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Is PIXE still a useful technique for the analysis of atmospheric aerosols? The LABEC experience

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At the 3-MV Tandatron accelerator of LABEC (INFN) an external beam facility is fully dedicated to particle-induced X-ray emission (PIXE) and particle-induced γ -ray emission (PIGE) measurements of atmospheric aerosol elemental composition. All the elements with $Z > 10$ are simultaneously detected by PIXE in a few minutes and an automatic system for positioning, changing and scanning of the samples allows the analysis of the aerosol collected by different kinds of devices: long series of daily PM_x samples can be measured 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: as a consequence, they are very effective in the study of natural aerosols, like, for example, mineral dust archived in polar ice cores (for environmental and paleoclimatic studies) and 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. Examples regarding recent monitoring campaigns, performed in urban and remote areas, both on a daily basis and with high-time resolution (hourly samples), are presented to evidence how PIXE can still provide unique information in aerosol studies or can play a complementary role to X-ray fluorescence or induced coupled plasma mass spectroscopy analysis. Copyright © 2011 John Wiley & Sons, Ltd.

Introduction

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.^[1,2] However, recently, other competitive techniques, such as those based on atomization by induced coupled plasma and detection by atomic emission spectroscopy (ICP-AES) or mass spectrometry (ICP-MS), have been developed. Furthermore, traditional X-ray fluorescence (XRF) systems have been replaced by more efficient modern devices and synchrotron radiation XRF has started to be used for elemental analysis.^[3] PIXE has many advantages for elemental analysis of aerosols^[1,2]: only 5–10 min of bombardment are sufficient to detect up to 20 elements from Na to Pb, including important anthropogenic elements (S, V, Ni, Cu, Zn, As and Pb) and all the crustal elements (Al, Si, K, Ca, Ti, Mn and Fe), and its high efficiency is very useful when hundreds of samples have to be analyzed, a quite common need in aerosol studies. Compared to traditional energy-dispersive XRF (ED-XRF), PIXE offers sensitivities that are typically at least one order of magnitude better and requires much less sample mass, thus allowing the use of samplers with high time and size resolution (e.g. streakers^[4] and Small Deposit area low pressure impactors (SDI)^[5]). Since PIXE is a nondestructive analysis, further measurements with other complementary techniques can be carried out. Moreover, no sample preparation or extraction is necessary, thus reducing the contamination from chemical reagents and possible loss of volatile elements in the sample. For instance, the sample mineralization by concentrated HF prevents the determination by ICP of Si, one of the most relevant crustal markers. Another advantage of PIXE over ED-XRF is that it can be complemented with other ion beam analysis (IBA) techniques, so that the light elements (H, C, N and O) that make up most of the aerosol mass can be measured as well.^[6]

However, one should realize that PIXE provides only part of the desired information with regard to 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^[7]) may lead to wrong results when applying multivariate receptor modelling for aerosol source apportionment; therefore, aerosol research exclusively based on PIXE is not sufficient anymore.

Anyway, the PIXE technique can continue to provide an invaluable contribution to atmospheric aerosol research by giving data for major, minor and trace elements in studies where large numbers of samples are involved. The data for the major elements (S, Na, Cl, Al, Si and Fe) are needed for the assessment of the climatic effect of aerosols for the estimate of the contributions of important aerosol types (e.g. sea salt and crustal material) and for the achievement of the chemical mass closure. Furthermore, multi-elemental data set as a whole (which comprises data for various anthropogenic tracers) can be used for disentangling the contributions from different source categories by applying multivariate receptor modelling.^[8] Finally, PIXE is unrivalled when highly size-resolved aerosol samples or with high time resolution have to be analyzed. In this article, we present some examples

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taken from our experience at the LABEC laboratory to show how PIXE can still give an important contribution to aerosol studies.

The LABEC Experimental Setup for Aerosol Analysis

A proper experimental setup is important to fully exploit PIXE capabilities. At LABEC, an external beam line is fully dedicated to PIXE and particle induced γ -ray emission (PIGE) measurements of atmospheric aerosols. The setup is extensively described in studies by Chiari *et al.*^[6] and Calzolari *et al.*^[9] Briefly, the proton beam, typically 3.0-MeV energy, is extracted in air through a 7.5- μm Upilex window and the aerosol samples are positioned at a distance of about 1 cm from the window. The beam size is usually 1 mm \times 2 mm, but can anyway be easily changed by simple collimation in vacuum in the last section of the beam line.

To obtain efficient simultaneous detection of all the elements, we use two detectors optimized for low and medium–high X-ray energies, respectively. The latter is a Si(Li) detector, whose entrance window is shielded by a 450- μm Mylar foil to attenuate the low-energy X-rays. To detect low-Z element X-rays, a traditional Si(Li) has been substituted by a silicon drift detector (SDD), which offers an excellent energy resolution (145 eV Full Width Half Maximum) at moderate cooling (-10°C , achievable with a Peltier cell). Thanks to the ultra-thin entrance window (8- μm beryllium) and to the use of a helium flow into the volume in front of the detector, it can detect with good efficiency X-rays of very low energies, down to ~ 1 keV (Na $K\alpha$ line). One of the advantages in using SDD is represented by the possibility of managing high count rates (up to 50 kHz at 0.5 μs shaping time of the amplifier). This implies, in turn, the possibility of using high beam currents (30–60 nA), thus drastically reducing the measurement time. Finally, γ -rays for PIGE analysis are detected by a Ge detector.

To make the analysis of daily samples automatic to exploit the intrinsic speed of the PIXE technique and to analyze a large number of samples in a short time period, we use a remote controlled multi-target holder, which manages the change and the scan of 32 filters or 64 half filters. The measurement time is typically about 5–10 min per sample (with a beam current ranging from 5 to 50 nA depending on the substrate) to be compared with 1 h for typical ED-XRF analysis. In this way, daily samples collected during a 1-year campaign can be analyzed in a 3-day measurement run. With respect to the ICP techniques, the analysis time is similar (ICP-AES) or little shorter (ICP-MS), but ICP methods need long times for sample preparation.

With the same setup, we can also analyze samples collected by the so-called stalker sampler.^[4] This device collects the fine and coarse fractions of the aerosol on two stages, which are paired on a cartridge rotating at constant speed. This produces, on both stages, a circular continuous deposit of particulate matter ('streak'), which can be analyzed 'point by point' by PIXE using a beam size corresponding to 1 h of aerosol sampling.^[6] The scan of the whole streak, corresponding to 1 week with 1-h resolution (168 spots), requires about 9 h. The interest for a detailed, size-resolved and high-time resolution particulate matter (PM) characterization is due to the fact that there exist source emissions that can heavily affect air quality with very high loading of toxic elements during a few hours: the knowledge of the timing and the intensity of certain episodes may be important for the assessment of human exposure as well as for source identification and apportionment.

Finally, we can analyze samples collected by the SDI sampler, specifically developed to collect aerosol for PIXE analysis.^[5] It collects particles in 12 size fractions in the size range of 45 nm–8.5 μm . Its relatively high sample flow rate and the small particle collection area (8-mm diameter) increase the sensitivity even when the sample concentration is low. Since in an external setup, it is not possible to work with beams that are large enough to cover all the particulate collection area (8-mm diameter), a homogeneous scanning of the deposit area is performed. Typical measuring time for each stage is ~ 1000 s.

Air Quality Investigations: the Particolato Atmosferico in Toscana (PATOS) Case Study

As mentioned above, a complete aerosol characterization calls for the use of multiple analytical techniques. In campaigns involving the collection of daily samples for a long period, we use low volume (2.3 m³/h) sequential samplers equipped with two inlets so that aerosol can be simultaneously collected on Teflon and Quartz fibre filters (47-mm diameter), thus allowing the application of different analytical techniques. Samples on Teflon are cut into three parts. On one half of the filter, PIXE is used to measure the concentrations of all the elements with atomic number $Z > 10$ (a subset of samples are also analyzed by proton elastic scattering techniques to obtain H, C, N and O concentrations^[6]). At the Chemistry Department, the water-soluble fraction of inorganic ions (e.g. Na, NH₄, K, Mg, Ca, Cl, NO₃, SO₄, Methanesulfonate (MSA), acetate, formate, glycolate and oxalate) is measured by ion chromatography (IC) on one quarter of the filter; ICP methods are used to determine the 'soluble fraction' (in the acidic extraction conditions) of several major (ICP-AES) and trace (ICP-MS) metals on the remaining quarter of the filter. By comparing data obtained by PIXE and by ICP-AES or ICP-MS, we can assess the 'soluble fraction' (in different conditions, depending on the strength of the acidic solubilization) of several elements. In this way, PIXE and ICP techniques appear to constitute a powerful complementary method, able to obtain a more complete data set of the aerosol chemical composition.

Samples collected on Quartz fibre filters are analyzed at the Chemistry Department by gas chromatography and gas chromatography mass spectrometry to determine n-alkanes and Polycyclic aromatic hydrocarbons concentrations. A 1.5-cm² punch of the filter is used for organic and elemental carbon assessment by Thermo Optical Transmission analysis (using a Sunset Lab analyzer^[10]) at LABEC.

As an example of the role of PIXE in the characterization of aerosol composition in a specific region, we present some results from the "Particolato Atmosferico in Toscana" (PATOS) campaign. Tuscany is known all over the world for its fantastic landscape and beautiful old towns; however, there are some areas within the region, including Florence itself, in which the limit values for PM₁₀ are exceeded. As a consequence, the Regional Government has promoted the PATOS project, the first extensive field campaign for the aerosol characterization in Tuscany, to give to policymakers the knowledge and the tools for a significant reduction in anthropogenic emissions. PM₁₀ samples were collected in six sampling sites, representative of areas of different typology (urban background, urban traffic, sub-urban background), on a daily basis, from September 2005 to September 2006, using three samplers that were shifted every 15 days from three sites to the other three.

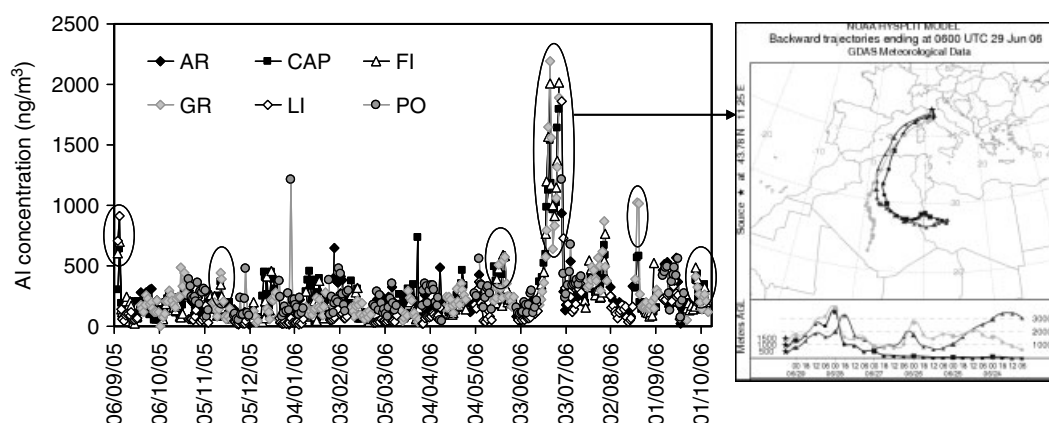


Figure 1. PM₁₀ Al concentration time trends measured during the PATOS campaign in the six sampling sites (AR: Arezzo, CAP: Capannori, FI: Florence, GR: Grosseto, LI: Livorno and PO: Prato). Simultaneous peaks due to Saharan-dust intrusions are highlighted (circles). Backward air trajectory calculations (HYSPLIT transport model by NOAA Air Resource Laboratory) for the most intense episode are also shown.

Nowadays, the determination of the contribution of marine aerosols and Saharan-dust intrusions to pollution levels in Italy is a still debated important issue. PIXE analysis allows an easy identification and quantification of important tracers of such long-range transport of marine (Na and Cl) and Saharan (Al, Ca, Ti, Fe, Sr and, in particular, Si) aerosols. As far as the concentrations of soil-related elements are concerned, differences among the six sampling sites, due to different local soil contributions, have been observed, but we also observed some cases with a simultaneous increase in all the sites and for all the crustal elements (Fig. 1), pointing at a common source that might be the impact of air masses coming from Sahara. This hypothesis has been confirmed by back-trajectories calculations and by satellite images. Since PIXE is a quantitative technique, it allowed obtaining a further proof of the Saharan origin by the observation of the inter-elemental ratios, whose values are different for the desert and the local dust. For example, in Florence the Al/Fe, Si/Ca and Ti/Ca ratios changed from 0.88, 1.0 and 0.031 during normal days to 0.36, 0.64 and 0.022 during these Saharan episodes, respectively, and similar changes were observed in all the sampling sites.

Saharan dust is a major component of PM on a global scale and its atmospheric concentrations have relevant effects on climate and environment; in southern Europe, it gives an important contribution to PM and it can episodically increase significantly the PM₁₀ and PM_{2.5} levels. The EU Air Quality Directives specify that PM₁₀ limit values have not to be applied to events defined as natural, which include 'long-range transport from arid zones'. Diffusion models and satellite images observation can be very effective in the study of Saharan-dust transport; however, the advection of air masses coming from Sahara does not necessarily imply high PM₁₀ concentrations at ground level. Therefore, only field campaigns, followed by elemental analysis, can assess the real impact of the Saharan-dust episodes on the air quality, so deserving a key role to the PIXE technique. An estimate of the soil dust component concentration can be calculated considering the crustal elements as oxides.^[7] During the PATOS campaign, it accounted from few $\mu\text{g}/\text{m}^3$ to $\sim 10 \mu\text{g}/\text{m}^3$, but during the most intense Saharan episode, in June, it gave a higher contribution, up to $30 \mu\text{g}/\text{m}^3$, $\sim 50\%$ of the PM₁₀ mass, causing the exceeding of the $50 \mu\text{g}/\text{m}^3$ limit value in all the sites. During the year, other Saharan-dust episodes were detected but their contribution to PM₁₀ was estimated to be much lower.

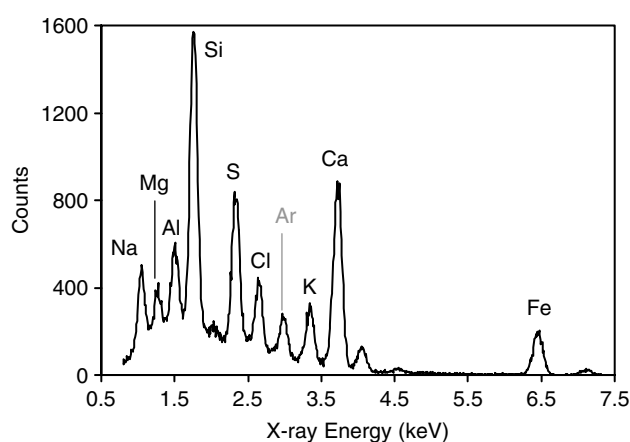


Figure 2. SDD PIXE spectrum of a PM₁₀ daily sample collected on a Teflon filter by a low-volume ($2.3 \text{ m}^3/\text{h}$) sampler, measured in 30 s at a proton beam current of 50 nA. The Ar peak is mainly due to argon in the air behind the sample.

It is worth noting that, due to the high sensitivity of PIXE for crustal elements, when the main objective of an aerosol investigation is the determination of the soil component, and in particular of the Saharan dust, with an SDD detector (which can manage high counting rates) and high beam currents (30–60 nA), a measurement of 30–60 s per sample is sufficient to obtain good counting statistics (Fig. 2); in this way, hundreds of filters can be analyzed in 1 day. This is a relevant, specific feature of the PIXE measurements.

Since aerosol particles retain elemental composition characteristics of their origin, the simultaneous detection of groups of elements by multi-elemental techniques, such as PIXE, can be of great help in the study of aerosol sources. We applied positive matrix factorization (PMF) analysis to the whole set of PATOS data (not only PIXE data) to identify the aerosol sources and their contribution to PM₁₀ mass. As an example, the source apportionment for the most polluted site (Capannori-Lucca) is shown in Fig. 3. An unexpected high contribution of the biomass-burning source (the dominant one during the winter period in which strong pollution events took place) was found. This component has been associated to a biomass-burning source since it was characterized by high loadings of K, nitrate, glycolate and carbon components

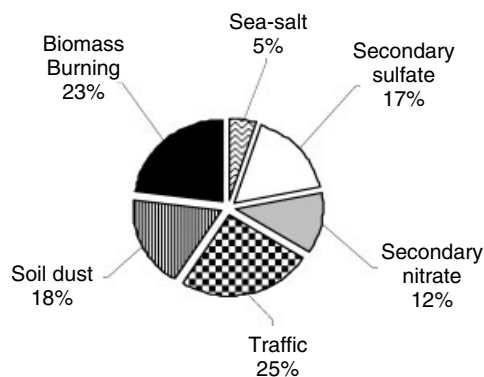


Figure 3. PMF source apportionment: identified source annual (September 2005–September 2006) average percentage contributions to PM₁₀ in Capannori.

and its time trend showed higher values during winter months (November–March). Although K, the main marker of this source, may have also other origins (e.g. soil), during the days of higher impact of this source it showed very high enrichment factors with respect to the soil composition and it turned out to be mostly soluble (as shown by the comparison between PIXE and IC data). Further information came from the analysis of hourly concentrations (Fig. 4). K shows periodic pattern with peaks starting at about 19:00 and lasting ~10 h, suggesting wood burning for domestic heating; the same time pattern is also shown by the biomass burning source identified by the PMF analysis applied to streaker data. In Fig. 4, the Cu time pattern is also shown; it is characterized

by concentration peaks during traffic rush hours suggesting traffic as main source. Actually, the traffic source identified by PMF shows the same time pattern. Other examples of the utility of the use of 1-h concentration data may be found in Refs.^[11–14]

Comparing data obtained by PIXE and ICP-MS, we assessed the soluble fraction (at pH 1.5) of several elements; we observed that Ni, Cu, Zn and V and other metals arising from anthropogenic sources resulted mainly soluble, while an opposite behaviour was found for crustal metals (such as Al, Fe and Mn).

Analysis of Low Mass Samples for the Study of the Aerosol Collected in Remote Areas

Insoluble mineral aerosol (dust) deflated from continental surfaces is an important player in Earth's climate by its influence on the Earth-Atmosphere radiative budget. To reconstruct the past atmospheric concentration of mineral dust and to correlate its variations with climatic changes, dust stratigraphies have been obtained by the chemical and physical analyses on ice cores drilled in polar areas. For the Southern Hemisphere, ice core drilled in Antarctica can give relevant information on the hydrological cycles of the southern South America (the most relevant dust area for Antarctica during glacial periods) and on the different transport processes of air masses from medium latitude, as a function of the changes in the climatic belts.^[15]

The isotopic and geochemical composition of Antarctic dust particles both in present-day aerosol and in ice cores is used to infer dust source locations and to study the geochemical evolution, in turn linked to paleo-environmental conditions, of

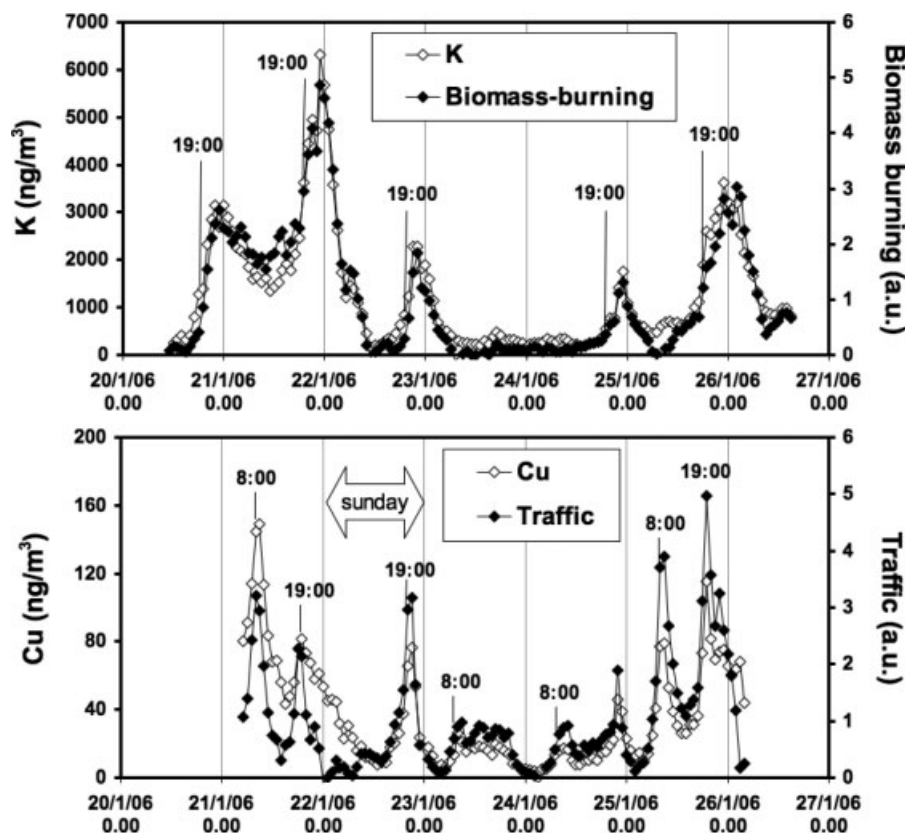


Figure 4. Hourly concentration time trends of K (fine fraction) and Cu (fine + coarse fraction) obtained by PIXE analysis of streaker samples collected in Capannori. The time trends of the Biomass-burning and Traffic sources obtained by PMF are also reported (in arbitrary units).

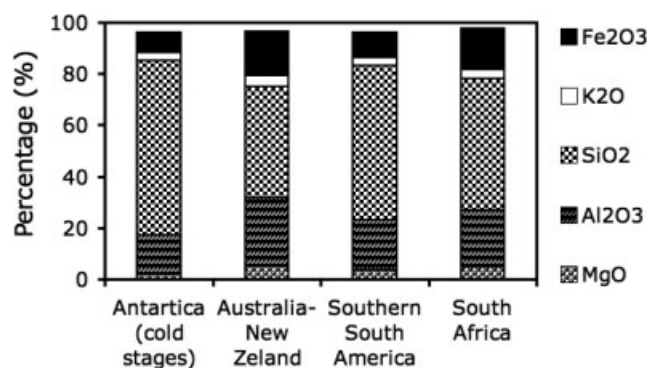


Figure 5. Average composition, expressed as percentage contribution of the main oxides, for the different groups of particulate samples: Antartica ice core samples from the last cold stages and sediment samples from southern South America, South Africa and Australia.

dust at the source. The extremely low elemental concentrations usually present in the insoluble particulate in Antarctic ice cores (pg to μg per kg of ice) make these analyses particularly challenging. In this context, the PIXE technique has proven to be a reliable tool for major and minor elements investigation. Ice-core sections are melted and the liquid is filtered through a narrow-area membrane to concentrate the insoluble dust to obtain detectable concentrations. No other sample pre-treatment is needed, thus minimizing contaminations (compared to ICP-MS).^[16,17]

In collaboration with the analytical chemistry group at the Chemistry Department, we analyzed samples from the ice core drilled at Dome C, in the framework of the European Project for Ice Coring in Antarctica (EPICA) project.^[15] The analyzed samples pertain to the main cold events of the last 220 000 years, when dust atmospheric concentrations were higher. Ice-core samples were melted and the dust particles were collected on a 1-cm² spot of a Nuclepore membrane.^[16] Soil sediment samples collected in the main 'potential source areas' (PSAs) for Antarctica, i.e. southern South America, Australia and South Africa, were also analyzed to compare their elemental composition with the ice-core dust one. For a reliable comparison, a soil-particle size selection has been done on PSA samples,^[16] since long-range transport causes a strong dimensional selection of the dust particles in the atmosphere [Antarctic dust is only composed of fine particles (diameter <5 μm)]. After the proper preparation, all the samples were analyzed by PIXE and PIGE, since the absolute quantity of the lighter elements (such as Na, Mg, Al and Si) can be somewhat underestimated because of the X-ray self-absorption inside each individual aerosol particle.^[16] Each sample has been irradiated for about 1000 s with a beam intensity ranging from 5 to 30 nA, depending on the sample load. For ice-core samples, the quantity of dust collected ($\sim 1\text{--}2 \mu\text{g}/\text{cm}^2$ in the scarcest samples) was sufficient to obtain good statistics for both PIXE and PIGE. Blank values for elements of interest were always largely below the measured concentrations. In Fig. 5, very preliminary results on the elemental composition of the first analyzed samples are reported; in accordance with recent literature,^[17] the ice dust composition during the cold stages turned out to be more similar to the southern South American one, while it differs significantly from both the Australian and the South African ones.

A similar analysis will be applied also to ice samples corresponding to interglacial periods (such as the today's Holocene), when the atmospheric concentrations of dust were lower (about two orders of magnitude): in this case, the absolute quantities of

aerosol which may be collected are even scarcer and avoiding any sample contamination by pre-treatment processes is even more mandatory.

Conclusions

From our experience, we can conclude that PIXE is still a useful technique for the analysis of aerosols, especially when used in a complementary and synergic way with other analytical techniques. PIXE is unrivalled for the study of natural aerosols such as mineral dust or marine aerosols. If only these components are of interest, one sample may be analyzed in less than 1 min, thus allowing the analysis of hundreds of samples in 1 day. The simultaneous detection of several important source tracers is fundamental for the application of receptor models such as PMF. The measuring times for the analysis of standard daily samples are far shorter than those typical of XRF systems and similar to the ICP methods (but PIXE does not need any sample treatment) and this makes it possible to analyze many samples in short times.

Another field in which PIXE has a main role is the study of high-time resolution samples, which is very useful to identify the aerosol sources, to understand physical-chemical processes and to assess real human exposure.

Finally, the PIXE capability of analysis of very low mass samples together with no need of sample pre-treatment (which may be a source of contamination) makes it quite useful for the analysis of the aerosol collected in remote areas, such as the Antarctica plateau, Arctic areas or high-altitude sampling sites.

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References

- [1] S. A. E. Johansson, J. L. Campbell, K. G. Malmqvist, *Particle-Induced X-Ray Emission Spectroscopy*, John Wiley and Sons, London, **1995**.
- [2] W. Maenhaut, K. Malmqvist, in *Handbook of X-ray Spectrometry* (Eds: R. E. Van Grieken, A. A. Markowicz), Marcel Dekker, Antwerp, **2001**, pp. 761–771.
- [3] K. D. Perry, S. S. Cliff, P. Jimenez-Cruz, *J. Geophys. Res.* **2004**, *109*, D23S28.
- [4] Website: <http://pixeintl.com/Streaker.asp> [accessed 23 February 2011].
- [5] W. Maenhaut, R. Hillamo, T. Mäkelä, J. L. Jaffrezo, M. H. Bergin, C. I. Davidson, *Nucl. Instr. Meth.* **1996**, *B109–110*, 482.
- [6] M. Chiari, F. Lucarelli, F. Mazzei, S. Nava, L. Paperetti, P. Prati, G. Valli, R. Vecchi, *X-Ray Spectrom.* **2005**, *34*, 323.
- [7] D. D. Cohen, J. Crawford, E. Stelcer, V. T. Bac, *Atmos. Environ.* **2010**, *44*, 320.
- [8] P. Paatero, U. Tapper, *Environmetrics* **1994**, *5*, 111.
- [9] G. Calzolari, M. Chiari, I. Garcia-Orellana, F. Lucarelli, A. Migliori, S. Nava, F. Taccetti, *Nucl. Instr. Meth.* **2006**, *B249*, 928.
- [10] M. E. Birch, R. A. Cary, *Aerosol Sci. Technol.* **1996**, *25*, 221.
- [11] H. J. Annegarn, G. M. Braga Marcazzan, E. Cereda, M. Marchionni, A. Zucchiatti, *Atmos. Environ.* **1992**, *26*, 333.

- [12] A. D'Alessandro, F. Lucarelli, P. A. Mandò, G. Marazzan, S. Nava, P. Prati, G. Valli, R. Vecchi, A. Zucchiatti, *J. Aerosol Sci.* **2003**, *34*, 243.
- [13] S. Nava, F. Becherini, A. Bernardi, A. Bonazza, M. Chiari, I. García-Orellana, F. Lucarelli, N. Ludwig, A. Migliori, C. Sabbioni, R. Udisti, G. Valli, R. Vecchi, *Sci. Total Environ.* **2010**, *408*, 1403.
- [14] F. Mazzei, F. Lucarelli, S. Nava, P. Prati, G. Valli, R. Vecchi, *Atmos. Environ.* **2007**, *41*, 5525.
- [15] EPICA community members, *Nature* **2006**, *444*, 195.
- [16] F. Marino, G. Calzolari, S. Caporali, E. Castellano, M. Chiari, F. Lucarelli, V. Maggi, S. Nava, M. Sala, R. Udisti, *Nucl. Instr. Meth.* **2008**, *B266*, 2396.
- [17] F. Marino, E. Castellano, D. Ceccato, P. De Deckker, B. Delmonte, G. Ghermandi, V. Maggi, J.-R. Petit, M. Revel-Rolland, R. Udisti, *Geochem. Geophys. Geosyst.* **2008**, *9*, Q10018.