X-Ray Spectrometry

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Investigating Technical Solutions to Improve the Near Real Time Measurement of Low-Z Elements in Atmospheric Particulate Matter by Energy Dispersive X-Ray Fluorescence Spectroscopy

Cosimo Fratticioli[1,2] | Chiara Ruberto[1,2] | Anna Mazzinghi[1,2] | Giulia Calzolai[2] | Luca Carraresi[1,2] | Fabio Giardi[2] | Franco Lucarelli[1,2] | Marco Manetti[2] | Silvia Nava[1,2] | Francesco Taccetti[2] | Massimo Chiari[2]

[1]Dept. of Physics and Astronomy, University of Florence, Sesto Fiorentino, Italy | [2]National Institute for Nuclear Physics (INFN), division of Florence, Sesto Fiorentino, Italy

Correspondence: Cosimo Fratticioli (cosimo.fratticioli@unifi.it)

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ABSTRACT

The measurement of the elemental composition of atmospheric Particulate Matter (PM) is of paramount importance in air pollution studies, providing fundamental information for identifying aerosol sources and understanding their contributions. In this context, online instruments integrating an energy-dispersive X-ray fluorescence (ED-XRF) spectrometer into an aerosol sampler offer the capability to both collect PM and perform near-real-time elemental analysis. However, these instruments face limitations, particularly in detecting low-Z elements such as Na, Mg, and Al, which are critical tracers for natural PM sources. In order to investigate potential solutions to this limitation, different technical solutions were implemented on a compact ED-XRF spectrometer that was developed for this specific purpose. The spectrometer's performance was evaluated through comparative analyses with a commercially available online metals analyzer for PM (Xact 625i) and particle induced X-ray emission (PIXE) technique. Results demonstrated greater sensitivities and lower MDLs for low-Z elements compared to a commercial online spectrometer for PM (Xact 625i) while scatterplots of measured elemental concentrations showed good correlation with both Xact 625i and PIXE. Moreover, fairly good MDLs, even if higher than those of Xact 625i, were achieved also for mid-high-Z elements. Finally, the spectrometer also demonstrated its capability to analyze PM samples collected on filters of various sizes, beyond the commonly used 47 mm diameter ones, overcoming the typical limitations of standard ED-XRF benchtop instruments.

1 | Introduction

Atmospheric Particulate Matter (PM) is a significant pollutant in the earth's atmosphere, with critical impacts on climate, ecosystems and human health. Its distribution and physico-chemical properties are monitored globally for both research and regulatory purposes. Among the different properties, its elemental composition (i.e., the concentration of different elements in a given PM sample) provides essential insights for identifying the PM sources [1]. Additionally, it enables the quantification of each source's contribution to the total PM concentration at a specific site using receptor models [2].

Within different techniques that are currently used to measure PM elemental composition, Energy-Dispersive X-ray Fluorescence (ED-XRF) spectroscopy is a valuable and widely used method. While traditionally applied in benchtop spectrometers to analyze PM samples collected on various substrates, ED-XRF has, over the past decade, been adapted for use in "online" multi-metal analyzers for PM [3, 4]. These instruments incorporate a compact ED-XRF spectrometer and a PM sampling line, allowing for both collection and subsequent elemental analysis within a single device. Online instruments save considerable time in laboratory filter analysis and provide high-resolution temporal data (down to 15 min). Consequently, online ED-XRF multi-metal analyzers are highly effective for both long-term monitoring of PM elemental composition and field campaigns requiring high time resolution [3, 5–8].

The main advantages of ED-XRF analysis of PM samples include short analysis times, no need for sample pre-treatment, and the ability to obtain multi-elemental information in a single measurement. However, ED-XRF has limitations, particularly its higher Minimum Detection Limits (MDLs) compared to other techniques like Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Another challenge lies in analysing PM samples collected on non-standard filters or substrates that differ from the widely used 47 mm diameter, with dimensions possibly smaller than the primary X-ray beam spot. These include filters used in hourly samplers like STRAS [9] or the streaker sampler [10] as well as 25 mm filters (moreover, in ring-supported 25 mm PTFE filters, the PM collection area diameter is reduced to 21 mm due to the filter supporting ring). These filters can not be effectively analyzed by commercial benchtop ED-XRF spectrometers; for instance, while spinning the sample, the Malvern Panalytical Epsilon5 ED-XRF spectrometer shows a homogeneous circular beam spot area of about 16 mm diameter with a halo extending up to 22 mm diameter, while in the Spectro Xepos ED-XRF spectrometer, the beam spot appears as a circular ring with inner and outer diameters of about 24.5 mm and 27.5 mm, respectively. This mismatch with the filter size can result in irradiation of areas outside the filter, for instance, the supporting ring, potentially leading to inaccurate analysis results.

Online multi-metal analyzers offer the significant advantage of delivering reliable, high-resolution data while reducing laboratory analysis time. However, they are generally unable to detect low-Z elements like Na and Mg, since the analysis is done with the sample in air at ambient pressure, and exhibit relatively high MDLs for Al. This limitation can be problematic, as low-Z elements like Na, Mg, and Al are essential tracers for natural aerosols, such as desert dust and sea spray [11, 12]. Thus, poor capabilities of online multi-metals analyzers in detecting low-Z elements could result in lost information regarding natural PM sources which, on a global scale, are the dominant ones and play an important role in the Earth's radiative balance.

To address these limitations, a compact ED-XRF setup (Compact XRF spectrometer for Particulate Matter—CXPM) was developed at the Laboratory of Nuclear Techniques for Environment and Cultural Heritage (LABEC) of the National Institute for Nuclear Physics (INFN) in Florence, Italy [13]. This spectrometer was designed with the goals of *(i)* achieving a compact form suitable for integration into a PM sampler for online elemental composition measurements, *(ii)* effectively detecting low-Z elements like Na, Mg, and Al, *(iii)* using it also as a benchtop spectrometer to analyze PM samples collected on non-conventional supports with high time resolution. To meet these objectives, technical solutions that were previously employed in the ED-XRF spectrometers for Cultural Heritage studies within the INFN-Cultural Heritage network (CHNet) [14, 15] and analysis of PM samples [16] were adapted. Finally, to evaluate the performances of CXPM, an intercomparison with Particle Induced X-ray Emission (PIXE) measurements was carried out in different measurement conditions. For this exercise, 25 mm PTFE PM samples collected during a previous field campaign were analyzed with CXPM. Moreover, the same filters were analyzed by means of Xact 625i used as a benchtop spectrometer. Surface concentrations, sensitivities, and MDLs obtained from CXPM were then compared with the ones of Xact 625i, allowing for a performance assessment against a commercially available online PM multi-metal analyzer.

The primary goal of this study was to explore technical modifications that enhance the sensitivity of compact ED-XRF analyzers to low-Z elements. To achieve this, we assembled and tested a versatile compact ED-XRF analyzer that can be integrated into a PM sampler for online analysis or used as a benchtop spectrometer for non-standard PM filters or substrates.

2 | Spectrometer Description & Methods

The design of the ED-XRF spectrometer (Figure 1) was carried out to reach these three aforementioned main goals: being as compact as possible, being able to detect low-Z elements (especially Na, Mg, Al, Si) with low-enough MDLs, and to measure PM samples deposited on non-conventional supports.

In order to minimize the spectrometer dimensions, a compact X-ray tube (Moxtek 40 kV, 100 μA, Rh transmission anode) and Silicon Drift Detectors, SDD (AMPTEK FastSDD, 17 mm^2 collimated area, 8 μm Be window, energy resolution of 131 keV FWHM at 5.9 keV and AMPTEK FastSDD, 50 mm^2 collimated area, 12.5 μm Be window, energy resolution of 131 eV FWHM at 5.9 keV FWHM) were used. These were installed onto a custom designed 3D-printed support. The tube was placed perpendicular to the PM samples, while the detector was placed at a 45° angle. In order to maximize both the intensity of primary X-rays on the analysis area and the collection of X-ray fluorescence emitted by the PM, the detector and tube were placed as close as possible to the sample, mounted onto manual linear stages that allowed for adjusting their distance from the sample. The tube was inserted in a brass case to avoid diffusion of X-rays in the surrounding area and collimated in order to obtain a 5 mm diameter spot on the sample, as measured using a commercial radiochromic film, while keeping the distance from the tube collimator and the sample at about 5 mm. This solution allows to analyze both 25 mm PTFE filters, which can not always be analysed by benchtop ED-XRF spectrometers due to the size of the primary X-ray spot, and non conventional supports (e.g., stripes from hourly samplers and impactors). The detector was placed as close as possible to the analysis area to maximize the

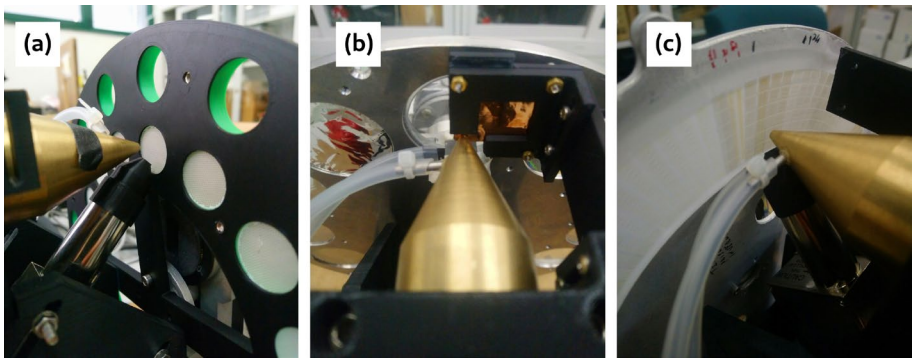

FIGURE 1 | CXPM measuring (a) 25 mm PTFE filters by fluxing He in front of both the tube and the detector, (b) thin elemental standards on Mylar by using a Cu foil to filter the primary X-ray spectrum, (c) PM samples collected with the STRAS sampler at hourly time resolution. [Colour figure can be viewed at wileyonlinelibrary.com]

detector solid angle and thus its collection efficiency. The detector distance from the analysis area was kept constant at about 20 mm. The X-ray tube and SDD assembly occupies a volume of $20 \times 15 \times 5\,cm^3$, that could be further reduced using OEM solutions for the detector and preamplifier system.

To test the spectrometer's performance and enable its use for benchtop analysis of non-conventional filters, a filter-supporting wheel was 3D-printed and mounted onto a stepper motor. This setup allows both rotation (to change the filter being analyzed) and scanning of the filter during analysis, thus allowing the targeting and scanning of non-conventional supports and sequentially analysing PM samples deposited onto 25 mm PTFE filters.

The X-ray tube was controlled by a FTC200 controller (Moxtek) which allows for manual regulation of both the tube current and voltage. Then, spectra from the FastSDD detector were acquired by using the PX5 Digital Pulse Processor and the DPPMCA acquisition software, both provided by AMPTEK.

2.1 | Metal Foils to Increase the Signal-To-Background Ratio

In order to improve the detection of elements by ED-XRF analysis, different metal foils were used to filter the primary X-ray radiation. This technique allows for an increase in the peak-to-background ratio in a given energy region of the acquired spectrum [17]. Here, the energy region where the peak-to-background ratio increases depends on the material of the metal foil. When placing the filters, the distance of the tube from the sample had to be increased by a few millimeters in order to allow for the presence of the metal foil support. Moreover, a thin (~1 mm) Lead shielding foil had to be inserted between the tube and the detector in order to avoid the detection of X-ray fluorescence emitted directly by the metal foil. Different metal foils were tested in order to improve the detection of elements in different energy regions. These were Aluminium (72 and 36 μm), Zinc (50 μm), Copper (16 and 24 μm) and Palladium (40 μm). Amongst the different filters, the Al one was used to improve the detection of low-Z elements (1–4 keV X-ray energy region), while the others were used to improve the detection of mid-high-Z elements (above 4 keV X-ray energy).

2.2 | Helium Flux to Improve Detection of Low-Z Elements

In order to optimize the detection of low-Z elements, the spectrometer was designed to allow for a helium flow on both the sample and the tube. This allows for a strong reduction in the attenuation of low-energy X-rays emitted by the low-Z elements. Moreover, the reduced attenuation of low-energy primary X-rays emitted from the tube enhances the excitation process, thereby improving the production of X-ray fluorescence from low-Z elements in the sample. The helium flow was obtained by a custom design of the X-ray tube brass case and by mounting a 3D-printed plastic nozzle on the X-ray detector extender. Both the case and the nozzle were designed in such a way that the tubes for fluxing helium did not interfere with the primary X-rays emitted by the tube, nor with the X-ray fluorescence directed towards the detector. A helium (He) flux of approximately 2 L/min was used during the measurements involving He flow.

2.3 | Spectral Deconvolution and Quantitative Analysis

The analysis of the acquired spectra was carried out by means of the PyMCA software [18]. Here, X-ray spectra obtained from the irradiation of both PM samples and thin elemental standards on 6.3 μm Mylar foils (MicroMatter Technology Inc.) were deconvoluted by using PyMCA fitting tools in order to obtain the peak areas of different elements. In the fit procedure, the background of each spectrum was subtracted by using the STRIP background removal algorithm provided by PyMCA.

With the aim of performing quantitative analysis of the PM samples, peak areas obtained by the analysis of PM samples were compared to the peak areas obtained by the analysis of thin elemental standards of known areal concentration, under the same irradiation conditions (X-ray tube voltage and current). This procedure was iterated for each analyzed element. In order to take into account impurities that are present on the PTFE and Mylar supports, concentration values measured on both the blank PTFE filter and on the blank Mylar supports were subtracted

when needed. Thus, the elemental concentration, C_i, of a given element i on the PM sample was given by

$$C_i = \frac{A_i^{filt} - A_i^{filtBLK}}{A_i^{std} - A_i^{stdBLK}} \frac{T_{std}}{T_{filt}} C_i^{std},$$

where A_i^{filt} and $A_i^{filtBLK}$ are the peak areas of the i element measured on the analyzed PM filter and on the blank PTFE filter, respectively, A_i^{std} and A_i^{stdBLK} are the peak areas of the i element measured on the respective thin elemental standard and on the Mylar blank filter, respectively, T_{std} and T_{filt} are the measurement times of the standard and filter measurements, respectively (please, note that both measurements were carried out with the same anode current), and C_i^{std} is the concentration of the i element reported on its respective thin elemental standard. Typical uncertainties in the concentrations range from 5% to 15%. The 5% uncertainty arises from the certified concentration for the elemental standard (C_i^{std}), while the remaining uncertainty (ranging from 0.1% to 10%) is attributed to the fitting procedure. Lower relative uncertainties are obviously associated with higher measured concentrations, whereas higher relative uncertainties are associated with lower concentrations. Finally, uncertainties due to repeatability for ED-XRF measurements on PM filters can be estimated as 5% or better [19], which are of the same order as the uncertainties attributed to the fit and spectral deconvolution procedure.

In order to evaluate the spectrometer performances, sensitivities and MDLs were evaluated for each measurement condition. The sensitivities were obtained by the analysis of the spectra obtained from the irradiation of the thin elemental standards [16]. Sensitivities were expressed as counts per second per milliAmpere per microgram over square centimetre. Typical uncertainties on the sensitivities are about 5% dominated by uncertainty on the certified concentration C_i^{std} given by the manufacturer.

On the other hand, MDLs were obtained by the analysis of the spectra obtained from the irradiation of PM samples [16] MDLs were expressed as micrograms over square centimetre. Typical uncertainties on MDLs are about 10%, dominated by the uncertainty on the background area $A_{B,I}$ and elemental concentration C_i.

2.4 | Comparison With PIXE and Xact 625i

With the aim of evaluating the spectrometer's ability to properly measure the elemental concentrations on PM filters, measurement of the elemental concentrations on different 25 mm PTFE filters was carried out. The PM filters used for this exercise were previously collected during a sampling campaign in an electronic waste recycling plant [20]. Due to the characteristics of the sampling site, the selected filters were characterized by the presence of several elements spanning a wide range of concentrations. Thus, these filters were optimal to evaluate the performance of the spectrometer. A set of eight filters was selected and measured once with both the spectrometer, the PIXE technique by means of the 3 MV Tandem accelerator of LABEC, and by the Xact625i online multi-metals analyzer used as a benchtop offline XRF spectrometer [5]. In order to evaluate the correlation between the elemental concentrations measured with CXPM, PIXE, and Xact 625i, orthogonal regressions on the measured concentrations were performed by means of the SciPy Orthogonal Distance Regression module in Python.

The PIXE technique represents a valuable technique for the elemental analysis of atmospheric PM samples, thus being widely used in air pollution studies [21–23]. Its main advantages with respect to the other techniques reside in the low analysis time (down to one minute), detection of all of the soil-related elements, no requirement for sample pretreatment, and non-destructiveness. Moreover, this technique was already used in previous studies to provide a comparison with ED-XRF measurements on PM filters [24–27]. In this exercise, PM samples collected on 25 mm PTFE filters were bombarded with a 3 MeV proton beam on the external beamline for aerosol analysis of the 3 MV Tandem accelerator of LABEC [28]. The X-ray spectra were collected using an array of three SDDs (one Ketek SDD, 30 mm^2 collimated area, 8 μm Be window and two Ketek SDDs, 80 mm^2 collimated area, 25 μm Be window plus 450 μm Mylar absorber) and then they were analyzed by means of the GUPIXWin software [29] to obtain the elemental composition of the different samples.

Xact 625i (Cooper Environmental Inc.) is an online multi-metals analyzer for PM. It is currently used in atmospheric studies both for field campaigns and for long term monitoring of PM elemental composition [3, 5–8]. The instrument is capable of sampling PM on a PTFE filter tape and analyze it subsequently by ED-XRF technique while a new sample is being collected on the filter tape. Thus, the sampling and total analysis time are equal. The analytical module is equipped with a 50 kV, 2 mA, 50 W X-ray tube with Rh anode and an SDD detector (AMPTEK FastSDD, 17 mm^2 collimated area, 12.5 μm Be window). Metal filters (Al, Pd and Cu) are used to filter the primary X-ray radiation and increase the peak-to-background ratio of elements in different energy regions. The ED-XRF measurement is carried out under three different sets of the X-ray tube parameters, called Energy Conditions (EC). These are EC1 (25 kV, 2000 μA, Al filter) to detect elements in the range Al-Mn plus Cs, Ba, La, Ce, EC2 (48 kV, 1000 μA, Pd filter) to detect elements in the range Fe-Mo and Pt-As, and EC3 (48 kV, 1000 μA, Cu filter) for elements in the range Pd-Te. For a 1 h sampling and analysis time, EC1 lasts about 12 min, while EC2 and EC3 last 24 min each. The quantitative analysis is carried out automatically by the XRS-FP software (AMPTEK). Here, individual spectra obtained from the irradiation of thin elemental standards (MicroMatter Technology Inc.) are fitted to the spectrum acquired from the sample. In this way, surface concentration on the filter and volume concentration in air are obtained for each analyzed filter. Xact 625i can also be used as a benchtop spectrometer to analyze 25 mm PTFE filters by inserting them manually into the analytical module [5].

3 | Results

3.1 | Comparison of Different Measurement Conditions

Sensitivities and MDLs were obtained by irradiation of MicroMatter standards for 5 min and PTFE filters for 24 min, respectively. These were evaluated for different measurement

TABLE 1 | List of the different measurement conditions used for testing the spectrometer. For each condition the use of metal foils to filter the primary X-rays, the use of He, the SDD dimensions and the target elements are reported. Effect of the different measurement conditions on MDLs and sensitivities with respect to the Xact 625i ones are reported in the right columns.

Measurement condition	Filter	Helium	SDD	Target elements	Effect on MDLs	Effect on sensitivities
STD	–	–	17 mm^2	All	+ (Z < 19)	+
Al72	Al 72 μm	–	17 mm^2	Na, Mg, Al, Si, S	+ (Z < 19)	+
Al72 + He	Al 72 μm	Y	17 mm^2	Na, Mg, Al, Si, S	+ (Z < 19)	+
Al36 + He	Al 36 μm	Y	17 mm^2	Na, Mg, Al, Si, S	+ (Z < 19)	+
He	–	Y	17 mm^2	Na, Mg, Al, Si, S	+ (Z < 19)	++
50 mm^2	–	–	50 mm^2	All	+ (Z < 19)	+
Cu, Zn, Pd	Cu, Zn, Pd	–	17 mm^2	Ti, Cr, Mn, Fe, Ni, Cu, Zn, Pb	–	=

conditions and compared with the ones of Xact 625i to provide a comparison of CXPM with a commercially available online metals analyzer for PM. Xact 625i MDLs are provided by the manufacturer and are reported here at 3σ for 1 h sampling and analysis time (which corresponds to about 24 min of XRF analysis in EC2, 1000 μA anode current, and 12 min of analysis in EC1, 2000 μA anode current). For what concerns sensitivities, these were obtained by a reanalysis of Xact 625i spectra obtained from the irradiation of thin elemental standards by means of the PyMCA software. Please, note that Xact 625i tube current is 10 to 20 times higher than the one of CXPM. The different measurement conditions are reported in Table 1.*Standard measurement condition (STD).*

MDLs and sensitivities for the standard measurement condition (i.e., no He flow, 17 mm^2 detector, no metal foils used as filters) are shown in Figure 2. Looking at MDLs, it can be observed that Xact 625i performs better for medium-high-Z elements (Z ≥ 20), with Xact 625i MDLs that are about one order of magnitude lower with respect to CXPM. Nevertheless, MDLs of the order of 10^{-3}—10^{-2} μg/cm^2 that were obtained for Z ≥ 20 with CXPM can be considered as fairly good for air pollution studies that require hourly time resolution. In fact, by considering a surface deposition of about 3 cm^2 (as it is for the case of 25 mm PTFE filters) and a flux of 2.3 m^3/h (in accordance with EU standards—EN 12341), MDLs of the order of 10^{-3}—10^{-2} μg/m^3 can be obtained for volume concentrations measured in air. MDLs are well in line with Xact 625i ones for Cl and K, while are about one order of magnitude lower for low-Z elements like Al, Si and S. Moreover, both Na and Mg can be detected and their MDLs was quantified. It has to be remarked that Xact 625i does not measure at all neither Na nor Mg. Looking at sensitivities, we can observe that CXPM presents much higher sensitivities than the ones of Xact 625i (about 1 to 2 orders of magnitude higher).

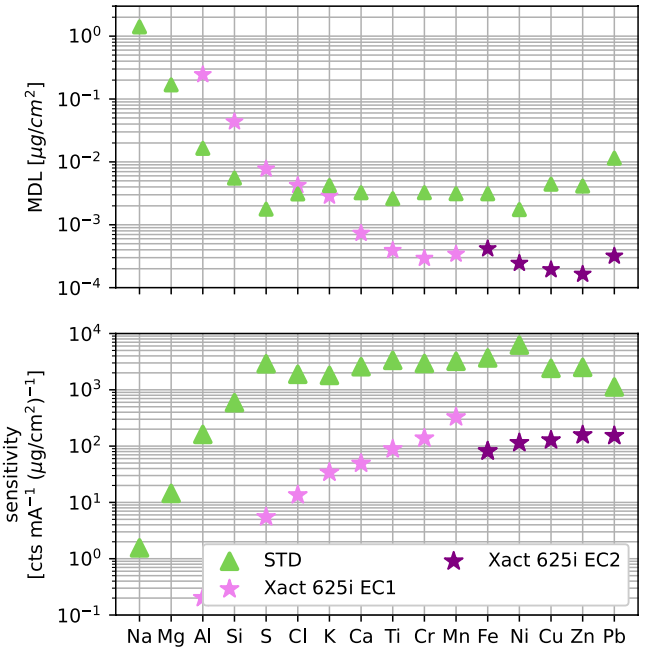

FIGURE 2 | MDLs and sensitivities for several elements measured with the standard measurement condition. Sensitivities are reported in counts per second (cps) per milliAmpere per microgram over square centimetre. ED-XRF measurement time was equal to 24 min. Xact 625i MDLs are provided by the manufacturer and are reported here at 3σ for a 1 h analysis time, corresponding to approximately 12 min of measurement in EC1 (25 kV, 2000 μA, Al filter) and 24 min in EC2 (48 kV, 1000 μA, Pd filter). Xact 625i sensitivities were calculated by reanalysing its spectra using the PyMCA software. [Colour figure can be viewed at wileyonlinelibrary.com]

3.1.1 | Aluminium Foils to Improve Detection of Low-Z Elements

Aluminium metal foils were used to filter primary X-ray radiation. The main goal of using Al filters was to improve the peak-to-background ratio in the low-Z energy region. Moreover, it allowed reducing the intensity of the escape peak of the Rh L_α line (0.957 keV) which is partially over imposed with the Na K_α line (see Figure 3). Moreover, the use of He to reduce the attenuation of low energy X-rays emitted by low-Z elements was tested. Thus, different conditions were tested. These are *(i)* 72 μm Al foil, *(ii)* 72 μm Al foil + He flow, and *(iii)* 36 μm Al foil + He flow. MDLs and sensitivities obtained in these conditions are reported in Figure 4.

The obtained MDLs are lower with respect to the standard measurement condition only for Na, while they are equal to the standard case for Mg, K, and Ca and about one order of magnitude higher for the remaining elements. Regarding sensitivities, these are lower than the standard case for all of the considered elements, but Na. For elements from Na to Si, the use of He significantly increases the sensitivities, while no effect is observed for elements in the range S-Ca. Nevertheless, the obtained sensitivities are always higher than the one obtained from Xact 625i.

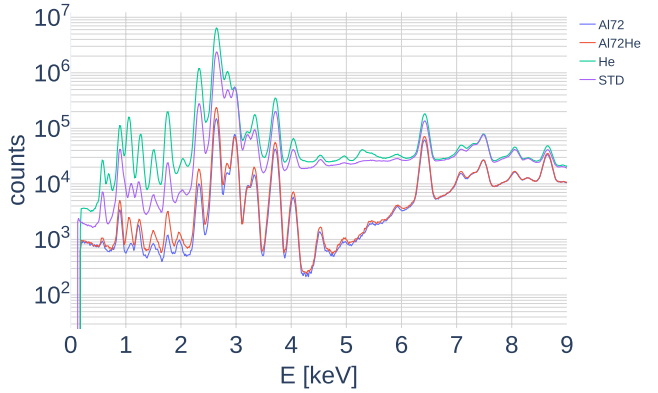

FIGURE 3 | ED-XRF spectra obtained from the irradiation of PM deposits on the same PTFE filter. Each spectrum is obtained in different conditions: 72 μm Al foil to filter primary X-ray radiation (Al72), 72 μm Al foil + He flow (Al72 He), standard measurement condition (STD), and Helium flow (He). [Colour figure can be viewed at wileyonlinelibrary.com]

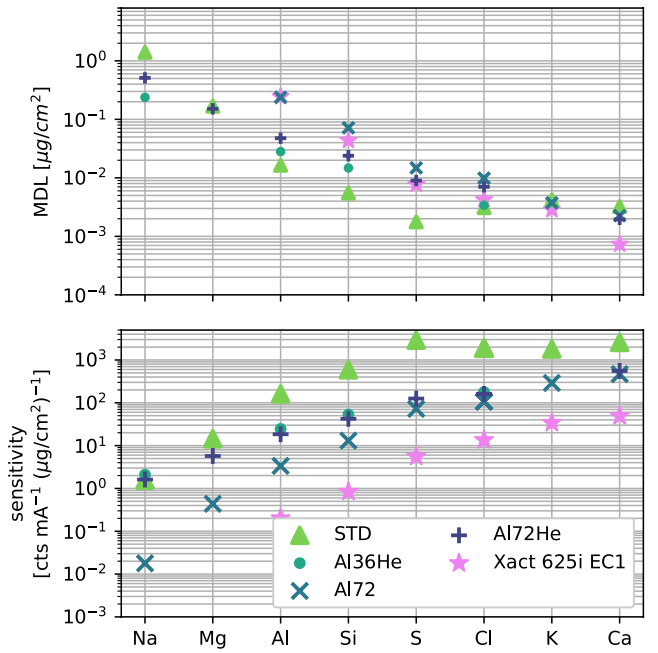

FIGURE 4 | MDLs and sensitivities for low-Z elements measured with Al foils as filters (and He). These are: 72 μm Al foil (Al72), 72 μm Al foil + He (Al72He) and 36 μm Al foil + He (Al36He). The standard CXPM measurement condition (STD) is reported for comparison. Sensitivities are reported in counts per second (cps) per milliAmpere per microgram over square centimetre. ED-XRF measurement time was equal to 24 min. Xact 625i MDLs and sensitivities are reported for comparison as described in Figure 2. [Colour figure can be viewed at wileyonlinelibrary.com]

3.1.2 | Helium Flux to Improve Detection of Low-Z Elements

In order to optimize the measurement of low-Z elements, an He flow was maintained between the tube, the sample, and the detector. The enhancement of the peak-to-background ratio with respect to the standard measurement condition can be observed by looking at Figure 3. The obtained MDLs and sensitivities are shown in Figure 5 and compared with both Xact 625i and the standard case. It can be observed that MDLs are significantly lower than the standard case (up to two orders of magnitude) for elements in the range Na-Cl. Even when compared with Xact 625i, CXPM's MDLs are up to two orders of magnitude lower. In the same way, sensitivities are increased both with respect to the standard case (up to 2 orders of magnitude higher) and with respect to Xact 625i (up to 3 orders of magnitude higher).

3.1.3 | 50 mm² SDD

The possibility of using a SDD with a larger area to increase the solid angle, and thus the peak-to-background ratio, was investigated. A 50 mm² collimated area, 12.5 μm Be window FastSDD from AMPTEK was used for this case. Results for this case are shown in Figure 6. Here, MDLs were reduced by about 40%–50% of their value in the standard case. On the other hand, sensitivities were increased by a factor of 2.16 on average for all the

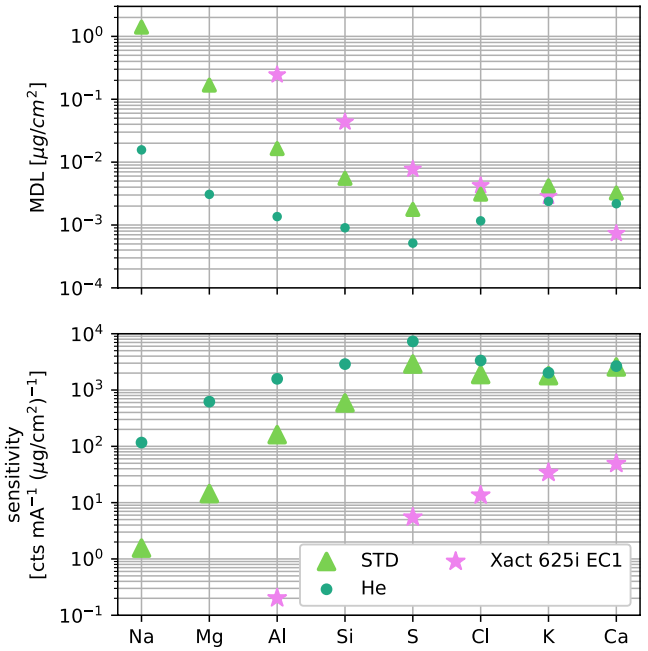

FIGURE 5 | MDLs and sensitivities for low-Z elements measured with He flow. Sensitivities are reported in counts per second (cps) per milliAmpere per microgram over square centimetre. The standard CXPM measurement condition (STD) is reported as a comparison. ED-XRF measurement time was equal to 24 min. Xact 625i MDLs and sensitivities are reported for comparison as described in Figure 2. [Colour figure can be viewed at wileyonlinelibrary.com]

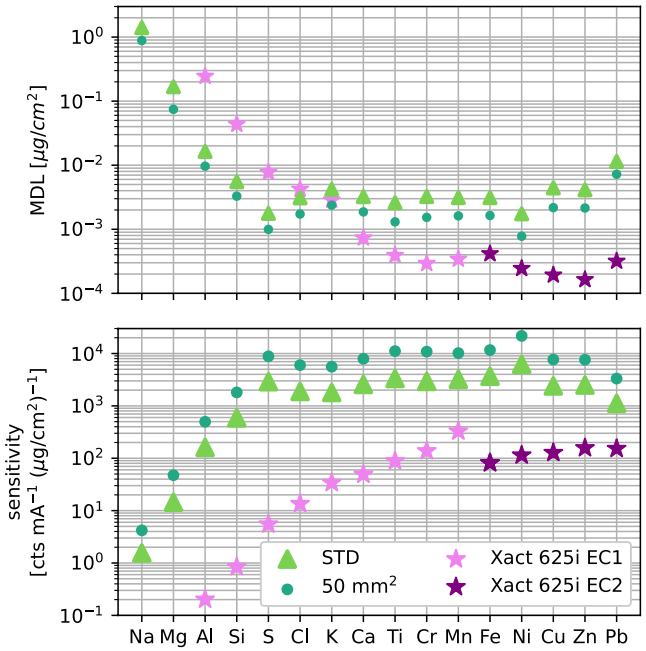

FIGURE 6 | MDLs and sensitivities for low-Z elements measured with 50 mm^2 collimated area FastSDD detector. Sensitivities are reported in counts per second (cps) per milliAmpere per microgram over square centimetre. The standard CXPM measurement condition (STD) is reported as a comparison. ED-XRF measurement time was equal to 24 min. Xact 625i MDLs and sensitivities are reported for comparison as described in Figure 2. [Colour figure can be viewed at wileyonlinelibrary.com]

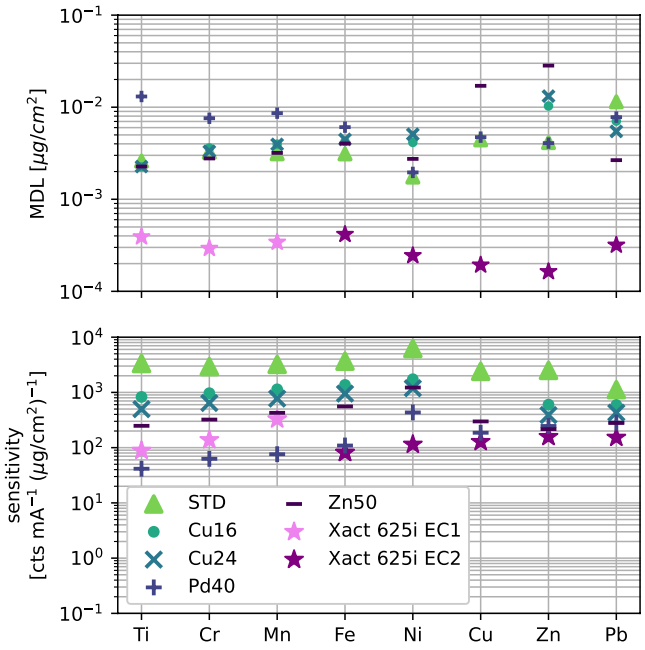

FIGURE 7 | MDLs and sensitivities for low-Z elements measured with Cu, Zn and Pd foils as filters. These are: 16 μm Cu foil (Cu16), 24 μm Cu foil (Cu24), 40 μm Pd foil (Pd40) and 50 μm Zn foil (Zn50). The standard CXPM measurement condition (STD) is reported for comparison. Sensitivities are reported in counts per second (cps) per milliAmpere per microgram over square centimetre. ED-XRF measurement time was equal to 24 min. Xact 625i MDLs and sensitivities are reported for comparison as described in Figure 2. [Colour figure can be viewed at wileyonlinelibrary.com]

elements. A lower increase in sensitivity (factor 1.7) was observed for Na, most probably because of the stronger attenuation of Na X-rays in the thicker Be entrance window of the 50 mm^2 detector with respect to the smaller one (12.5 vs. 8 μm).

3.1.4 | Cu, Zn and Pd Foils to Improve Detection of Mid-High-Z Elements

Finally, the possibility of using Cu, Zn, and Pd foils to filter primary X-ray radiation in order to improve the detection of medium-high-Z elements was tested. Obtained MDLs for Ti, Cr, Mn, Fe, Ni, Cu, Zn, and Pb were at least one order of magnitude higher than those of Xact 625i. Sensitivities resulted in up to one order of magnitude higher than those obtained by Xact 625i, as it was in the case of Al foils. MDLs and sensitivities for these conditions are shown in Figure 7.

3.2 | Comparison With PIXE

In order to compare CXPM with a recommended technique, 25 mm PTFE filters previously sampled in an electronic waste recycling plant were measured by both CXPM and by PIXE at the 3 MV Tandem accelerator of the LABEC laboratory. Results are shown in Figure 8. Good linearity was observed for all of the considered elements, with most of the slopes in the range 1.0 ± 0.4, which are in agreement with other intercomparisons between ED-XRF/PIXE measurements on PM samples [25, 26].

Offsets were (almost) consistent with zero for many of the analyzed elements, with greater discrepancies obtained for Na, Fe, and Zn. The observed offsets different from zero could be attributed to an incorrect background subtraction due to the complexity of the blank spectrum. The obtained results showed that CXPM quantitative analysis agrees well with that of a commonly used technique for elemental analysis like PIXE.

3.2.1 | Comparison With Xact625i

An intercomparison with Xact 625i was carried out by measuring the same filters used in the intercomparison with PIXE. Here, each filter was measured both by CXPM and by Xact 625i used as a benchtop spectrometer, as reported by [5]. Results from this intercomparison are shown in Figure 9. Good linearity was observed for all of the analyzed elements. Most of the slopes obtained by the orthogonal regressions were included in range 1.0 ± 0.3, with exceptions for Al and K. Concentration for Al was underestimated by 69% for Al and overestimated by 44% for K, respectively, by CXPM with respect to Xact 625i. Looking at offsets, these are (almost) consistent with zero for most of the analyzed elements, with the main exceptions represented by Al, Fe and Zn. Discrepancies for Fe and Zn can be attributed to incorrect background subtraction as already described in the comparison with PIXE measurements. On the other hand, discrepancies for Al could be attributed to a wrong quantification of Al by Xact 625i. In

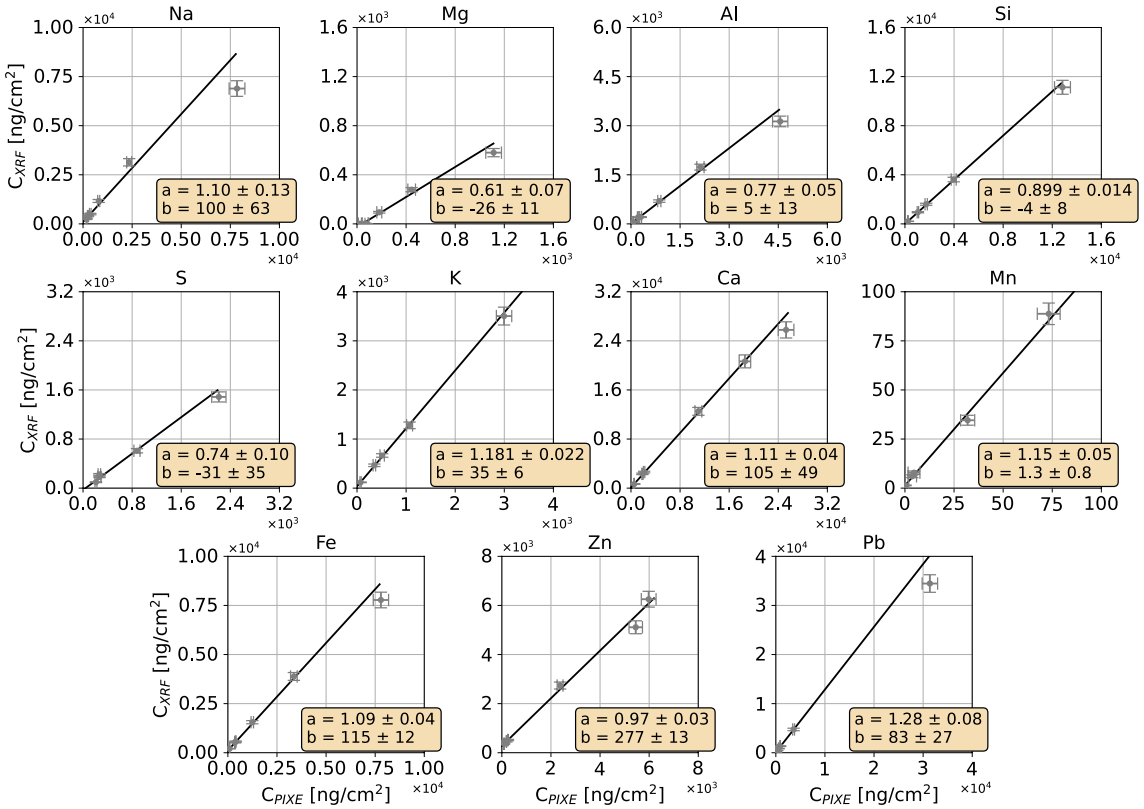

FIGURE 8 | Scatter plots between elemental concentrations measured by the spectrometer (C_{XRF}) and by PIXE (C_{PIXE}) for different elements. Results from orthogonal regressions performed on the data to fit the linear equation y = ax+b are reported in the boxes, for each element. [Colour figure can be viewed at wileyonlinelibrary.com]

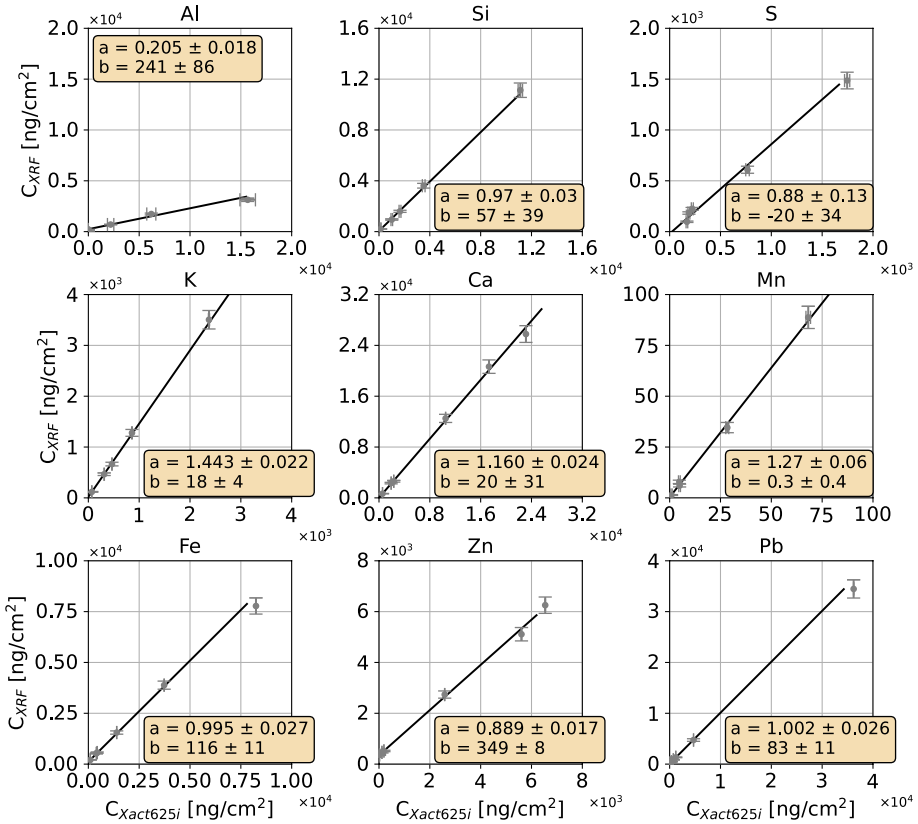

FIGURE 9 | Scatter plots between elemental concentrations measured by the spectrometer (C_{XRF}) and by Xact 625i ($C_{Xact625i}$) for different elements. Results from orthogonal regressions performed on the data to fit the linear equation y = ax+b are reported in the boxes, for each element. [Colour figure can be viewed at wileyonlinelibrary.com]

fact, Xact 625i presents very low sensitivity to Al and other studies reported discrepancies between Xact 625i and other techniques. For example, slopes included in range 0.24–0.39 were observed for Al when comparing half-hourly Xact 625i measurements with daily ICP-MS measurements [30].

3.3 | Conclusions

Compared to a commercial online multi-metals analyzer for PM, the Xact 625i, CXPM demonstrated significantly higher sensitivities, even when operating at a current approximately ten times lower. This improvement was achieved through careful optimization of the measurement geometry, which was found to be critical for enhancing the overall performance of the system. Additionally, CXPM achieved much lower Minimum Detection Limits (MDLs) for low-Z elements such as Al, Si, and S, while also enabling reliable detection of Na and Mg using a helium (He) flux.

Comparisons between CXPM, Particle Induced X-ray Emission (PIXE) and ED-XRF analysis by Xact 625i confirmed good linearity between CXPM and these methods. Intercomparison with PIXE measurements showed the possibility to determine calibration factors to correct the spectrometer quantitative measurements, while comparison with Xact 625i showed good correlation with a commercially available online multi-metals analyzer for PM. The capability of CXPM to analyze PM samples on non-standard filters or substrates was also successfully demonstrated, overcoming a limitation that can be found in some traditional benchtop ED-XRF spectrometers.

This study highlights the advantages of CXPM, particularly its ability to combine high sensitivity with flexibility in analysing PM samples under different conditions. By addressing key challenges such as the detection of low-Z elements and the analysis of non-standard filters or substrates, the new system offers a valuable improvement in the field of PM elemental compositional analysis. These results underline the potential for future integration of CXPM into PM samplers, paving the way for more efficient high time resolution measurement of PM elemental composition, in particular for source apportionment of natural aerosols, such as dust and sea spray. Nevertheless, technical feasibility of the proposed upgrades to existing online PM instrumentation remains to be assessed.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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