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Study of atmospheric aerosols by IBA techniques: The LABEC experience

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ABSTRACT

At the 3 MV Tandetron accelerator of the LABEC laboratory of INFN (Florence, Italy) an external beam facility is fully dedicated to PIXE-PIGE measurements of the elemental composition of atmospheric aerosols. All the elements with Z > 10 are simultaneously detected by PIXE typically in one minute. This setup allows us an easy automatic positioning, changing and scanning of samples collected by different kinds of devices: long series of daily PM (Particulate Matter) samples can be analysed in short times, as well as size-segregated and high time-resolution aerosol samples.

Thanks to the capability of detecting all the crustal elements, PIXE-PIGE analyses are unrivalled in the study of mineral dust: consequently, they are very effective in the study of natural aerosols, like, for example, Saharan dust intrusions. Among the detectable elements there are also important markers of anthropogenic sources, which allow effective source apportionment studies in polluted urban environments using a multivariate method like Positive Matrix Factorization (PMF).

Examples regarding recent monitoring campaigns, performed in urban and remote areas, both daily and with high time resolution (hourly samples), as well as with size selection, are presented. The importance of the combined use of the Particle Induced Gamma Ray emission technique (PIGE) and of other complementary (non-nuclear) techniques is highlighted.

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1. Introduction

Atmospheric aerosols or Particulate Matter PM) have been shown to have negative impacts on human health, atmospheric visibility, and radiative forcing [1,2]. The source identification and quantification of PM are crucial to understand aerosol chemical processes and develop effective PM abatement strategies.

The Particle induced X-ray emission PIXE) technique has been widely used since its birth for the study of the aerosol composition, and for a long time, it has been the dominating technique for its elemental analysis [3,4] because only few minutes were sufficient to detect up to 20 elements from Na to Pub, including important anthropogenic elements S, V, Ni, Cu, Zn, As and PBS) and all the crustal elements Al, Si, K, Ca, Tic, Man and Fe). However, nowadays other competitive techniques play a dominant role, such as Inductively Coupled Plasma Mass Spectrometry ICP-MS) [5], Inductively Coupled Plasma Atomic Emission Spectroscopy ICP-AES) [6], Energy Dispersive X-ray Fluorescence ED-XRF) [7] and Synchrotron Radiation XRF SR-XRF) [8]. Therefore, for a successful use of PIXE to aerosol studies it is important to find specific applications where it can give unique information or can give final results in a far simpler way with respect to other competing techniques.

One advantage is the very short measuring time, ~ 60 s versus 1 h for typical ED-XRF analysis. ICP techniques have the analysis time only a little longer, but ICP methods need long times for sample preparation. This can be a key aspect when hundreds or thousands of samples collected in big sampling campaigns must be analyzed.

The analysis of samples with very low mass such as collected with high time resolution is possible. In most of the field campaigns PM is collected with a 24-h time resolution. However, many particulate emissions change within a few hours (industrial emissions, traffic rush hours, construction works, ...); moreover, as many meteorological parameters, like wind intensity and direction, change within a 1-h time scale and the boundary layer evolution shows strong diurnal patterns, atmospheric transport and dilution processes change within a few hours. Consequently, the aerosol concentration and composition may significantly change within a few hours and daily samples are not capable of tracking these rapid changes. For this reason, the measurement of the PM composition with high time resolution is important to assess health and environmental effects, understand transport processes and determine source contributions.

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Mineral dust (coming e.g. from the Saharan desert) together with sea-salt particles are dominant on a global scale. It influences the earth system through the interaction with the radiation, the influence on the cloud formation and the fertilization of the Ocean, which has a role in CO_2 absorption. Furthermore, it gives an important contribution to PM in urban areas and it can episodically increase significantly the PM10 and PM2.5 levels. Therefore, good data on the composition and concentration of mineral aerosol is necessary with PIXE. All the soil related elements are easily detected by PIXE [9] (Si is not easily detected or not detected at all by ICP).

No sample preparation or extraction is necessary, thus reducing the contamination from chemical reagents compared to ICP-MS and possible loss of volatile elements in the sample. This is fundamental for very low mass samples e.g. remote sites aerosol) [10].

Finally, compared to traditional ED-XRF, PIXE offers sensitivities that are typically one order of magnitude better and requires far shorter measuring times also with very low mass samples. Since PIXE is a non-destructive analysis technique, further measurements with other complementary techniques can be carried out (not on organic compounds) or it can be complemented by other Ion Beam Analysis techniques like Particle Induced γ-ray Emission (PIGE).

However, one should keep in mind that PIXE provides only part of the desired information regarding the chemical composition; it is also mandatory to perform at least measurements for important ionic species e.g. ammonium, nitrate), for organic carbon and elemental carbon. The use of PIXE data alone even if proxies coming from IBA techniques are used) may lead to wrong results when applying multivariate receptor modelling for aerosol source apportionment [11]; therefore, aerosol research exclusively based on PIXE is not sufficient anymore even if it continues providing an invaluable contribution to atmospheric aerosol research.

To fully exploit the potential of PIXE in the analysis of aerosol samples, a proper experimental setup is important. At the LABEC laboratory at Florence an external beam line fully dedicated to the analysis of aerosol samples has been developed since many years and it has been widely used for the analysis of aerosol samples.

The first part of the article will be devoted to the description of this set-up and of the experimental procedures adopted depending on the different kinds of samples to be analyzed (e.g. the choice of the optimal measurement parameters like the beam energy). The importance of the use of PIGE to overcome some problems for the correct quantification of low-Z elements is highlighted. Finally, some examples are given of applications performed in our laboratory to show the potentialities of the PIXE technique for aerosol studies.

2. The LABEC external beam set-up

Since 1989 there exists at the Florence laboratory an external beam line fully dedicated to the analysis of aerosol samples [12]. We emphasize how convenient an external beam is for these measurements. Apart from the trivial but not insignificant advantage of being able to handle big samples holders and the ease of changing them or the scanning of the filter, the possible loss of volatile elements like Cl and Br is eliminated or reduced. It is possible to use high proton currents because the local heating due to the energy deposited by the beam is dissipated (even better in the He atmosphere with respect to air). Furthermore, all the detectors may be placed closer to the sample, increasing the solid angle.

The extraction window originally used in our laboratory consisted of a 7.5 μm thick Upilex-S ($C_{22}H_{10}N_2O_4$, density 1.47 g/cm^3) foil. However, this polymer undergoes a progressive thinning/degradation during irradiation [13] and eventually a final rupture can happen, after a time which depends on the beam current density used for the measurements (with a beam current of 100 nA about 2–3 h are enough to reach the limit of rupture). Therefore, we have replaced the Upilex window with a Silicon Nitride membrane more durable under proton beam irradiation. We have chosen a 500 nm thick, 3 mm width Si_3N_4 membrane supplied by Selsun Ltd. The Si_3N_4 extraction window has been used for more than 3 years without any need to change it.

The aerosol samples are positioned at about 1 cm from the exit window. The beam size is usually 1 mm × 2 mm, but can be easily changed by simple collimation in vacuum in the last section of the beam line. The charge flown during the measurement is simply measured by integrating the beam current on a graphite Faraday cup positioned just behind the sample. The movement of the samples (perpendicular to beam direction) on the x–y axes (to scan all the samples surface and to reduce the beam charge density on the sample) and the change of the samples by rotation of the sample holder are both remotely controlled by the acquisition system.

To obtain efficient simultaneous detection of all the elements, we used since the beginning two detectors optimized for low and medium–high X-ray energies, respectively, to consider the differences in the X-ray production cross sections, spanning over several orders of magnitude. Such set-up has been constantly improved taking advantage of the technological advancements in terms of X-ray detectors [13–15]. The two original Si(Li) detectors have been replaced by Silicon Drift Detectors (SDDs), which provide better resolution with modest cooling (down to −40 °C) achievable with Peltier cells and can cope with higher counting rates (up to 50 kHz at 0.5 μs shaping time).

As concerns the SDD dedicated to low-Z elements, we use a 40 mm^2 (collimated to 30 mm^2 by a Ta–Cr–Ti–Al multilayer collimator, to shield the outer part of the area, where incomplete charge collection may happen), 450 μm thick SDD, having 140 eV FWHM energy resolution at the 5.9 keV Mn Ka line and 1 μs shaping time. The use of a thin (8 μm) Be window and the saturation of the volume between the entrance window and the target with helium enables the detection of X-rays down to around 1 keV, i.e., the detection of elements down to Na (Z = 11). The SDD is positioned at about 135° with respect to the beam direction, at about 9 cm distance from the target; a magnetic proton deflector (NdFeB permanent magnet, 0.5 T, length 8 cm, distance between magnets 8 mm) is installed to prevent the damage to the detector by backscattered protons; it is designed to deflect protons up to 4 MeV in energy.

As concerns the detection of the medium-high Z elements, two identical KETEK SDDs are used to double the statistics of the acquired spectra. Their characteristics are: 113 mm^2 area (collimated to 80 mm^2), 450 μm thickness, 165 eV FWHM energy resolution at the 5.9 keV Mn K_α line and 1 μs shaping time, and 25 μs thick Be entrance window. A further absorber (450 μm Mylar foil) is mounted to attenuate the low energy X-rays. Both detectors are placed at 135° with respect to the beam direction, at about 2–2.5 cm from the target. As a whole, the SDD array of the upgraded set-up covers a total solid angle of 400 msr. The LABEC experimental set-up is shown in Fig. 1.

The PIXE spectra are fitted using the GUPIX code [16] and elemental concentrations are obtained by a calibration curve from a set of thin standards of known areal density (Micro matter Inc., Surrey, Canada).

Depending on the type of samples we analyze (standard daily samples, samples with 1-h time resolution, size segregated samples) the optimal measurement parameters must be chosen.

Aerosol sampling campaigns usually involve the collection of daily samples for a long period. Teflon $(CF_2)_n$ filters are frequently used because they are easily weighted, they have very good blank

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