



TXRF analysis of airborne particulate matter captured in liquid medium using a cyclone bioaerosol sampling approach[☆]

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ABSTRACT

A deep investigation of the aerobiome is necessary to assess air quality and the effect of environments on people's health. Characterization of airborne particulate matter (PM) is essential to study inorganic elements present in aerobiome. This study proposes a proof-of-concept method integrating an innovative liquid-based sampler, named Corlios Micro®, with Total Reflection X-ray Fluorescence (TXRF) analysis for rapid and multielemental analysis of airborne PM. TXRF is a suitable analytical technique since it requires small sample amount for analysis, making it ideal for low masses collected in liquid. Nevertheless, sampling in liquid medium poses some challenges associated with the heterogeneity and representativeness of the sample. To address these effects, we compared two sample preparation approaches - pre-concentration and lyophilization. Pre-concentration was applied because of its simple procedure and fast analysis time. This approach revealed low repeatability, which pointed to the problem of representativeness in highly dilute suspensions for the chemical analysis. On the other hand, lyophilization, which enabled the analysis of the whole collected sample, demonstrated low variability between replicates. This sample preparation method allowed to quantify the concentration of elements and identify the differences among various locations in indoor and outdoor sites. This optimized procedure demonstrates the potential of combining TXRF analysis with liquid-based airborne PM sampling for environmental exposure assessment in complex indoor and outdoor environments.

1. Introduction

Air pollution, which is a serious public health hazard, contributing to a rise in global morbidity and mortality, is caused by the presence of chemical and biological contaminants. It is known that airborne particles serve as a carrier of microorganisms, organic compounds, and inorganic pollutants like metals and metalloids [1] and can travel long distances [2,3]. The aerobiome comprises the community of microorganisms and biological particles suspended in the atmosphere, such as bacteria, fungi, pollen, spores, and biologically derived fragments [4]. Notwithstanding the data suggest that aerobiome characteristics may

have a protective immune system effect [5–7], airborne microorganisms interact with chemical pollutants, influencing their toxicity, causing cardiovascular and neurodegenerative disease (like Alzheimer's), asthma, and cancer [8,9]. Since the aerobiome's composition varies significantly depending on the season, weather and environment conditions [10,11], it is necessary to evaluate the presence of chemical compounds such as black carbon (BC), particulate matter (PM₁₀ and PM_{2.5}), ground level ozone (O₃), sulfur dioxide (SO₂), nitrogen dioxides (NO₂), heavy metals and volatile organic compounds (VOCs) [12,13] to better understand the interaction between chemical pollutants and airborne biological components. Determination of heavy metals in

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airborne PM has a particular importance due to their persistence. The concentration of heavy metals in airborne PM differ between indoor and outdoor environments [14]. The main sources of outdoor airborne PM are traffic emissions, industrial processes, burning of biomass, soil resuspension, and long-range atmospheric transport [15], while chemical composition of indoor PM is greatly influenced by human occupancy and activities [16,17], building materials, ventilation efficiency [18], and cleaning methods. Integrated monitoring techniques that can capture the pollutants in both environments offer important insights into pollution sources, and potential health implications [19,20]. Air sampling is commonly performed using various active or passive sampler. Sampling and determination of chemical pollutants is carried out in accordance with normatives [21–24], there is a lack of standardized methods for bioaerosols, which are defined as material released by organisms (e.g., spores, pollen) live and dead microorganisms with a size range: 0.05–100 μm [25]. The commonly used sampling techniques are filtration, impaction, impingement, or cyclone separation, which each one has distinct benefits and drawbacks. One of the most employed methods for sampling airborne PM is the use of filter-based samplers [26,27]. Air is drawn through quartz, Teflon, or glass fiber filters by high- or low-volume air samplers, which retain particles for elemental, chemical, or gravimetric analysis [28,29]. Although filters have high collection efficiency and are compatible with standardized techniques, they present problems for biological analyses. Size-selective sampling and morphological analysis are made possible by impaction-based samplers, which collect aerosols by forcing airflow onto solid or semi-solid substrates. Particle fractionation based on aerodynamic diameter is particularly possible with cascade impactors [30,31]. Integrated sampling of the aerobiome and airborne chemical pollutants can reduce sampling bias and sample loss, improve consistency between datasets, and simplify analytical and operational procedures. Bioaerosol sampling is performed employing liquid impingement and cyclone-based bio-sampler. These techniques allow for simultaneous chemical and microbiological analyses while maintaining biological integrity by directly collecting airborne particles into a liquid medium. Cyclone-based bio-aerosol samplers, such as the Coriolis Micro®, collect particles from large air volumes into small liquid quantities by using centrifugal forces [25,32,33]. The sampling time ranges from minutes to several hours, the liquid samples can be used for a various analysis, including microscopy, culturing, biochemical assays, and molecular techniques such as PCR and sequencing [34].

The most used instrumental analytical techniques for determination of ions, metals and metalloids present in atmospheric aerosols are ion chromatography (IC), flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), plasma-based techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS), neutron activation analysis (NAA) [32,35]. ICP-OES and ICP-MS are classified as techniques with low detection limits for trace metals and are recognized as standardized methods for quantitative elemental analysis in environmental investigations [36,37]. However, when dealing with filter membranes, they require the acid digestion, which complicates analysis and increases the risk of contamination or analyte loss. Energy-dispersive X-ray fluorescence (EDXRF) and Laser-Induced Breakdown Spectroscopy (LIBS) [38] offer rapid, non-destructive elemental analysis, catering to in-situ and real-time monitoring requirements. Although EDXRF allows to perform direct elemental analysis of PM loaded on filter membranes and it is suitable for air quality monitoring, for low-mass samples and ultra-trace elements, its sensitivity might be restricted. Total reflection X-ray fluorescence (TXRF) spectroscopy is widely used in environmental samples like soils [39], water [40] and employed to characterize PM loaded on filter membranes prepared using the SMART STORE® approach because it permits direct analysis and satisfies the requirements of green sample preparation methods for analytical techniques [41–43]. TXRF is proposed as a potential

analytical alternative to FAAS and ICP-based techniques because of some features such as microanalytical capability that requires low mass sample, no treatment or minimal sample preparation, reduced matrix effects as the sample is deposited as a thin layer, and better detection limits than EDXRF due to the total reflection X-ray geometry. TXRF is successfully applied on solid samples prepared as a suspension [44–49], especially when dealing with mass-limited samples. This approach involves the deposition of small aliquots, usually 10 μL , on reflector. However, the repeatability is not due to the TXRF technique itself, but it is affected by suspension heterogeneity and the drop deposition [50]. For this reason, optimization of sample preparation is essential to obtain reliable results for environmental analysis.

While TXRF has demonstrated potential for the direct analysis of PM collected on solid substrates (e.g. membranes), its application to aerosols collected in liquid media remains largely unexplored. This study presents a proof of concept for using TXRF to liquid aerosol samples by using an innovative cyclone-based air sampling approach, focusing on the development and optimisation of sample preparation method. Pre-concentration and lyophilization were tested as two sample preparation approaches for liquid samples collected from both indoor and outdoor settings.

2. Material and methods

2.1. Air sampling

A residential area, an academic setting (the Faculty of Medicine, Università di Brescia), and an office on the first floor of the Unit of Microbiology and Virology, ASST Spedali Civili di Brescia were selected as different sampling locations to represent various environmental conditions. The first sampling campaign was held during 2024. Air samples were collected using Coriolis Micro® bio-sampler from both indoor and outdoor environments, such as offices, living room, as well as a university courtyard, balcony and home terrace. The terrace and living room are located far from the university. The advantage of Coriolis Micro® bio-sampler is that it can be placed in small spaces because it weighs 2 kg and measures $22 \times 33 \times 36 \text{ cm}^3$ (length x width x height). Every sampling event was preceded by a cleaning and sterilization process to prevent cross-contamination. Cones, screw caps, tubes, and aspiration sections were all cleaned with denatured alcohol and subsequently sterilized under UV-C light for 15 min. Airborne aerosol samples are collected in a volume of 15 mL of ultrapure water (Milli-Q®) (VWR HiPerSolv CHROMANORM® water) in a sterile plastic cone, reaching a minimum volume of about 8 mL. During the sampling, the Coriolis Micro® was set at 300 L/min, which is its maximum flow rate [32]. The bio-sampler, used in the absence of the pre-separator, has been designed to capture particles size from 0.5 to 20 μm and does not provide the required PM_{10} or $\text{PM}_{2.5}$ aerodynamic cut-off separation for regulatory air-quality monitoring. This cyclonic collection mechanism leads to higher collection efficiency for larger particles with higher inertia and the sampled material is more representative of the coarse aerosol fraction ($d > 2.5 \mu\text{m}$).

Indoor environments were sampled with multiple replicates in order to assess occupancy effects and evaluate the reproducibility of the methodology. Regarding the outdoor sampling, it was used as a baseline for comparison with indoor sites and to test the instrument's capacity to identify the differences between various locations.

For the indoor sampling site, Coriolis Micro® was positioned at 80 cm from the ground; for the home terrace and university balcony sites, it was positioned 1.5 m and approximately 4 m from the ground, respectively (see Table 1 for all the investigated locations and sampling conditions). For each sampling locations, one field blank was deployed using the same reagents and containers and processed in parallel with the collected samples. All cones were sealed after sampling and kept at $-80 \text{ }^\circ\text{C}$ for a maximum of 24 h before being processed further (see Section 2.2.1). To stabilize biological material for microbiological

Table 1

Details of the monitoring site, locations, number of collected samples, sampling time, and sample preparation method for elemental chemical analysis.

Monitoring Site	Locations	Points	Number of collected samples	Sampling Time	Sample Preparation
Indoor	University Office	Room 1	$n = 2$	8 h	Lyophilization
		Room 2	$n = 3$ (in different days)	8 h	
	Living room	$n = 1$	45 min		
	Hospital Office	$n = 12$ (in different days)	8 h		
Outdoor	University Courtyard		$n = 4$ (in different days)	4–8 h	Lyophilization
	University Balcony (around 4 m distance from the soil)		$n = 1$	7 h	
	Home Terrace		$n = 1$	20 min	

analysis, aliquots of each collected sample were put into sterile vials with 3 mL of eNat® preservation solution.

A second experiment was performed fixing the sampling time, extended to 8 h. A total of 12 indoor air samples were collected for two weeks in an office on the first floor of the Unit of Microbiology and Virology, ASST Spedali Civili di Brescia. The sampling period was concentrated over several weeks spanning April and May 2025. Throughout the experiment, the office was regularly used for work activities, meetings, and doors and windows were opened when needed.

The cones were rinsed in running water, then with 99.9% ethanol, and a second rinse with 70% ethanol. After, the cones were exposed to ultraviolet (UV) light for 30 min to eliminate residual nucleic acids. Each sterilized cone was subsequently filled with 15 mL of MilliQ sterile water suitable for molecular biology applications. After sampling, the liquid samples were transferred to storage at 4 °C until further processing.

2.2. Sample preparation

2.2.1. Lyophilization

The liquid samples collected in sterile cones during the first campaign were frozen at -80 °C overnight to ensure complete solidification prior to freeze-drying. The samples were subsequently transferred to a laboratory-scale freeze dryer (5 Pascal, Milan, Italy) connected to an Edwards Modulyo vacuum system (Edwards Vacuum, UK) and dehydrated under vacuum conditions until complete lyophilization was achieved. After that, the dried sample was fully recovered and suspended in 45 μ L water solution of Triton X-100 1% wt [51]. Gallium (Ga-ICP Standard Solution, Fluka, Sigma Aldrich) was used as internal standard (IS). Each suspended sample was mixed with 5 μ L of Ga standard solution at a concentration of 10 mg/L, to obtain a final concentration of 1 mg/L. After, 10 μ L of the prepared sample was deposited on a previously cleaned and siliconized (Serva GmbH & Co, Germany) quartz sample carrier and dried at 50 °C on the heating plate under laminar flow hood. For each sample, three replicates were analysed. The workflow is shown on the left-hand side of Fig.1.

2.2.2. Pre-concentration

Samples collected during the second campaign were processed through a two-step centrifugation procedure, which concentrated microbial biomass and removed coarse particle matter. Samples were centrifuged at 1000 rpm for 10 min at 4 °C to remove macroscopic particles. The recovered supernatant was centrifuged at 14000 rpm g for 20 min at 4 °C to remove bacterial cells. After centrifugation, we carefully remove the supernatant and resuspend the pellet in 300 μ L of sterile ultrapure water. Only 40 μ L was used for elemental chemical analysis.

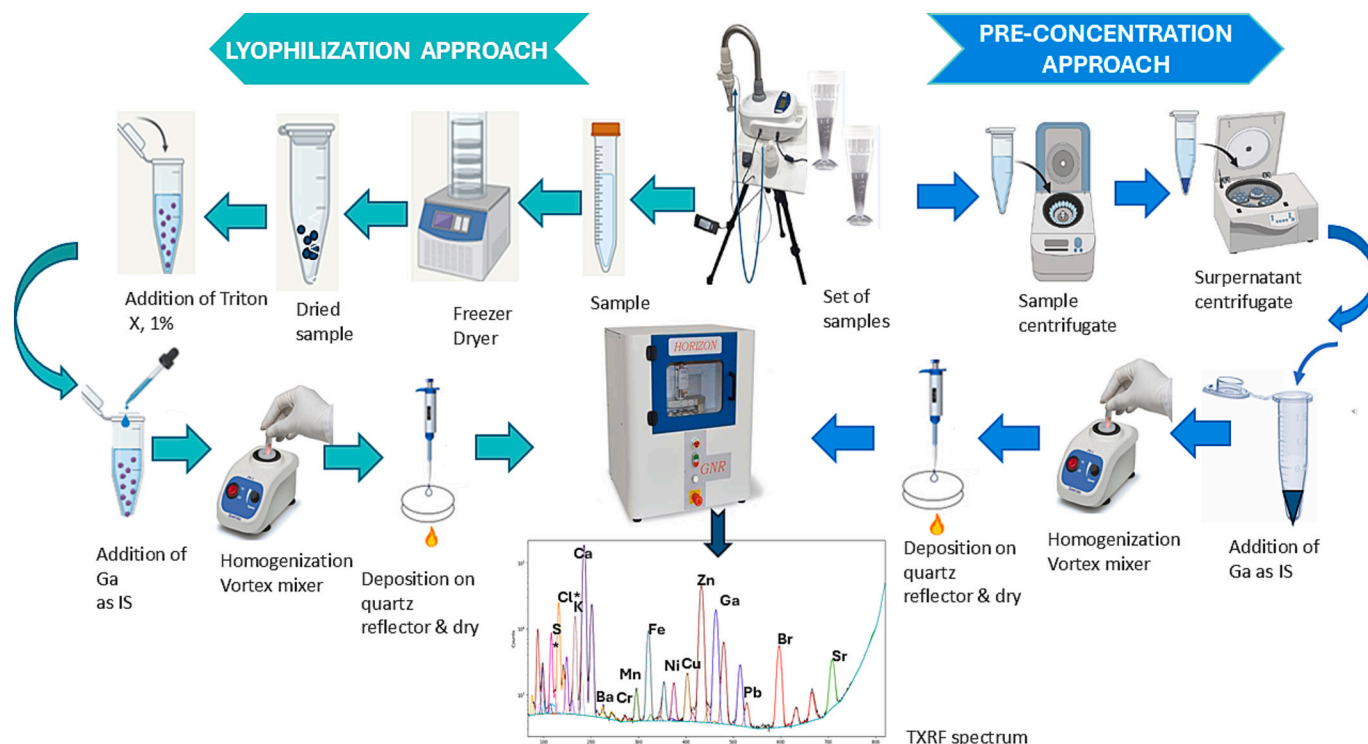


Fig. 1. Schematic layout of two sample preparation methods for TXRF analysis: lyophilization (left-hand side) and pre-concentration (right-hand side).

For TXRF analysis, IS was added in the samples to obtain a final concentration of 0.1 mg/L. The following steps are the same as reported in Section 2.2.1. In this case, four replications were analysed. The workflow is shown on the right-hand side of Fig. 1.

2.3. TXRF analysis

A benchtop TXRF spectrometer (Horizon, G.N.R., Italy) equipped with a Mo—K α (17.44 keV) X-Ray tube coupled with a W/Si multilayer monochromator, a 40 mm² Silicon Drift Detector from KETEK GmbH, fitted with a 1 μ m graphene window, was used for elemental analysis of airborne aerosol samples. The measurements were made in air at 40 kV and 15 mA, and spectra were acquired for 600 s real time.

Quantitative analysis was performed based on the internal standard method and relative sensitivity curves. The ratio of the target element's absolute sensitivity to that of the internal standard (Ga) is known as the relative sensitivity. Aqueous solutions of certified reference materials with known concentrations were previously used to create these curves.

3. Results and discussion

Sampling locations and monitoring sites were chosen as representative environments with different events. Beyond the traditional use of Coriolis Micro® in microbiological investigations [33,34], we applied this cyclone-based liquid sampling technique combined with TXRF analysis for airborne PM characterization of indoor and outdoor samples collected in various locations.

As mentioned in the sampling section, e-Nat solution was added to preserve the sample prior to microbiological investigation. For elemental analysis by TXRF, the use of the e-Nat solution as a storage medium caused the presence of an intense sulfur peak (see Fig. S1) in the TXRF spectrum that covered the background of the spectrum compromising the analytical sensitivity and limits the quantification of other elements, especially at low concentrations. Its intense spectral tails overlap with other elemental regions (such as Cl) while other elements (i.e Cr, Cu, Ni) were not detected. Thus, the collected samples were analysed shortly after sampling to avoid e-Nat addition.

The pre-concentration is used as pre-treatment sample preparation approach when analysing samples with very low elements concentrations [52]. This method allows to enhance the detection limit of TXRF analysis as reported by Barros et al. 2010 [53]. Pre-concentration is operationally simple and maintains the PM in suspension.

Fig. 2 shows the TXRF spectra of an indoor sample collected over a period of 8 h in Hospital Office prepared by pre-concentration method. TXRF spectra were normalized to the maximum counts of Ga peak (9.25 keV) to compensate for variations in experimental conditions (i.e sample deposition). This normalization allows a direct comparison of spectra repeatability. As showed in Fig. 2, four replicates of the same sample exhibited low repeatability. In particular, the intensities of certain elements, such as Cr and Fe, were up to one order of magnitude higher in one reflector compared to other three. Sample heterogeneity is a frequent problem in elemental analysis of suspensions, and in highly diluted samples its effect is more evident. Some strategies are employed to overcome this effect include particle size reduction such as sonication, thorough mixing or agitation prior to analysis, and the use of dispersing agents to improve particle distribution. Nevertheless, for complex environmental samples, these strategies may not fully eliminate sedimentation or non-uniform particle distribution. In this case, the airborne PM was collected in relatively large liquid volumes (roughly 7–8 mL), which led to suspensions with a diverse range of particle sizes, densities, and elemental compositions. For TXRF analysis, very tiny aliquots are prepared and usually 10 μ L are deposited on reflector; these aliquots constitute a very small portion of the entire collected volume. The deposited mass might not accurately represent the suspension's composition. The TXRF signal is influenced by the non-uniform distribution of metal-rich particles in the suspension, which is affected by

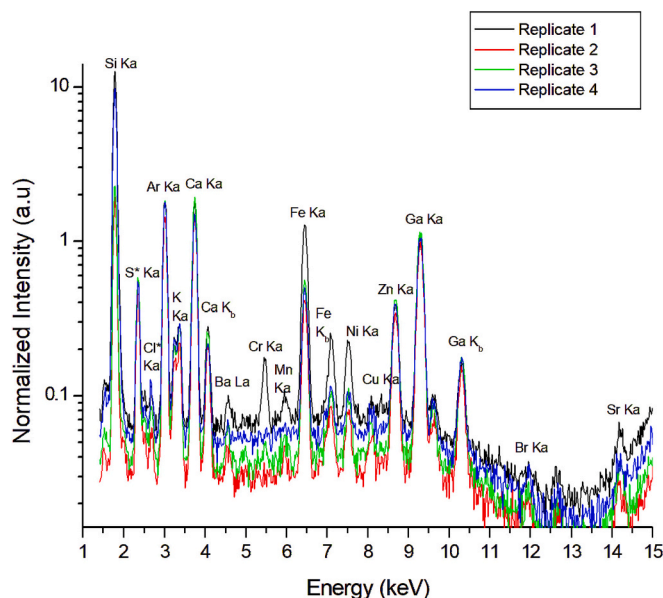


Fig. 2. TXRF spectra of four replicates from an indoor sample, after normalization to the intensity of Ga K α peak (~9.25 keV), collected in Hospital Office over an 8 h sampling period and prepared using pre-concentration approach. The S* and Cl* peaks are considered only for qualitative analysis because of their concentration is underestimated under the measurement conditions. Si peak is coming from the quartz reflector.

various physicochemical factors such as particle size, density, sedimentation behaviour, sample agitation method and random settling [54,55]. These effects are significant in highly diluted suspensions, where the measured signal can be affected by small variations in the particle content among the replicates. Compared to the traditional airborne PM sampling techniques such as filter-based, the impactor guarantees a more uniform particle distribution on the filter surface [56]. Despite this essential limitation of the pre-concentration approach, the impact of indoor human activity was still evident. Higher Ba, Fe and Ni concentrations (see Fig. S2 in supporting information) were found in samples taken during times of increasing occupancy, confirming that indoor activities contribute to metal levels [15].

From an analytical point of view, this approach leads to high coefficients of variation (CV%). Although pre-concentration is a simple analytical approach, the significant variation between the replicates demonstrated the limited representativeness of the analysed aliquots with respect to the entire collected samples and cannot be used for accurate quantitative TXRF analysis.

To address these limitations and enhance analytical robustness, lyophilization has been explored as an approach that allows the analysis of the complete collected sample. This procedure minimizes losses, redistribution of analytes by removing water through sublimation at low temperatures and low pressures, preserving the sample's chemical and physical integrity [57]. Lyophilization avoids the sedimentation that can happen during liquid-phase handling by preserving the entire suspended solid fraction, including biological and inorganic particulate matter.

TXRF spectra of three replicates from an indoor sample collected in University Office over a period of 8 h and prepared by lyophilization method are presented in Fig. 3. After the normalization, the spectra demonstrate good overlap profile among the replicates revealing high consistency for a major part of the elements, with minor differences for any element (i.e Fe) due to the variations in counting statistics. While TXRF spectra of an outdoor sample collected in a Home Terrace is shown in Fig. S3 (see Supplementary Information).

Comparison between Fig. 2 and Fig. 3 demonstrated that lyophilization greatly increases repeatability. Qualitative analysis revealed the presence of S, Cl, K, Ca, Ba, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Br and Sr.

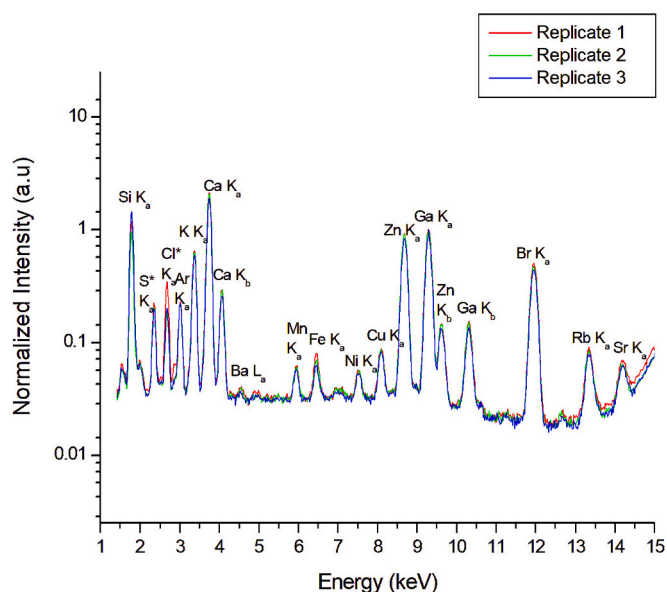


Fig. 3. TXRF spectra of three replicates from an indoor sample, normalized to the intensity of Ga K α peak (~9.25 keV), collected in University Office over an 8 h sampling period and prepared using lyophilization approach.

Quantitative analysis using internal standardization approach was applied to collected samples and field blanks prepared by lyophilization. Quantitative data reported from K because the concentration of S and Cl are underestimated under the current measurement conditions [40,50]. Elemental mass of the selected elements (K, Ca, Ba, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Br and Sr) was calculated by summing the elemental masses obtained from the three replicate TXRF deposits prepared from the same lyophilized sample. Elemental concentrations could not be expressed in terms of mass per collected PM fraction because the amount of lyophilized material was insufficient to accurately determine the total PM mass collected. For this reason, the results are expressed as elemental mass per cubic meter, considering the volume of sampled air and the sampling time. Table 2 presents the differences of relative standard deviation (RSDs %) obtained after TXRF analysis of samples prepared using pre-concentration (calculated from four replicates) and lyophilization (calculated from three replicates) approach. The RSD% ranges from 1 to 20% for the elements, showing better results achieved by lyophilization with respect to pre-concentration, where RSD values were significantly higher, particularly for Cr and Pb. This is attributed to their low concentrations close to the instrumental detection limits. Under these

Table 2

Comparison of the Relative Standard Deviations (RSD%) obtained by TXRF analysis of samples prepared using the pre-concentration approach ($n = 4$ replicate aliquots), and the lyophilization approach ($n = 3$ replicate deposits).

Elements	RSD (%)	
	Pre-concentration	Lyophilization
S	6	4
Cl	34	4
K	12	6
Ca	12	5
Ba	42	19
Cr	85	18
Mn	27	18
Fe	31	5
Ni	16	5
Cu	33	8
Zn	10	5
Pb	69	11
Br	43	5
Sr	43	5

conditions, measurements are more affected by signal-to-background ratio, counting statistics, and small variations in sample deposition caused by sample heterogeneity (see TXRF spectra in Fig. 2). These effects are particularly significant in highly diluted suspensions, where the non-uniform distribution of metal-rich particles can strongly influence the measured signal. Additional information about TXRF results obtained by analysis of two different certified reference materials was included in Table S1 in supporting information.

Table 3a and Table 3b present the total element mass summing the three measurements (ng/m^3) in samples collected in the outdoor and indoor investigated locations, respectively. The results are reported after subtracting the contributions measured in the corresponding field blanks. Different elemental fingerprints were detected at several outdoor locations, particularly for K, Ca, Br, and Sr. The elemental profiles are dominated by major crustal elements (K and Ca), with Ca having the highest concentrations, especially in Home Terrace. Similar trend was also observed for Fe. Ca, K, and Fe are classified as crustal elements [58], therefore, these results suggest a dominant contribution from coarse particles generated from soil dust resuspension and small contributions from human activities like transportation and local infrastructure. The observed data align with the configuration of the sampling system which is expected to collect coarse PM ($d > 0.5 \mu\text{m}$). Other elements like Mn, Ni, Cu, Zn, and Pb were found in lower quantities (few nanograms). Pb concentration was lower in the University Balcony sample, while did not show significant differences between university courtyard and home terrace locations. Cr was detected only in the University Courtyard samples. Comparing TXRF results [59] with the meteorological air quality parameters of the corresponding area reported in Table S2, is observed that sampling was performed during high atmospheric pressure, high relative humidity, and low wind speed (less than 15 km/h) that are favourable to the accumulation of air PM [60,61]. Sample 1 (24-01-2024) collected on the University Courtyard was characterized by elevated average PM₁₀ and PM_{2.5} concentrations, reaching 70.3 and 56.6 $\mu\text{g}/\text{m}^3$, respectively. This sample revealed the highest concentration of K (4.79 ng/m^3), Ca (83 ng/m^3) and Fe (18.33 ng/m^3) from this outdoor location, supporting their origin mostly from resuspension of soil dust [58]. Notwithstanding the observed correlation between PM levels and elemental concentrations, it should be noted that the elemental mass quantified by TXRF analysis represent only a limited fraction of the total PM mass. Consequently, under the current TXRF measurement conditions, a major amount of atmospheric PM, which is made up of organic and elemental carbon, sulphates, nitrates, ammonium, biological material, and other low-Z elements, could not be determined. Therefore, the TXRF results should be interpreted as a characterization of the inorganic elemental fraction of airborne PM rather than a complete mass closure of PM₁₀ or PM_{2.5}.

Changes in wind direction, which affect the relative contribution of local and transported particulate sources, may be connected to the variations in Ca, Br, and Sr concentrations found in the Home Terrace sample.

Indoor samples had significantly lower overall elemental concentrations than outdoor locations. Results revealed difference in the elemental quantities among the indoor locations. Living room showed the highest concentration for the main part of the elements and were in a good agreement with the results obtained from the outdoor samples collected at the same site. This agreement for crustal-related elements (i.e. Ca, K, Fe, and Sr associated with soil and resuspended dust) confirms that outdoor PM is a significant source of indoor elemental load. Indoor PM chemical composition is influenced by the outdoor derived particles during air exchange processes such as ventilation system or window openings, as well as from building materials. Regarding Room 1 and Room 2 deriving from the same location, TXRF results demonstrated similar elemental pattern, where Zn seems to be the more abundant element compared to Ba, Mn, Fe, Ni or Cu. From an analytical point of view, we obtained reproducible results for the majority of elements (K, Ca, Fe, Cu, Zn, and Br) in samples collected in different days at the same

Table 3

Elemental concentration (ng/m³) in a) outdoor and b) indoor locations prepared by lyophilization. TXRF results are expressed as the total element mass summing the three measurements \pm expanded uncertainty (Uc). Elemental concentrations are reported after subtraction of the corresponding field blank values.

a)																		
Elements	Outdoor Locations																	
	University Balcony			University Courtyard										Home Terrace				
				Sample 1			Sample 2			Sample 3			Sample 4					
K	3.1	\pm	0.9	4.79	\pm	0.66	2.19	\pm	0.36	2.39	\pm	0.66	4.78	\pm	0.35	551	\pm	87
Ca	47	\pm	18	83	\pm	12	32.0	\pm	9.7	35.0	\pm	10.4	35.1	\pm	10.0	2201	\pm	212
Ba	0.51	\pm	0.03	2.79	\pm	0.03	0.57	\pm	0.04	0.27	\pm	0.03	0.49	\pm	0.02	3.97	\pm	0.30
Cr	—			0.186	\pm	0.004	0.31	\pm	0.01	0.123	\pm	0.004	0.175	\pm	0.003	—		
Mn	0.183	\pm	0.003	0.98	\pm	0.01	1.31	\pm	0.06	0.31	\pm	0.01	0.33	\pm	0.01	0.18	\pm	0.02
Fe	1.9	\pm	0.1	18.3	\pm	0.5	4.81	\pm	0.22	8.14	\pm	0.47	15.7	\pm	0.8	10.7	\pm	0.5
Ni	—			0.057	\pm	0.001	0.062	\pm	0.001	0.020	\pm	0.001	0.034	\pm	0.001	0.69	\pm	0.02
Cu	0.077	\pm	0.005	1.19	\pm	0.02	0.77	\pm	0.02	0.228	\pm	0.015	0.57	\pm	0.01	8.56	\pm	0.39
Zn	0.463	\pm	0.003	2.14	\pm	0.03	1.74	\pm	0.07	0.703	\pm	0.027	0.97	\pm	0.03	0.60	\pm	0.01
Pb	0.020	\pm	0.001	0.176	\pm	0.003	0.31	\pm	0.01	0.081	\pm	0.003	0.137	\pm	0.002	0.328	\pm	0.007
Br	0.080	\pm	0.004	0.054	\pm	0.001	0.018	\pm	0.001	0.022	\pm	0.001	0.011	\pm	0.001	3.24	\pm	0.08
Sr	0.146	\pm	0.001	0.020	\pm	0.001	0.084	\pm	0.002	0.086	\pm	0.000	0.021	\pm	0.002	6.65	\pm	0.17

b)																		
Elements	Indoor Locations																	
	University Office Room 1						University Office Room 2						Living Room					
	Sample 1			Sample 2			Sample 1			Sample 2			Sample 3					
K	0.870	\pm	0.064	0.513	\pm	0.033	1.73	\pm	0.17	1.38	\pm	0.15	1.39	\pm	0.143	46	\pm	8
Ca	2.971	\pm	0.346	5.352	\pm	0.923	16.8	\pm	4.5	16.7	\pm	5.8	15.8	\pm	4.8	749	\pm	285
Ba	0.015	\pm	0.001	0.028	\pm	0.002	0.061	\pm	0.003	0.057	\pm	0.002	0.020	\pm	0.001	4.59	\pm	0.31
Mn	0.012	\pm	0.001	0.024	\pm	0.001	0.082	\pm	0.003	0.032	\pm	0.001	0.021	\pm	0.001	0.099	\pm	0.003
Fe	0.013	\pm	0.001	0.023	\pm	0.001	0.056	\pm	0.002	0.103	\pm	0.004	0.109	\pm	0.004	0.37	\pm	0.01
Ni	—			—			0.024	\pm	0.001	0.018	\pm	0.001	0.015	\pm	0.001	0.14	\pm	0.01
Cu	0.012	\pm	0.001	0.016	\pm	0.001	0.044	\pm	0.002	0.055	\pm	0.002	0.047	\pm	0.002	1.61	\pm	0.05
Zn	0.18	\pm	0.01	0.409	\pm	0.001	0.48	\pm	0.02	0.71	\pm	0.03	0.60	\pm	0.03	4.65	\pm	0.15
Br	0.076	\pm	0.003	0.050	\pm	0.002	0.16	\pm	0.01	0.164	\pm	0.006	0.165	\pm	0.010	1.10	\pm	0.03
Sr	0.008	\pm	0.000	0.028	\pm	0.001	0.037	\pm	0.001	0.068	\pm	0.002	0.012	\pm	0.001	1.83	\pm	0.05

room (University Office, Room 2). This result demonstrates the importance of developing and optimizing sample preparation methods for reliable TXRF analysis of airborne PM collected using liquid-based sampling techniques. Since TXRF uses small aliquots for analysis, it is essential to guarantee that the measured fraction represents the whole collected sample. In our case, lyophilization enhanced representativeness by increasing the effective measured mass, reducing the effects of particle redistribution. Thus, improving the data repeatability and enabling the comparison of results between indoor and outdoor samples.

4. Conclusions

This work presents a proof of concept to use a cyclone-based bio-sampler combined with TXRF analysis to characterize airborne PM. TXRF is a suitable analytical technique for rapid and simultaneous multielement analysis requiring small sample masses, making this a relevant advantage for airborne PM characterization where restricted mass is available.

In this study, air sampling was performed in six different locations in indoor and outdoor monitoring sites. Pre-concentration and lyophilization were tested as two sample preparation strategies for airborne PM analysis. Pre-concentration was adopted as a rapid preparation method, allowing quick processing of liquid samples. Notwithstanding its simplicity, TXRF results demonstrated high variability among replicates. This low repeatability reveals a limited representativeness of the analysed aliquots with respect to the entire collected samples and the effect of sample's heterogeneity is more evident in highly diluted suspensions. Lyophilization has been developed as an alternative sample preparation strategy, which allows the analysis of the entire collected sample mass. Thus, reducing the effect of particle-distribution and improving

analytical parameters. TXRF results showed better repeatability especially for trace and minor elements. Data highlight differences in elemental concentrations among the studied locations, with evident changes observed between indoor and outdoor. All outdoor samples revealed higher overall metals concentrations and site-specific elemental profiles mostly for K, Ca, Fe, Br and Sr. While Zn appeared as a dominant trace element in indoor samples. This work shows lyophilization as an enabling preparation approach which preserves the entire particle fractions and paired with TXRF technique resulted suitable for airborne PM characterization. Beyond the analytical optimization, the environmental relevance of this work lies in the possibility of applying liquid-based airborne PM sampling coupled with TXRF analysis to real-world indoor and outdoor exposure scenarios.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the author(s) used artificial intelligence tools for language editing and writing support. After using this tool, the author(s) reviewed the content as needed and take(s) full responsibility for the content of the publication.

CRediT authorship contribution statement

Fabjola Bilo: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Data curation. **Laura Borgese:** Writing – review & editing, Data curation, Conceptualization. **Simona Fiorentini:** Writing – review & editing, Methodology, Data curation. **Gloria Bignotti:** Writing – review & editing, Software, Investigation. **Vlad S. Popescu:**

Resources. **Stefano Renzetti**: Writing – review & editing. **Cláudio Roque**: Writing – review & editing. **Carolina M. Pinheiro**: Writing – review & editing. **Paula Coutinho**: Writing – review & editing, Visualization. **Donatella Placidi**: Writing – review & editing, Conceptualization.

Declaration of competing interest

Fabjola Bilo, on behalf of all co-authors of submitted manuscript “TXRF Analysis of Airborne Particulate Matter Captured in Liquid Medium Using a Cyclone Bioaerosol Sampling Approach”, declares that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.sab.2026.107572>.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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