (from hours to minutes) and provides reliable results. The analysis of solid samples by TXRF can be performed directly on particles (suspension or slurry of finely powdered materials), on thin foil or on deposited material. In this manuscript we show that TXRF can be a good alternative to other standardized methods for PM filter analysis. In particular, we introduce a new method for samples analysis that was recently patented [32].

This method offers the possibility to analyze filter samples without digestion, making TXRF extremely competitive compared to other techniques such as AAS and ICP. This approach allows non-destructive analysis of filters to obtain quantitative information about heavy metals in airborne particles [31,33]. However, it requires suitable reference samples to convert the measured fluorescence intensities into concentrations.

The proposed method was applied to investigate the concentration of manganese (Mn) in air filters sampled in the Italian province of Brescia (see Fig. 1). Samples were collected both in the pre-Alps valley of Vallecamonica in the vicinity of Mn–Fe-alloy industries and in a reference area in the southeastern Garda Lake area of the province. This exposure assessment was part of the previously mentioned EU-FP6 Integrated PHIME Project.

2. Materials and methods

2.1. Air filter sample collection

Atmospheric aerosols were collected on commercial filters (37 mm diameter, PTFE-Teflon) for PM$_{10}$ in selected municipal districts of Brescia, one of the largest provinces in the Lombardia Region of Italy, with a total land surface area of 4784 km^2. The filters were collected with personal samplers on volunteer student adolescents. The samplers used were 10 μm particle diameter cut-point Personal Environmental Monitors (PEMs) of 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 of 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, the 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. Samplers were kept in a special case that reduces the noise significantly. 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 [14] an increased prevalence of Parkinsonism was observed in the vicinities of Mn–Fe-alloy plants located in Vallecamonica, a narrow valley in the pre-Alps in the northern part of the Brescia province which once contained three active Mn–Fe-alloy foundries. Based on the results of an initial environmental survey, the potentially most polluted areas for Mn in the Brescia province have been selected [34] and a total of 188 filter samples were collected and analyzed. They included 31 samples collected in the village of Breno, located in the central area of Vallecamonica. Breno was the site of one of the largest and most active of these foundries that operated from 1902 until 2002. In addition, 94 samples were collected in other municipal districts

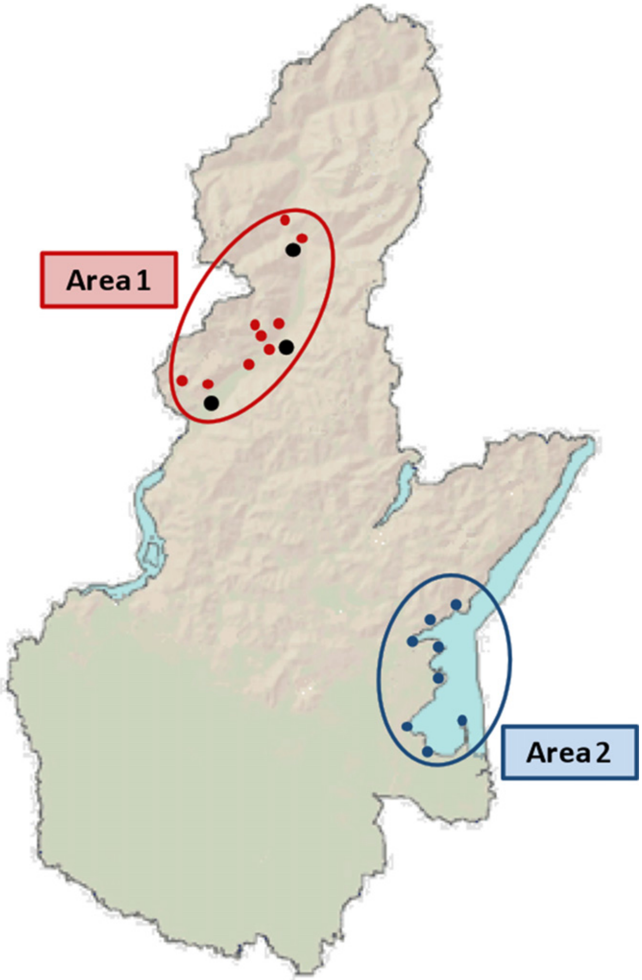

Fig. 1. Map of Brescia province. The red points indicate Breno (the most polluted municipal district for Mn presence) and surrounding valley sampling locations (area 1). Blue points represent locations where samples were collected in the Garda Lake reference area (area 2). Black points show the location of the Fe-alloy plants. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of Vallecamonica, and 63 samples were collected from the Garda Lake area, a tourist area in the southeastern corner of the province, where there are no industrial sources of metals and thus, it was considered as a reference area. The samples were collected during the entire 2008–2009 school year from September to June. To yield good comparison between the two areas of Vallecamonica and the Garda Lake, sampling was scheduled alternatively in the two areas every other week.

Fig. 1 shows the site locations in the Brescia province. Red points, in area 1, indicate the investigated municipal districts of Vallecamonica (for example Breno, where the highest level of Mn was detected). Blue points show the location of samples in area 2 (Garda Lake reference area). Black points show the location of the Fe–Mn-alloy plants.

2.2. Filter preparation and analysis by TXRF

The prerequisite to perform quantitative analysis by TXRF is a minute amount of sample placed as a thin flat layer or a thin-film-like sample on a clean carrier so that matrix effects are negligible. This is a condition that can be fulfilled for particulate filters prepared in the following manner.

In this work a new approach that was recently patented (Pat. #: PCT/IT2008/000458), is proposed: the filter is sandwiched between two thin sheets of polypropylene, each with a thickness of 125 μm, to obtain a thin sample that can be directly placed onto a quartz glass sample carrier and inserted in the instrument for measurement. As it will be shown in this work, the proposed method has the following advantages: it is simple and fast; 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 which allows improved limits of detection in determining the composition of the particulate matter deposited on the filters; the samples remain 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. Finally, intensity is enhanced at the glancing angle, because the samples were sandwiched with low-density material, i.e. as organic films [35]. This is the novelty of the proposed procedure.

The measurements were performed with the portable Bruker TXRF system S2 PICOFOX, air cooled, molybdenum (Mo) tube, Silicon-Drift Detector, with operating values of 50 kV and 1000 μA. This low rating makes it possible to use a simple air-cooling. The small portable generator produces the necessary energy for the equipment. This spectrometer is fitted with a Peltier-cooled X-Flash detector. The compact devices are safe and can easily be operated. This spectrometer is able to detect a wide range of elements rapidly, simultaneously and quickly; in the present case the acquisition time was 600 s.

The PICOFOX software facilitates calibration, evaluation, and storage of the data. Low detection limits (a few ng/cm^2) can be achieved for elements with atomic numbers greater than 13 (aluminum). The software database contains the fluorescence reference spectra of almost all the detectable elements. All the series excitable by the Mo tube are considered, and the ratios between intensities are tabulated: for example, for Pb, the M and L series are considered and for As and Rb, the K and L series are considered. The quantification procedure is performed by the software on each measured spectrum; peak area is calculated (after baseline subtraction) and the concentration of each element is obtained.

2.3. Preparation and use of reference filter

To evaluate the absolute concentration of the elements in the filters, we used as an external standard reference the air particulate standard filter produced by the U.S. National Institute of Standards and Technology (NIST-SRM 2783). The material deposited on this standard filter is representative of that collected in a typical urban industrial area [36]. The NIST-SRM 2783 filter was prepared for TXRF analysis in accordance with the previously mentioned method (see Section 2.2), with the filter being sandwiched between two thin polypropylene sheets.

The quantitative analysis was performed using the NIST-SRM 2783 as a multielemental reference. The area of each element's peak, of the measured standard filter spectrum is related to the certified surface concentration (ng/cm^2) of the specific element. We can consider the peak area of each metal present in the standard as a reference to evaluate the quantity of the same element in the collected filters. The peaks areas of the analyzed filter sample spectra are compared with those of the standard to evaluate the surface concentration of each element in the collected filter samples.

As the elements are identified and quantified by means of the area of their fluorescence peaks, the lowest detection limit (LLD) of each element can be defined on the basis of a statistical inspection of the peak area and the subjacent spectral background. An element is considered to be detected if the peak area is three times larger than the area of the background, following the so-called "three-sigma" procedure.

The LLD of each element in the present work is calculated as the average of five LLDs obtained for five measures of the NIST-SRM 2783. The obtained LLDs are reported in Table 1. We can see that LLD values are of the order of a few nanograms for all the elements, except for Ba, whose value is about 200 ng. This can be ascribed to the partial superposition of the Ti and Ba fluorescence peaks.

Table 1
Detection limits of elements, for air particulate matter filters, calculated considering five measures of the Standard Reference Material NIST 2783.

Element	LLD (ng)
Ti	31
Cr	15
Mn	14
Fe	11
Ni	7
Cu	6
Zn	4
Rb	6
Ba	211
Pb	4

The total amount of each element present on the entire filter sample surface is obtained by multiplying the PM covered filter surface area by the calculated surface concentration in ng/cm^2. Then, the air concentration (ng/m^3) is calculated using the air volume collected for each sample. The virtual absence of matrix interference makes the quantification more reliable than that achievable by conventional techniques.

3. Results and discussion

In a common procedure for TXRF quantitative analysis [37], filter samples are digested with nitric acid in a microwave oven and gallium is added, as the internal standard, to quantify the elemental concentrations. Filter samples can also be analyzed with two other reference methods: (1) ICP-MS [38] and (2) AAS [39], but in both cases sample digestion is required.

For liquid samples, the calibration is performed adding a known quantity of metal to the solution and analyzing a micro-droplet residue deposited on a sample carrier. In the case of solid samples, standard film samples can be used [33].

Table 2
Comparison between certified mass of elements deposited on filter sample 2783 and the absolute quantification performed on Standard Reference Material NIST filter 2783, on the basis of TXRF spectra (see Fig. 2). Cu (404 ng) was taken as an internal standard.

NIST-SRM 2783		
Element	Certificate values (ng)	TXRF results (ng)
Ti	1490 ± 240	1032 ± 84
Cr	135 ± 25	141 ± 15
Mn	320 ± 12	250 ± 6
Fe	26500 ± 1600	24688 ± 746
Ni	68 ± 12	57 ± 5
Cu	404 ± 42	Internal standard
Zn	1790 ± 130	2037 ± 74
Rb	24 ± 5.5	25 ± 3
Ba	335 ± 50	410 ± 92
Pb	317 ± 54	346 ± 30

The advantage of the new method described in this paper is the elimination of the need for the lengthy, sample destructive and possibly result-modifying method of sample digestion.

Fig. 2 shows the TXRF spectrum collected on the NIST-SRM 2783. The presence of Si, S, Pb, Sr, Ba, Br, As, Se, Zn, Ni, Cu, Fe, Mn, Cr, Ti, Ca, K, and Cl is evident. It can be seen that TXRF is quite sensitive to metals: indeed, Ni and Rb peaks (with a concentration respectively of 6.8 and 2.4 ng/cm^2) can be detected. In addition, the large difference in concentration ranges of the metals does not affect the measurement, yielding quantification from integrated area calculation, without the need of dilution or concentration procedures. In the TXRF spectrum shown in Fig. 2 several peaks overlap (Sr, Rb, and Si). Also, As overlaps with Pb, Ba overlaps with Ti, and Mn overlaps with Fe. The PICOFOX software takes into account the possibility of peaks overlapping (see Section 2.2), however in some cases it can lead to over- or under-estimation of signals of lower concentration elements.

The mass values, of some selected elements (Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Ba, and Pb), certified in the NIST-SRM 2783 data sheet are compared in Table 2 with those obtained by our TXRF analysis method, using Cu as internal standard. All the values are reported with their absolute error.

Most of the reported values are in very good agreement. However in the case of Mn the agreement between the two data is not satisfactory, probably because of a partial overlapping of Mn and Fe peaks. The average relative difference for the nine elements (not including Cu, which was used as an internal standard) is 13%. Nonetheless the calculated concentrations, ranging from a few ng/cm^2 (for Ni and Rb) to μg/cm^2 (for Fe), are in agreement with those expected for elements that are typically abundant in urban particulate matter.

Thus, this quantification process appears to be reliable; however overlapping peaks may make detection of elements that are in very low concentration more difficult.

The high signal/background ratio is mainly due to the low matrix contribution in the TXRF pattern. The chemical information in this approach is similar to that obtained by standard sample analysis after digestion [31]. However, the analysis of a significant filter area compared with the analysis of one drop of a few microliters of digested filter allows a signal increase, together with an increase in the detection of very low amounts of contaminants. Moreover, insoluble phases, that may have been lost during a sample digestion procedure, are directly measured with the other filter components.

There is no paper in the literature dealing with direct TXRF analysis of filter samples, but recently the first direct analysis of standard particulate matter on air filters was reported by Wang et al., using Synchrotron Radiation X-ray Fluorescence (SRXRF) [40]. In this work, filters containing several micrograms (e.g. 150 μg for Ca and Fe) were analyzed. This work is very interesting because it shows experimentally that, for some elements (such as Ca and Fe) with higher concentrations in particulate matter on filters, the intensity versus metal concentration exhibits a linear behavior until the mass is about 50 μg of material. For the elements with lower concentrations, with respect to the previous ones (for example Ti and Pb), the calibration curve is linear until the mass is in the order of 5 μg. Considering the certified masses of the elements reported in Table 2 for the NIST-SRM 2783, we can verify that these masses are in the range of a linear calibration curve: for Fe about 26 μg and for Ti about 1 μg; Pb is less than 1 μg. The metal concentrations for the samples reported by Wang et al. [40] are generally much higher than those usually found in PM filters, such as the NIST-SRM 2783 as well as our experimental filters from this study.

These considerations suggest that the proposed TXRF technique proves much more suitable for filters with lower amounts of particulate matters. The advantage of TXRF is that elements can be effectively analyzed from a sample either with a shorter collection time, a lower sampling flow rate or a lower ambient concentration. In addition, since this analysis method is non-destructive, the filter can be archived for later alternate analysis methods.

In Fig. 3 the TXRF spectrum of the NIST-SRM 2783 standard filter is compared with that of a filter sampled in Breno. Some of the metal concentrations in the Breno samples are 1.5–2 times higher with respect to the standard (see for example Fe and Zn peaks), while for some other elements (Cu, Ni and Cr) they are comparable. Mn shows an integrated area 4–5 times larger than the standard (see magnification of Fig. 3).

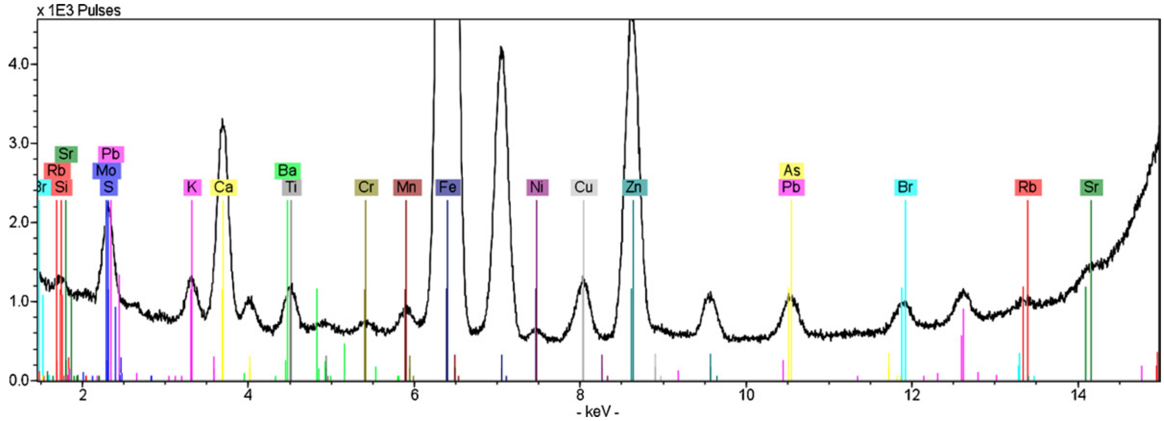

Fig. 2. TXRF spectra collected on standard filter sample by NIST, treated in accordance with PCT/IT2008/000458. The presence of Si, S, Pb, Sr, Ba, Br, As, Se, Zn, Ni, Cu, Fe, Mn, Cr, Ti, Ca, K, and Cl is evident.

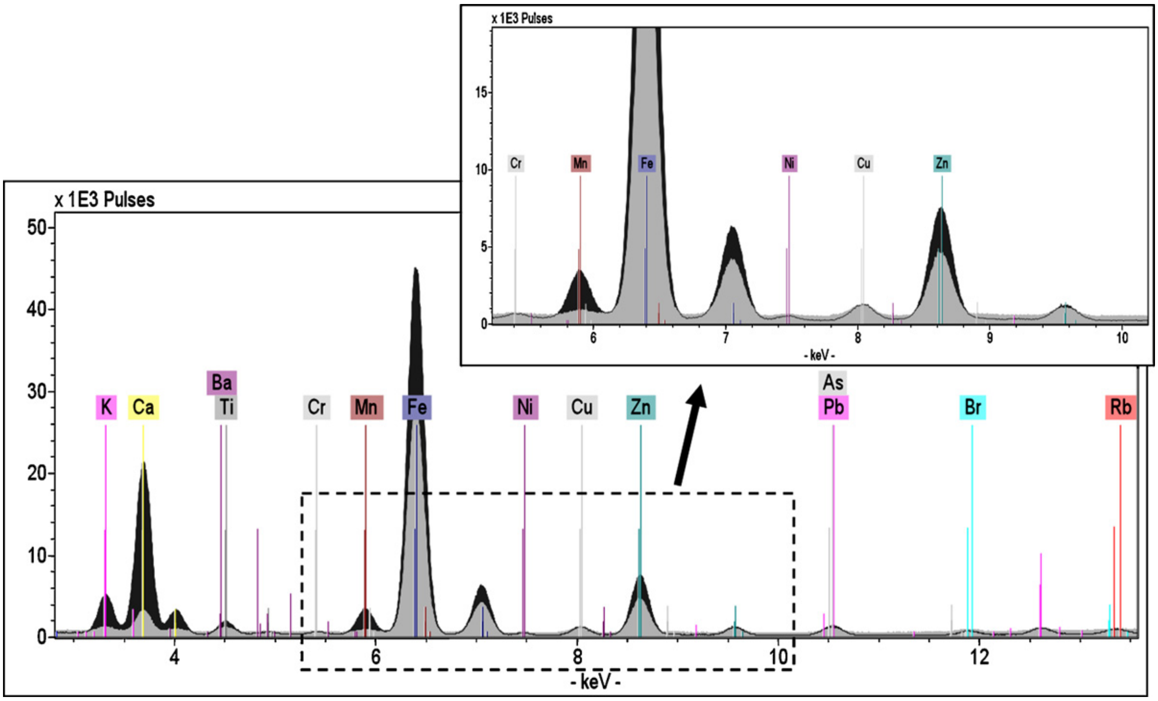

Fig. 3. Direct comparison of spectra collected on the NIST standard filter (gray) with that collected on sample 22 (taken in Breno) (dark gray), showing concentrations of many metals about 1.5–2 times higher on sampled filter, with respect to the standard one (see for example Fe, and Zn peaks). Other elements (Cu, Ni and Cr) are comparable in intensities (Mn shows an integrated area larger by 4–5 times in relationship to the standard concentration (see magnification).

Since the PHIME Project focuses primarily on Mn exposure assessment, the integrated area of the TXRF spectra Mn peak of the NIST-SRM 2783 filter is compared to that of the other filter TXRF patterns in order to obtain the estimated Mn surface concentrations in the collected samples.

The analysis and quantification are performed for 188 samples. The Mn mass concentration in the air is calculated considering the pump flow rate and sampling time of 24 h and the results are shown in Fig. 4. The samples are divided into two groups: area 1 which includes the samples collected in the municipal districts of Vallecamonica, shown in alphabetical order; and area 2 which includes the samples of the Garda Lake area taken as the less-polluted reference area. The figure shows the highest Mn concentrations in Breno, site of the former largest and most active of the three former Fe–Mn-alloy plants. Values elevated above the reference area levels are also seen in Cedegolo, Darfo Boario and Esine, all of which are situated near one of the three foundries. The Mn values obtained in the areas where metallurgical plants were active are, on average, twice or three times larger than those obtained in the Garda Lake reference area. These results are in accord with the preliminary

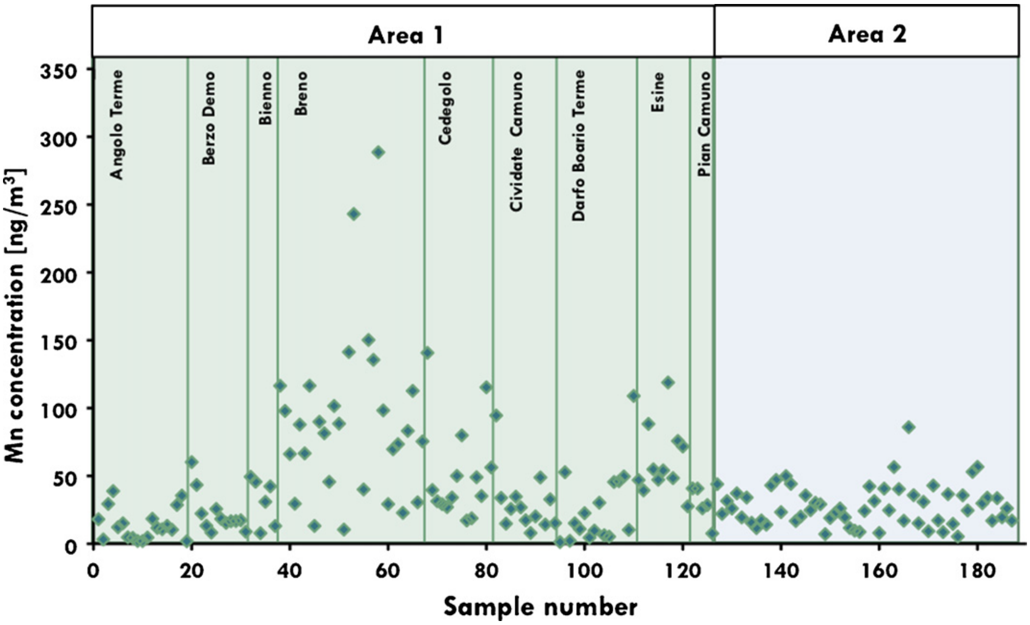

Fig. 4. Mn mass concentration in the air, calculated considering the pump flow rate and sampling time of 24 h. The samples are divided into two groups: area 1 which includes the samples collected in the municipal districts of Vallecamonica shown in alphabetical order and area 2 which involves the samples of Garda Lake area taken as reference.

data reported on these areas based on an earlier settled dust study [34].

Since TXRF allows the detection of all metals present in the filter simultaneously, useful comparisons of metals and interpretations of their sources are possible. Although the purpose of this study was to present the development of this new application of TXRF, the large number of filters analyzed provides a useful example of this principle. Since the presence of elevated Mn levels in the Vallecamonica area are most likely due to the presence of metallurgical plants, the Fe levels are also evaluated. We have already shown [34] that Mn and Fe have higher concentrations in this studied area in settled dust, and that the origin of Fe is probably both crustal and anthropological (i.e. from the metallurgical processes). In a comparison of the Fe concentration as a function of Mn calculated by TXRF, despite some deviations from the data (due to the fact the Fe also has crustal origins [34]), it is possible to see a positive relationship, demonstrating that Fe and Mn concentrations are correlated. This strongly supports the hypothesis of the same origin for these metals, most probably due to the metallurgical plants, even if some plants have been closed for several years. This is due to the persistence of these metals in the environment.

4. Conclusion

This work proposed and discussed a new method for the analysis of PM collected on air filters based on direct TXRF analysis without filter digestion which avoids errors due to current digestion sample preparation methods. Also, after the analysis, the sample can be archived for subsequent re-analysis.

As an example, this procedure has been applied to the quantification of Mn in air samples collected in the province of Brescia, Italy, because elevated Mn concentration was expected in the air near former Fe–Mn-alloy industries that were present in the Vallecamonica study area compared to the reference area. The Mn values in areas where metallurgical plants were active, are on average two to three times higher than those in the reference area of Garda Lake. However, since the results are variable, this demonstrates the need for a large amount of sampling data and thus the necessity of regular monitoring of critical sites. This can be realistically accomplished only by a fast, yet accurate and reliable method such as the one proposed here.

The advantages of this procedure, performed with compact TXRF instruments, are evident: (1) multi-elemental analysis allows the simultaneous identification of all elements; (2) the measurement is quite easy to perform and rapid (only 10 min); (3) data analysis is automatic; (4) samples are not destroyed by time-consuming digestion procedures, then protected filters can be stored (this is very important to produce a database of air analysis, and for forensics); (5) any risks of diluting the sample below detection limits are avoided; (6) utilization of potentially hazardous reagents and loss of volatile elements are avoided; (7) total method (including sample encapsulation and analysis) is very rapid; (8) the procedure is inexpensive, also due to the avoiding of digestion procedure; (9) the procedure is reliable. For the previously reported advantages, this method is more environmentally sustainable, than the standard ones.

TXRF has some disadvantages in comparison with other chemical techniques: overlapping peaks can complicate quantification of some elements, when their surface concentration is very low (in the order of a few ng/cm^2). This is the case for Pb and As that sometimes cannot be quantified. Peak superposition can also increase the LLD of some elements (as for example for Ba). In addition, because the Mo is the element used to generate the X-ray, it is impossible to detect and quantify molybdenum. Finally, optical alignment is critical (i.e. if sample is not in correct position, measurement must be repeated, increasing the total measuring time) and therefore the instrument requires frequent calibration.

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