



Elemental analysis of particulate matter by X-ray fluorescence methods: A green approach to air quality monitoring

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ABSTRACT

This review explores X-ray fluorescence (XRF) spectrometry for elemental analysis of particulate matter (PM) for air quality monitoring. The introduction presents PM classification based on size and composition, covering various elemental analysis methods while highlighting the increasing interest in XRF due to its non-destructive, rapid, and green features. The fundamental concepts of XRF and the experimental configurations commonly used are discussed, focusing on Energy Dispersive X-Ray Fluorescence (EDXRF) and Total Reflection X-Ray Fluorescence (TXRF). PM sampling devices and substrate are described, with a specific emphasis on filtering membranes for EDXRF and reflecting substrates for TXRF. Sample preparation strategies and procedures are presented. Qualitative and quantitative analysis is described, with a particular focus on the calibration approaches implemented for PM. Finally, the challenges faced by XRF in becoming a recognized reliable analytical technique for PM analysis, comparable to other standardized techniques for PM filters analysis, while capitalizing on its green advantages.

1. Introduction

Environmental pollution is a pressing global concern that poses significant threats to both ecosystems and human health. One notable contributor to this problem is particulate matter (PM), which includes tiny solid or liquid particles suspended in the air. These particles vary in size, composition, and origin. While some PM is directly emitted into the atmosphere as primary particles (e.g., dust, soot from combustion processes) [1,2], others are formed in the atmosphere from emissions of certain precursor pollutants such as SO₂, NO_x, NH₃ [3,4]. Therefore, PM can consist of both primary particles and those formed because of secondary processes. This diverse nature of PM makes its characterization and analysis essential for understanding and mitigating environmental pollution. PM can interact with other atmospheric components and can be associated with the formation of certain secondary pollutants, such as ground-level ozone and some harmful gases. These pollutants contribute to the deterioration of air quality, leading to smog, haze, and reduced visibility [5]. Furthermore, deposition of PM on soil and water surfaces can have adverse effects on terrestrial and aquatic ecosystems, disrupting their functioning and biodiversity.

PM is categorized based on aerodynamic equivalent diameter (AED), with PM₁₀ referring to particles with a diameter of ≤10 μm, PM_{2.5} indicating particles with an AED of ≤2.5 μm, and PM_{1.0} denoting particles with an AED of ≤1.0 μm. The size of these particles is directly linked to their potential for causing health issues. Respirable particles, including PM_{2.5}, pose the highest concern for their ability to penetrate the lungs, and even enter the bloodstream [6]. Prolonged exposure has been linked to various respiratory and cardiovascular ailments, including asthma, bronchitis, lung cancer, and heart attacks. These health effects can lead to a significant reduction in human life expectancy [7]. Health effects of respirable particles are particularly noticeable in specific population groups, including children, the elderly, pregnant women, and individuals with pre-existing respiratory or cardiovascular conditions. These particles can remain suspended in the atmosphere for extended periods and travel long distances from the emission source, thereby posing a significant threat to the population distributed over wide geographic areas.

PM is a diverse and heterogeneous mixture, whose composition continuously varies spatially and temporally. The chemical constituents of PM are extensive and encompass a range of substances. Some of the common components found in PM include nitrates; sulphates; elemental

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Abbreviations

AAS	Atomic Absorption Spectrometry
AED	aerodynamic equivalent diameter
CRMs	certified reference material
EDXRF	Energy Dispersive XRF
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LIBS	Laser-Induced Breakdown Spectroscopy
NAA	Neutron Activation Analysis
NIST	National Institute of Standards and Technology
PC	Polycarbonate
PIXE	Particle-Induced X-ray Emission
PM	particulate matter
PTFE	Polytetrafluoroethylene
RM	reference material
RSD	relative standard deviation
SOP	Standard Operating Procedure
TEM	Transmission Electron Microscopy
TXRF	Total Reflection X-Ray Fluorescence
XRF	X-Ray Fluorescence

and organic carbon; organic compounds (e.g., polycyclic aromatic hydrocarbons); biological compounds (e.g., endotoxin, cell fragments); and metals (e.g., iron, copper, nickel, zinc, and vanadium). It's crucial to recognize that the sources and concentrations of these elements in PM can exhibit significant variations upon several factors, including geographical location, degree of urbanization, industrial operations, and other contributing elements. Among these elements, Fe, Ni, and Zn are naturally abundant in the Earth's crust and are commonly found in both soil and dust. While, Cu and V are primarily present in soil and rocks, and their mobilization into the atmosphere typically occurs through processes like dust resuspension and soil erosion. The anthropogenic origins of these elements encompass a spectrum of industrial activities. These activities include metal production, iron and steel manufacturing, copper smelting, nickel mining, and processes like galvanization, which entail the application of zinc coatings to iron or steel surfaces. Furthermore, significant contributions arise from the combustion of fossil fuels, with particular emphasis on heavy fuel oils commonly utilized in shipping and power generation. Additionally, vehicle-related emissions, notably those generated through brake and tire wear, constitute substantial sources of these elements, especially in densely populated urban areas [8]. This highlights the complexity of its characterization needing multiple complementary analytical techniques to determine elemental, and phase composition.

Elemental composition of PM can be determined by means of various spectroscopic techniques such as Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Laser-Induced Breakdown Spectroscopy (LIBS), Neutron Activation Analysis (NAA), Particle-Induced X-ray Emission (PIXE), X-Ray Fluorescence (XRF). The first two are the most used and standardized techniques for PM characterization [9]. AAS is a technique that measures the absorption of specific wavelengths of light by atoms in the gaseous state. It is widely used for the determination of specific elements in PM [10]. AAS can be performed using flame, graphite furnace, or hydride generation systems, depending on the elements of interest and their concentrations. ICP-MS is a highly sensitive technique that combines inductively coupled plasma as the excitation source with mass spectrometry for the determination of element based on their mass to charge ratios. It allows for simultaneous analysis of a wide range of elements, with detection limits at the level of ng L^{-1} . ICP-MS offers excellent sensitivity, precision, and accuracy, making it suitable for elemental analysis of PM in various environmental [11,12] and biological samples. LIBS is a technique that utilizes a laser pulse to generate a plasma confined in the

volume containing PM both in the solid and the gas phase, making it suitable for online measurements. Following the emission of light in LIBS, the subsequent step involves analysing the emitted light using optical spectrometry to determine the elemental composition [13]. LIBS offers rapid analysis, requires minimal sample preparation, and can be combined with machine learning and chemometrics method for PM source apportionment [14]. NAA is another technique employed for PM characterization. It involves bombarding the sample with neutrons to induce radioactive isotopes. The emitted gamma rays from these isotopes are measured and used to determine the elemental composition. NAA provides high sensitivity and can analyse a wide range of elements, including trace elements (detection limits ranging from 0.1 to $1 \times 10^6 \text{ ng g}^{-1}$) [15] PIXE employs ion beams to induce X-ray emissions from the sample, enabling the identification and quantification of its constituent elements. Qualitative and quantitative analysis provide crucial data regarding the chemical composition of PM [16]. PIXE employs a range of ions to induce X-ray emissions, and the selection of the appropriate ion based on the unique demands of the analysis. Protons (H^+), helium ions (He^+ or α -particles), and their use are predominant in PIXE due to their versatility and wide applicability [17]. Alternative ions like heavy ions (e.g., carbon, oxygen, argon) or secondary ions (e.g., Li^+ , Be^+) may be harnessed, albeit less commonly. The choice of these ions is to meet specific factors such as the elements under investigation, the composition of the sample, and the desired depth of analytical penetration. XRF is a non-destructive analytical technique that measures the fluorescent X-rays emitted when a sample is irradiated with X-rays. By detecting and analysing these emitted X-rays, XRF provides multi element information of PM composition. It is widely used for both qualitative and quantitative analysis of PM, determining major and trace elements. The accessibility, low maintenance costs, and versatility of XRF laboratory and portable instrumentation combined with possibility of in situ analysis make it an attractive option for a wide range of application like geological exploration, environmental monitoring, and archaeology. XRF is considered a green analytical technique because it typically requires fewer chemicals and generates less waste compared to the other wet chemical methods. Furthermore, XRF instrumentation and operation are cost-effective with respect to other analytical techniques.

In Europe, the European Directive on ambient air quality and cleaner air for Europe [18] emphasizes the importance of employing standardized measurement techniques and uniform criteria for the number and placement of monitoring stations. While ICP-MS and AAS are mentioned, there is no reference to XRF as no European Standards (CEN) or International Standards (ISO) exist. This ensures that the data collected on air pollution is both representative and comparable through the Community. The directive also recognizes the potential use of methods for in-situ measurements to evaluate ambient air quality. Consequently, it is imperative to establish criteria governing the usage of such techniques and the accuracy standards they must meet. The European standard EN 14902:2005 'Standard method for the measurement of Pb/Cd/As/Ni in the PM_{10} fraction of suspended particulate matter' is nowadays the only available and specifies both sampling and analysis requirements referring to Graphite Furnace AAS (GFAAS) and ICP-MS as the reference techniques [19]. ICP-MS has a lower detection limit with respect to AAS [20]. Both techniques require sample treatment with nitric or hydrochloric acid [21,22], for the acidification of liquid samples or solubilization of solid. These procedures are time-consuming and may introduce potential sources of error. The potential of EDXRF to be equivalent to GFAAS and ICP-MS for the determination of elements in PM_{10} filters was evaluated by the Joint Research Centre of the European Commission, but it was never included in a standard method [23]. On the other hand, in the US, the EPA already included XRF in the Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air since 1999 [24]. In the last few years, there has been an increased interest in XRF for the analysis of PM, likely due to several advantages it offers over the other standardized techniques and the growing focus on aspects of green analytical

chemistry (see Fig. 1). Indeed, the simultaneous multi-element capability of modern XRF instrumentation, combined with improved automation, provides a distinct advantage with respect to sequential analysis of each element. This enables quick results, efficient data collection, and analysis, making XRF a unique tool also for screening of PM filters compositions. An increased interest in XRF analysis can also be attributed to the growing emphasis on green analytical chemistry, which seeks to minimize environmental impact and promote sustainable analytical practices [9]. This advantage is particularly beneficial in environmental monitoring studies where a large volume of samples needs to be processed within a limited timeframe, without the need for extensive sample preparation and destruction, and reduced consumption of dangerous compounds to be specifically disposed at the end of the analysis. This manuscript presents XRF based methods to obtain elemental mass concentrations in PM.

2. XRF experimental configurations

XRF relies on the excitation of atoms in the sample by high or low-energy X-ray photons. When the incident X-rays with sufficient energies interact with the atoms, inner-shell electrons are ionized or promoted to higher energy levels. This excitation destabilizes the atoms, and as they return to their ground state, they emit X-rays that are characteristic of the specific elements present in the sample [25]. Various experimental configurations are used in XRF instruments, each tailored for specific applications and sample types. The most common setup used for PM analysis is Energy Dispersive XRF (EDXRF) which uses a detector to measure the energy of X-rays emitted by a sample. Two additional XRF based techniques are used: Wavelength-Dispersive XRF (WDXRF) and Micro XRF (μ -XRF).

In EDXRF the angle between the incoming X-ray beam and the sample surface (glancing angle) and the angle between the detector and the sample surface define two geometrical configurations schematized in Fig. 2. The conventional configuration with angles $45^\circ/45^\circ$ (simply referred as EDXRF) and the configuration with angles $0^\circ/90^\circ$ commonly referred as Total Reflection XRF (TXRF). The TXRF configuration is mainly selected when the phenomenon of external total reflection of the incoming X-ray beam wants to be exploited, to enhance the analytical sensitivity. This condition occurs when the glancing angle is lower than the critical angle of the sample substrate and an X-ray standing wave (XSW) is generated through the constructive interference of the incident and reflected beams, amplifying the X-ray fluorescence signal of the elements present on the sample surface [26,27]. When TXRF is combined with X-ray absorption near edge spectroscopy (XANES) is also possible to get speciation information [28]. It is worth to notice that the condition of total reflection does not only depend on the glancing angle,

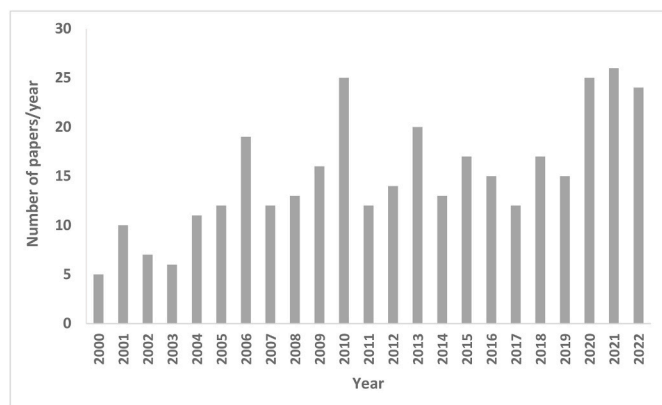


Fig. 1. Number of published papers per year using XRF based techniques for PM analysis from 2000 to 2022 (Total 346 paper, keywords: PM analysis and XRF or TXRF; source: Scopus.com).

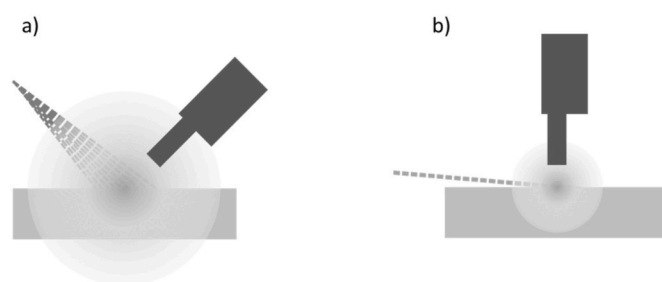


Fig. 2. Schematic diagram of the geometrical configurations used in: a) conventional EDXRF, and b) TXRF.

and it is strongly related with the sample characteristics, thus leading to multiple experimental cases where the above-mentioned condition is not or only partially fulfilled. In this case, the signal enhancement is absent or reduced and TXRF can be simply considered as a different geometrical variation of EDXRF where the advantage is due to the proximity of the detector to the sample surface enhancing the solid angle of collection [29]. The utilization of instruments at a configuration of 0° – 90° allows for the exploitation of signal enhancement at lower angles. This approach can be applied to samples that adhere to the thin film approximation, where a linear relationship exists between fluorescence intensity and element concentration. Determining the critical mass for multielement samples can be challenging. However, the thin film approximation can be verified by examining the direct proportionality between intensity and concentration using reference materials (RM). If the instrument permits angular scanning, the optimal measuring condition for determining an element in a sample corresponds to the maximum point on the angular scan curve.

WDXRF spectrometers are equipped commonly with Cu and Mo X-ray tube. Distinguishing themselves from the previously mentioned configurations, WDXRF sample chambers are often maintained under vacuum or controlled atmospheric conditions to minimize interference from air and other gases. WDXRF instruments employ crystal monochromators or analysers to precisely select and disperse X-rays of specific wavelengths. These optics play a critical role in separating the characteristic X-rays emitted by the sample into their constituent wavelengths, facilitating precise elemental identification. WDXRF instruments offer exceptional resolution, and elemental coverage being able to detect light elements down to C under vacuum [30] or excitation power tuning [31]. However, they do have certain drawbacks, such as being time-consuming, especially when analysing a wide elemental range. Additionally, their acquisition and maintenance cost together with the complexity of use can pose challenges. Additionally, most of WDXRF instruments are quite large, demanding substantial laboratory space, require a vacuum environment for operation and pure gas mixtures for operation and stand by. Achieving power optimization is feasible for only a few elements.

Micro-XRF instruments are equipped with microbeam X-ray sources, typically microfocus X-ray tubes. These sources generate highly focused X-ray beams, enabling spatially resolved analysis. These instruments employ polycapillary optics to focus and collimate the X-ray beam onto the sample. One of the key features of μ -XRF is spatial resolution which can span from micrometres to sub-micrometres depending on the instrument, enabling to analyse small portions of interest within a sample. In some μ -XRF instruments elemental mapping is possible, by scanning the sample in a controlled manner beneath the focused X-ray beam. The obtained spatially resolved data provide invaluable insights into the distribution of elements on the sample surface at the μm or even sub- μm scale. In the case of PM samples this feature is fundamental for understanding elemental variations among PM particles and identifying specific particles of interest for source apportionment studies and identification of exposure hotspots [32,33]. Nevertheless, μ -XRF does have some limitations, including sample size requirements, potential

time intensiveness, particularly when performing high-resolution mapping, and a limited ability for depth profiling. These instruments primarily provide information about the surface or near-surface composition of samples and mainly on a qualitative basis.

3. p.m. sampling devices and collection substrates

For PM monitoring, countries like the US [34] and European Nations (EN)/Union (EU) [35] successfully adopt cyclone-based and impactor-based samplers. Cyclones, impactors and virtual impactors are mechanical devices utilized to separate particulate matter based on particle aerodynamic diameter and later the mass of PM determined by weighing the collecting substrate before and after sampling [36]. Cyclone separators are essential stationary equipment widely employed in the field of air quality. By utilizing centrifugal forces, cyclone sampling techniques are effective in collecting airborne particles. The cyclone separator is known for its simple structure and geometry, absence of internal components, high efficiency, minimal maintenance requirements, and low manufacturing cost. However, it is worth noting that typical cyclones exhibit lower efficiency when it comes to capturing fine particles [37,38]. Thus, causing a lower “collection efficiency” and sampling representativeness if non filtering substrates are used. In impactors air containing particles is accelerated through an orifice or nozzle towards a plate placed below the orifice, which causes the airstream to change direction abruptly. Particles small enough to follow the streamlines remain suspended, while those unable to do so collide with or impact upon the plate. Various type of these air sampler are commercially employed: high [39], medium [40] volume air sampler, micro-orifice uniform deposit impactors [41] and cascade impactors [42–44].

It is important to select the appropriate substrate for PM collection based on the specific requirements of the study, the desired particle size range, the nature of the particulate matter, and the compatibility with subsequent analytical techniques. Substrate materials include cellulose, glass fibre, quartz fibre [45,46], polytetrafluoroethylene (PTFE) [47,48] greased quartz reflector [49,50], mixed cellulose ester, greased aluminium foils, or Si wafer [51]. The most widely used collecting substrate for EDXRF is a filtering membrane, offering a high capture efficiency, allowing for the collection of a wide range of particle sizes. While, in near real-time XRF instruments the substrate is a filtering tape [52]. Reflective substrates are sometimes used when TXRF measurements are performed. The European Union’s reference method for measuring heavy metals in PM consists in the analysis of air filtering membranes sampled at air monitoring stations [18]. Filters have different pore sizes and filtration efficiencies, allowing for the collection of particles of various sizes and types. Filter membranes such as Teflon are compatible with a range of analytical techniques and are often used for gravimetric analysis, chemical analysis, and microscopic examination of PM. Compared to the other substrates, filters enable comparability of results across different monitoring sites and studies [19]. Standardized protocols define the sampling duration, flow rate, and filter type, ensuring consistency in data collection. By adhering to these protocols, it can compare and combine data from different locations, enabling regional or global assessments of air quality [53]. PM collected on filter membranes can be easily preserved and archived for future analysis or reference purposes. The filter membranes can be stored under controlled conditions to maintain sample integrity and stability. This archiving capability allows for retrospective analysis, reanalysis of samples using new analytical techniques, or validation of previous results.

4. Preparation of PM loaded substrates for XRF analysis

While XRF measurements of PM collected on non-filtrating substrates, such as reflectors, typically require no sample preparation, various sample preparation methods are applied to PM filters. The

choice depends on many constrains, including whether the entire substrate, cut portions, or only the removed PM should be used. The main sample preparation methods used for EDXRF and TXRF analysis are summarized in Fig. 3. In EDXRF, a cut portion or the whole filter can be placed on an XRF sample cup and secured with a binding agent to be measured. Instead, TXRF is designed to analyse dried residues resulting from liquid deposition on a smooth, reflective substrate or thin films. Thus, the dedicated sample preparation strategies are tailored to achieve these specific conditions. For instance, filter solubilization or extraction can be utilized to obtain a liquid solution or suspension, which is then deposited on the reflector and dried for TXRF measurements. Alternatively, a representative portion of the filter can be cut and affixed to a reflective substrate. An innovative preservation method has been recently proposed, involving the plasticization of the entire filter for long-term storage and direct XRF measurement. More details about each procedure are following reported.

Metallic nanoparticles aerosolized on filters were measured by a TXRF instrument at a higher glancing angle, with a special carrier maintaining the filter in a flat position without further treatment, achieving the best sensitivity with polycarbonate (PC) filters compared with fibrous or sponge-like materials like mixed cellulose ester, PVDF, PTFE [54].

Extraction techniques are used to remove the PM from the filter for further analysis. Some commonly employed extraction methods include solvent extraction, sonication, or rinsing the filter with appropriate solvents. These techniques help in separating the PM from the filter substrate while maintaining the speciation of the analytes of interest [55,56].

Digestion is a chemical process in which a sample is dissolved or partially dissolved using strong acids or a mixture of acids. The purpose of digestion is to break down the complex matrix of the sample, such as organic materials, minerals, and other compounds, to release the target elements into a soluble form. To perform filter mineralization, microwave-assisted reaction systems are mostly used [57–59].

Ashing, also known as dry ashing or incineration, is a thermal process where a sample is subjected to high temperatures (typically between 450 °C and 800 °C) in a controlled environment, to oxidize organic components and obtain an inorganic ash residue. Cold plasma ashing is a variant of the traditional process that uses a plasma source for the oxidation, leading to operate in a low temperature environment. The use of pure oxygen minimizes contamination risks, however loss of volatile elements during the process may occur. Ashing offers distinct advantages over microwave-assisted digestion of PC filters which are completely ashed, increasing the signal-to-background ratio and enhancing the analytical sensitivity and accuracy of TXRF analysis [60]. Specifically, cellulose acetate filters are chosen for their ability to be decomposed by oxygen-plasma [9].

Preservation techniques are usually implemented to ensure that no PM is lost from the filter during storage and transportation. One effective method compatible with various XRF analysis methods [48] involves the encapsulation of the PM filter between two laminated polymeric sheets using an automatic device called SMART STORE®. This approach offers several advantages, including the preservation of the PM filter’s structural integrity, and protection against external contaminations. Furthermore, by removing the stretching ring of PTFE filters, this method enables the direct illumination of the filter surface by the X-ray beam in TXRF analysis [61–64].

5. Qualitative and quantitative elemental analysis of PM

Qualitative XRF analysis identifies the elements present in a sample exposed to X-ray photons of suitable energies based on their characteristic X-ray fluorescence emitted from the sample [65]. Fig. 4 shows a portion of the XRF spectrum acquired from a certified reference material (NIST SRM 2783 - Air particulate on filter media) prepared using the SMART STORE® and measured by a TXRF instrument equipped with

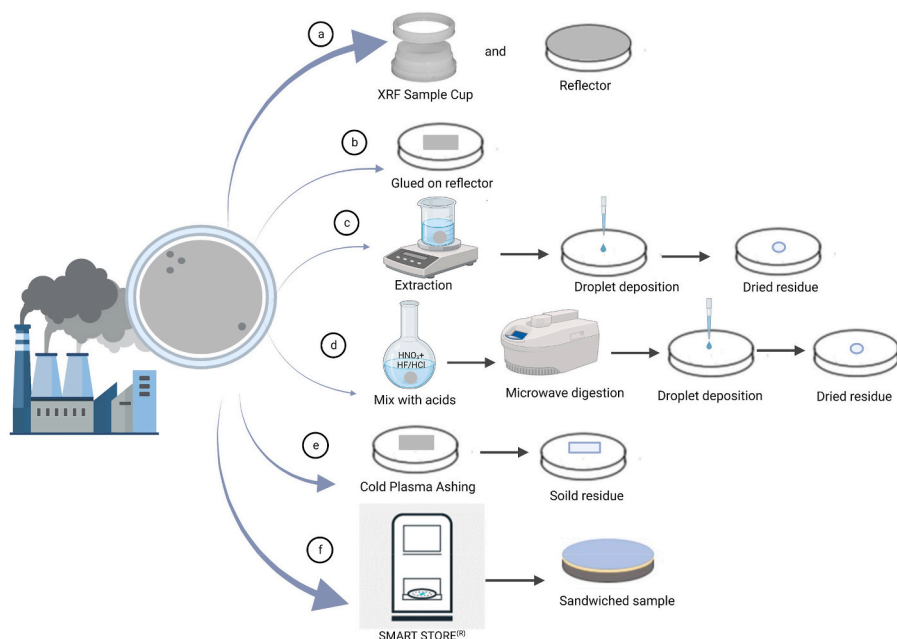


Fig. 3. Sample preparation methods of PM filters for XRF analysis: a) no treatment; b) portioning and glue; c) liquid extraction; d) microwave acid digestion; e) cold plasma or wet ashing; f) preservation (Created with [BioRender.com](#)).

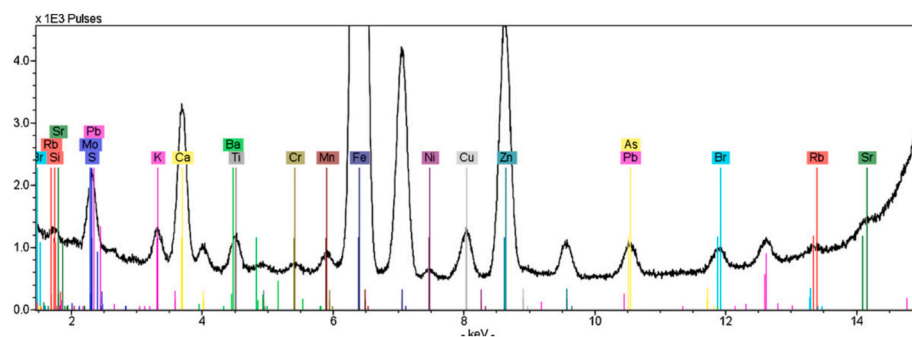


Fig. 4. TXRF spectrum of NIST SRM 2783 filter sample, treated in accordance with PCT/IT2008/000458. The y-axis illustrates X-ray intensity, while the x-axis denotes the energy levels (keV) of the elements present in the sample. (Licensed under journal Talanta, License Number: 5595941006555).

Mo-K α anode metal-ceramic X-ray tube, having a multilayer monochromator and XFlash® Si drift detector. Elements with characteristic X-ray fluorescence emission below the excitation energy (about 17.485 KeV) can be identified comparing the peak energy with that of the characteristic X-ray emission lines tabulated or stored in the software database. Fig. 4 shows the unambiguous presence of some elements identified by their K α lines: K, Ca, Cr, Mn, Fe, Cu, Zn, Br, Rb, and Sr. The main challenge in qualitative XRF analysis is to establish the presence of elements with overlapping XRF emissions. Generally, this is observed with the K lines of lighter elements and the L lines of heavier elements. In the spectrum of Fig. 4 one can observe the overlap of Ti with Ba, and As with Pb, all present in NIST SRM 2783. In this case, the fitting of the spectrum using software based on fundamental parameters, such as PyMCA [66] or reference spectra (such as the Bruker Spectra 5.1 evaluation software) can be useful to distinguish the presence of one or the other element or both. To address these challenges, advanced techniques such as high-resolution XRF or different excitation energies to resolve overlapping peaks can be also used.

Quantitative XRF analysis converts the characteristic X-ray emission signal from the elements present in the sample, measured as peak height or area, into mass or concentration amounts. The determination of relative concentration, usually in %, of the elements identified in the sample is often called semi-quantitative analysis. The conversion of

intensities into amounts is based on algorithms that are determined with three main methods, which we will call fundamental parameters, internal standard calibration, and matrix calibration. Each calibration method possesses own set of advantages and limitations, and the selection depends on many applications related factors.

The fundamental parameter method, also called reference-free is based on theoretical calculations that relate the measured X-ray intensities to the concentrations of elements in the sample. This approach considers the physical characteristics of the X-ray interaction with the sample and employs mathematical models to estimate element concentrations [51,67].

The internal standard calibration method is predominantly employed in TXRF analysis, leveraging the thin film approximation to assume a consistent matrix effect. In this approach, a known concentration of an element not naturally present in the sample, often Ga or Y, is introduced into the liquid sample. The quantity of other elements in the sample is subsequently determined in relation to the added element, which serves as an internal standard for calibration [68].

The matrix calibration uses regression of experimental data to calculate the calibration curve relating the XRF emission intensity (ordinate) of an element with its concentration or mass (abscissa). Experimental data are obtained measuring samples with known concentrations of elements of interest. The calibration curve equation is

then used to convert into the element concentration or mass the XRF emission intensity of each element identified in the spectrum of a sample with unknown composition [23,63]. This methodology is often referred as external calibration or empirical approach and it is widely used in many analytical techniques other than XRF.

6. Applications in air quality and environment

Regulatory measures, such as emission controls, stricter air quality standards, and the promotion of cleaner technologies, are crucial in reducing PM emissions at the source. XRF analysis is a powerful tool for characterizing PM filters for air quality monitoring purposes. It provides valuable insights into the elemental composition of particulate matter, assists in source identification, facilitates real-time analysis, and supports quantitative assessment. By utilizing XRF techniques, environmental monitoring programs can better understand the bad impacts of PM on human health and the environment can be mitigated to support the aim of the United Nations Sustainable Development Goals (n. 3, 11, 12, 13, and 15). Table 1 provides a summary of relevant literature reporting the use of XRF based techniques for elemental analysis of PM loaded substrates, including details of sample preparation methods, XRF configuration, quantification approach, and elements analyzed.

The elemental composition data obtained from XRF analysis are used to identify potential sources of air pollution and conduct pollution source apportionment studies [69]. By comparing the elemental signatures of PM samples with those of known emission sources, such as industrial emissions or vehicle exhaust, researchers can gain insights into the contribution of different sources to the overall pollution. This information is crucial for developing effective pollution control strategies

and targeted interventions. In the research conducted by Yeonjin Kim et al. [70], the objective was to determine the chemical composition of PM through XRF analysis. For this purpose, three filter samples were obtained from the living rooms of 8 households, each inhabited by individuals with asthma to assess the concentrations of heavy metals in PM_{2.5}. The collected filter samples were analyzed separately in a sequential manner using three different XRF spectrometers. The analysis included the assessment of twenty-five different heavy metals using XRF instruments across three distinct global research institutions. The high data correlation highlights the compatibility and reproducibility of XRF for the analysis of PM_{2.5} samples. It is recently found that handheld XRF may also provide elemental concentrations of environmental PM in good agreement with those determined by benchtop XRF spectrometer [71]. The progress in EDXRF instruments, enhanced by secondary targets and three-dimensional polarization optics, has proven to be a successful approach for the analysis of various inorganic elements present in aerosols collected on quartz fibre filters, as demonstrated in the study by Okuda et al., in 2013 [72]. The primary challenge in implementing XRF lies in achieving comparability with other established analytical methods used for PM elemental analysis. However, it has been demonstrated that results obtained using EDXRF align with those obtained using ICP-MS for PM samples collected on quartz fibre filters [72], and PTFE which is found to be preferable due to the absence of contamination [23,57,73]. Indeed, the presence of nickel (Ni) in the quartz fibre blank filters could not be ignored [72]. The comparison highlights that the primary drawback of ICP-MS is the requirement for sample solubilization, whose effectiveness also depends on the composition of the PM, thereby reducing the representativeness of the sample to be analyzed, especially for critical elements to dissolve such as Ti, Cr, and Al [57].

Table 1

Summary of XRF Techniques applied for elemental analysis of various PM loaded substrates. The table presents different substrates, sample preparation methods, XRF techniques used for elemental analysis, quantification approaches, and the analyzed elements. Reference sources are provided for each entry.

Substrate	Sample Preparation	XRF technique	Quantification	Elements	Reference
PTFE & quartz filter	Direct	ED-XRF	Fundamental parameters	Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Fe, Co, Ni, Mn, Cu, Zn, As, Br, Sr, Pb, Mo, Cd, Sn and Sb	[23]
Quartz fiber filters	Digestion (HCl: HNO ₃ , 1:3)	TXRF	Internal standard addition (Ga + Y)	Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Sr, Ti, V, Zn	[45]
Nuclepore and PTFE filters	Direct	ED-XRF	Matrix calibration	Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Ba, and Pb	[46]
PTFE filters	SMART STORE®	TXRF, SR-TXRF	Matrix calibration	Mn	[48]
Greased quartz reflector	Direct	TXRF	Internal standard addition (Y)	K, Ca, Ti, Mn, Fe, Cu, Zn, Ni, Rb, Sr, Pb	[50]
Si wafer	Direct	GIXRF	Fundamental parameters	C, N, O, Na, Mg, Al	[51]
Filter	Extraction	TXRF	Internal standard addition (Ga)	K, Ca, Fe, Zn and Pb	[55]
PTFE filters	Extraction	TXRF using synchrotron radiation	Internal standard addition (Ga)	K, Ca, Mn, Fe, Cu, Zn, Br, Sr, Ba and Pb	[56]
Whatman-41 filter	Cut + spike with IS	ED-XRF	Internal standard addition (Ga)	Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Zr, W, Pb, Bi	[69]
PTFE	Digestion	TXRF	Internal standard addition (Ga)		
Polycarbonate filter	Digestion	TXRF	Internal standard addition (Ga)	Al, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Ba, Pb	[58]
Polycarbonate filter	Ashing	TXRF	Internal standard addition (Ga)	S, Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb	[60]
PTFE	SMART STORE®	TXRF	Internal standard addition (Cu)	Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Ba, and Pb	[61]
PTFE	SMART STORE®	TXRF	Matrix calibration	Mn	[62]
PTFE	SMART STORE®	TXRF	Matrix calibration	Pb	[64]
PTFE	SMART STORE®	TXRF	Matrix calibration	Pb	[63]
Polycarbonate filter	Direct on filter	TXRF	Matrix calibration	ZnO, TiO ₂ , CeO ₂ , Al ₂ O ₃	[54]
Quartz fiber filter	Direct	EDXRF	Fundamental parameters	S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb	[72]
PTFE filters	Direct	XRF	Matrix calibration	Na, Mg, Al, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Zr, Pb.	[73]
PTFE filters	Direct	EDXRF	Matrix calibration	Al, As, Ba, Br, Ca, Cd, Cl, Cr, Cs, Cu, Fe, K, Mn, Ni, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Ti, V, Zn	[70]
PTFE filters	Direct	Handheld XRF	Matrix calibration	Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Al, Si, S, K and Ca	[52]
PTFE filters	Direct	EDXRF	Matrix calibration		
PTFE filters	Direct	Handheld and benchtop EDXRF	Matrix calibration	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Pb	[71]

Efforts have been made to utilize handheld XRF instruments for the elemental analysis of PM, as demonstrated in the study by Chatoutsidou et al., in 2022 [71]. The findings of this study revealed a notable concurrence between portable and benchtop XRF spectrometers, particularly for certain elements, along with comparable limits of detection.

In time-resolved and size-segregated elemental analysis of airborne PM, TXRF demonstrates superior performance compared to the conventional ICP-MS approach for samples collected on cascade impactors at high frequency. In this context, a significant challenge is to achieve traceability due to the variability in aerosol deposition patterns on impaction plates, necessitating reference samples that accurately mimic these deposits in both spatial distribution and elemental composition [74]. A comprehensive review summarizes the sample preparation methods used for qualitative and quantitative analysis of PM filters by TXRF [75]. In the pursuit of optimizing sample preparation techniques, Wagner et al., in 2010 [60] demonstrated the superiority of cold plasma ashing over conventional digestion methods for aerosol particles collected on polycarbonate filters, particularly in terms of streamlined sample preparation and reduced contamination risks. However, it's worth noting that additives, such as the fixatives employed to affix the filter material onto TXRF sample carriers, warrant further investigation to identify and mitigate potential sources of contamination. The thin film like correlation between XRF intensity and elemental concentration is clearly demonstrated when analysing atmospheric PM filters prepared with SMART STORE® measured in TXRF instruments with strong evidence of the possibility to realize matrix calibration curves [61,63]. This correlation forms the basis for conducting quantitative elemental analysis of PM filters, provided that appropriate calibration samples are available to validate the analytical method. The calibration samples enable the determination of a linear calibration range, as well as the establishment of limits of detection and limits of quantification. These parameters are crucial in ensuring accurate and reliable quantification of elements in PM filters [64]. The application of reference PTFE filters measured by XRF under grazing incidence (GI) conditions demonstrated a linear range from 0.028 to 4.239 $\mu\text{g cm}^{-2}$, and the RSDs were below 10 %, revealing a promising and precise results for Pb concentrations [63]. This determination was made through rigorous statistical analysis, including a comparison with a quadratic regression model. It's worth noting that the linear range's upper limit was capped to exclude the highest lead loading sample where absorption effects were not compensated, ensuring the accuracy and reliability of the linear relationship within this specified concentration range. Moreover, the Smart Store® procedure demonstrated to be versatile to be applied for many fluorescence based techniques: μ -XRF, EDXRF, TXRF and GIXRF, and synchrotron radiation (SR) [48]. Data obtained by SR-XRF showed that the instrumental configuration has a significant impact on the results. The more focused the beam, the more visible the inhomogeneity. Inhomogeneity clearly increases with mass deposition [48]. All the studies reviewed in the literature consistently highlight the numerous advantages of TXRF over ICP-MS in terms of sample preparation, analysis, and data outcomes. TXRF presents a streamlined and more straightforward sample preparation process, in addition to the simplicity of instrument use and maintenance, not requiring routine calibration, vacuum pumps and gases. In TXRF, samples are typically direct analysis, eliminating the need for extensive digestion procedures or dealing with difficult sample matrices. This approach drastically reduces the complexity of sample preparation. Furthermore, TXRF demands only few sample portions, making it exceptionally suitable for situations where sample quantity is limited. TXRF offers outstanding surface sensitivity, positioning it as the technique of choice for thin films, coatings, or surface layers. In contrast, ICP-MS, while incredibly sensitive, primarily provides bulk analysis and may not distinguish surface composition from interior composition as effectively. One noteworthy advantage of TXRF is its reputation as an environmentally friendly technique. TXRF reduces the uses of harmful reagents and minimized generation of chemical waste, meeting the

principles of green chemistry.

Although significant progress has been made in the XRF methods, comparable results with those obtained through standardized spectroscopic techniques, a recurring challenge emerges in various studies: the lack of certified reference materials. Consequently, considerable efforts have been dedicated to the development of both mono-element and multi-element reference materials [73,76,77]. Despite the validation of XRF measurements against other established methods like ion chromatography and ICP-MS for specific elements, the absence of a universally accepted Reference Method for determining the elemental content of PM makes difficult to choose the best analytical method. They are often considered as complementary to each other. This highlights the pressing need for universally recognized reference materials that rigorously assess all aspects of the measurement process, a necessity for the atmospheric PM monitoring community.

7. Trends and perspectives

The trend towards green analytical methods is gaining momentum, aiming to minimize the use of hazardous materials, lower energy consumption, and generate less waste. Embracing sample preparation approaches with minimal or no treatment aligns with the principles of green analytical chemistry. This reduction in waste generation and resource consumption allows laboratories to contribute to more sustainable practices while obtaining accurate and reliable and dependable analytical results. Emphasizing green sample preparation methods is crucial for advancing environmentally conscious research and fostering a greener future for analytical science [78].

In this context, XRF-based analysis of PM filters without the need for complex extraction or digestion procedures offers a valuable alternative with numerous advantages compared to standardized analytical techniques. The integration of multiple techniques can provide a comprehensive understanding of the elemental composition of PM, thereby contributing to air quality monitoring, health risk assessment, and regulatory compliance efforts. Ensuring data interoperability is crucial when analysing data from various techniques to achieve consistency, comparability, and seamless integration of results. Interoperability enables the combination of information from different sources and facilitates comprehensive data analysis. Particularly, the need for data interoperability between ICP and XRF becomes vital in addressing the challenges posed by PM pollution.

The challenge lies in establishing the reliability and accuracy of the XRF technique through calibration procedures that utilize fit-for-purpose RM. The accuracy of determination heavily relies on the selection of appropriate calibration samples, RM, or certified RM. Unfortunately, there is a lack of CRM specifically tailored for PM analysis. Presently, only one certified RM, NIST SRM 2783, provided by the US National Institute of Standards and Technology, is available in the market, but it is not suitable for all types of PM as it is specific to PM_{2.5}. While some RM are fabricated by depositing thin films of various compounds in a vacuum, only a few handmade secondary reference materials are mentioned in the literature and EPA methods [24]. These limited options suffer from low representativeness due to differences in matrix composition between thin films and actual particles, as well as the method of preparation. There are some important features to meet in order to obtain the ideal filter-based reference material such as: i) the material to be deposited should be a contemporary material, containing an elemental pattern representative of the real samples of interest; ii) the standard solutions should consider the whole range of size-fractionated, focusing more on the "inhalable fraction"; iii) a sufficiently large batches of uniform filters should be tested before distributing them as reference materials [79]. Recently, several attempts have been made to produce reference materials and calibration samples on various substrates. Aerosol generation systems are used to produce RM of analytes of interest on filter membranes with assigned mass loadings [69–72], or calibration samples by using nanoparticles suspension [54] or salt based

water solutions trying to mimic ambient or workplace aerosol composition [80–82].

As the importance of accurate and reliable particulate matter analysis will continue to increase, there is a growing interest in developing operating procedures to be translated into international standards supporting quality assurance processes that ensure the validity and recognition of analytical results. In this frame interlaboratory tests are crucial in ensuring consistent and comparable results across different analytical platforms and laboratories.

8. Conclusion

To sum up, XRF-based methods are a suitable holistic approach for PM analysis. Their adaptability and capacity to supply information on constituent elements, together with their user-friendly benefits, establish them as an excellent option for PM characterization across diverse applications. This underscores their critical role in environmental research and safeguarding public health. The adoption of green principles in elemental analysis emphasizes sustainability, efficiency, and reduced environmental impact, aligning with the growing demand for greener analytical practices. The entire analytical process optimization with a green mindset, from sample preparation to XRF analysis minimizes waste generation, reduces the use of hazardous reagents, significantly improving the sustainability of the elemental analysis process with respect to the traditional standardized techniques. The incorporation of automated devices further enhances the efficiency of sample preparation while reducing both time and reagent consumption. This forward-thinking approach fosters a greener and more sustainable future for analytical science. XRF techniques' compatibility with existing PM sampling methods on filters allows for seamless integration, and its application will drive innovation in the development of a comprehensive green methodology encompassing sample preparation, and measurement, coupled with quantitative analysis calibration using fit-for-purpose RM. Considering the advantages listed in the reviewed papers, the European and International standardization of XRF methods for PM analysis emerges as a pivotal stride toward harmonizing data collection, analysis, and interpretation across research and regulatory framework. The adoption of standardized methods not only fosters comparability between studies but also boosts the credibility of XRF analysis of PM, underpinning informed decision-making and safeguarding environmental and public health. In this way, researchers can make significant contributions to understanding air pollution, mitigating its harmful effects on human health, and protecting the environment, ultimately promoting environmentally responsible practices, and advancing the principles of green chemistry, paving the way for a healthier and more sustainable future.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT in order to improve language and readability. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Declaration of competing interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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