PIXE and XRF analysis of particulate matter samples: an inter-laboratory comparison

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Abstract

PIXE and XRF are very effective techniques in atmospheric aerosol investigation, therefore they are extensively used by the authors. In this work an inter-laboratory comparison of the results obtained analysing several samples (collected on different substrata) with both techniques is presented: the samples were analysed by PIXE (in Florence, at the 3 MV Tandetron accelerator of LABEC laboratory) and by XRF (in Genoa and Milan, where two Oxford XRF instruments are operational). The results of the three sets of measurements are in good agreement for all the analysed samples.

The aim of this work was also to compare PIXE and XRF performance in atmospheric aerosol analysis with the routine set-up currently in use at the three laboratories, to determine the best technique to be applied depending on the substratum used for aerosol sampling and the main elements of interest for each specific research project. Results of the comparison between the minimum detection limits of both techniques will be shown for all the measured elements, for different substrata (Teflon, polycarbonate and cellulose mixed esters).
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1. Introduction

PIXE (particle induced X-ray emission) and EDXRF (energy dispersive X-ray fluorescence) are multielemental analyses, very powerful in the detection of trace elements. Both EDXRF (hereinafter simply XRF) and PIXE are highly sensitive, do not require any pre-treatment of the sample (in our specific application, they analyse directly particles deposited on the filtering support), they are simultaneous for a wide range of atomic numbers and rapid. All these characteristics make them particularly suitable for the analysis of aerosol samples [1–5].

For several years, the research groups of the Universities and INFN of Florence, Milan and Genoa have been involved in many common projects on aerosol characterization in urban and remote areas as well as in the improvement of these techniques in this research field [6–8]. Usually, aerosol-monitoring studies require to fully characterise a large number of samples; therefore, thousands of samples are analysed every year in the three laboratories and, to avoid an overload of measurements at the single laboratory, quite frequently part of the samples are analysed in one lab and part in another one. For this reason the main purpose of this work is to optimise the elemental

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analysis with the joint and complementary use of PIXE (in Florence) and XRF (in Genoa and Milan), minimising the analysis time at the accelerator (which is heavily used also for other ion beam analysis or AMS applications) and maximising the detection efficiency for a number of elements. Therefore, we carried out: (a) a comparison of the results obtained in the three laboratories, with the two different techniques; (b) a study aimed at the identification of the optimal technique to be used, in relation to filter type and to the goal of the specific campaign; for this last intent, a comparison between PIXE and XRF MDLs (minimum detection limits) has been made, for different elements and filter types.

2. Experimental

Fourteen daily samples of PM_{10} and $PM_{2.5}$ collected on different substrata were taken into account (6 on Teflon, 3 on polycarbonate and 5 on cellulose mixed esters filters); these samples have been collected by standard low-volume sequential samplers in an urban sampling site and they can be considered representative for urban aerosol samples. They were first measured by XRF in Milan, then by XRF in Genoa and, finally by PIXE in Florence. To check whether any material loss or contamination had occurred during transport or sample-handling, XRF measurements in Milan were repeated after PIXE analysis, except for polycarbonate filters that become too fragile to be further analysed after proton bombardment. Both PIXE and XRF measurements were done under the typical conditions used for the routine analysis of aerosol samples.

2.1. PIXE measurements

PIXE measurements were performed at the 3 MV Tandetron accelerator of INFN-LABEC laboratory in Florence. Samples were bombarded with a 3.2 MeV extracted proton beam, with a 12 nA current (6 nA in case of Teflon filters), for about 10 min. The beam was collimated to dimensions of 2×1 mm^2; anyway, using a scanning mode, most of the area of the sample has been analysed. X-rays were collected by two detectors, a Silicon Drift Detector, for light elements, and a Si(Li), optimised for the detection of X-rays approximately in the range 4–20 keV; energy resolutions are 145 and 190 eV FWHM at 5.9 keV, respectively. The experimental set-up is described in detail elsewhere [9]. PIXE spectra were analysed with the GUPIX software [10].

2.2. XRF measurements

XRF measurements were carried out at the Physics Departments of the Universities of Genoa and Milan, using an ED-2000 spectrometer by Oxford Instruments [11]. Excitation X-rays are produced by a Coolidge tube ($I_{max} = 1$ mA, $HV_{max} = 50$ kV) with an Ag anode. Two measuring conditions were fixed to optimise the sensitivity

for groups of elements: runs with HV = 15 kV, $I = 100$ μA, no primary filter, live time = 1000 s, to detect "low Z" elements (from Na to P), while the "medium-high Z" elements (from S to Pb) were measured setting HV = 30 kV, $I = 500$ μA, Ag primary filter (about 50 μm thick), live time = 3000 s. The beam spot is elliptic with an area of about 1 cm^2; nevertheless, the automated spinning on the sample axis allows the investigation of a much wider area. X-rays were detected by a Si(Li) with energy resolution lower than 145 eV FWHM at 5.9 keV. XRF spectra were fitted using AXIL software package [12].

For both PIXE and XRF measurements, elemental thickness (μg/cm^2) was obtained by comparing the filter yields with a sensitivity curve measured in the same geometry on a set of thin Micromatter standards, with a ±5% uncertainty on areal concentrations. A check of the calibration was periodically performed analysing the NIST standard SRM2783 (Air Particulate on Filter Media).

3. Results

Amongst the detected elements, we selected only those with concentrations above their MDLs in at least 8 samples, both in PIXE and XRF measurements; therefore, we took into account Al, Si, S, K, Ca, Fe, Cu and Zn. Moreover, these elements are markers of aerosol sources, as mineral dust, sulfates, biomass burning and traffic. In both PIXE and XRF measurements, blank corrections were necessary to obtain accurate quantitative results. In the case of samples collected on cellulose mixed esters filters, we could not take into account Zn concentration data because of the high and inhomogeneous contamination of blanks.

XRF and PIXE measurements are in good agreement: differences between concentrations obtained by the two methods are reported in Table 1 and are always within 10%, except in two cases (being anyway at maximum 15%): this result is comparable with those reported in literature [13,14]. These discrepancies can be due to different X-ray spectra fittings, and to sample and blanks

Table 1
Results of the XRF versus PIXE comparison on 14 aerosol samples, collected on Teflon, polycarbonate and cellulose mixed esters filters: slopes and correlation coefficients, obtained by a fitting procedure, are reported (linear regression plots are shown in Fig. 1); intercepts were consistent with zero

	XRF (Genoa) versus PIXE		XRF (Milan) versus PIXE	
	Slope	r^2	Slope	r^2
Al	1.04 ± 0.02	0.96	0.89 ± 0.02	0.97
Si	1.03 ± 0.02	0.98	1.00 ± 0.02	0.98
S	1.04 ± 0.02	0.97	1.07 ± 0.02	0.97
K	1.00 ± 0.03	0.93	1.03 ± 0.03	0.97
Ca	1.02 ± 0.03	0.99	1.08 ± 0.03	0.99
Fe	1.07 ± 0.02	0.99	1.07 ± 0.02	1.00
Cu	0.99 ± 0.02	0.99	1.10 ± 0.02	1.00
Zn	1.12 ± 0.03	0.99	1.08 ± 0.03	1.00

inhomogeneities, because of the different area covered by proton and excitation X-rays beam. Sample thickness spanned a wide range of aerosol deposit ($\sim$30–500 μg/cm^2), so we can exclude any dependence on the mass deposited. In Fig. 1, linear regression plots for the eight elements selected are shown; slopes and correlation coefficients are reported in Table 1.

3.1. Comparison of PIXE and XRF MDLs

To evaluate the MDLs, the commonly accepted three-sigma criterion was used: an X-ray peak is considered detectable if its intensity exceeds a three-standard-deviation fluctuation of the underlying background [5]. In PIXE spectra the background is originated by Compton interactions in the detector and by secondary Bremsstrahlung, which is dominant for energies up to about 5 keV (with a 3 MeV proton beam); in XRF spectra, the background is a continuum due to the Bremsstrahlung radiation of the exciting beam, and its shape and intensity are strongly related to the selected primary filter.

MDL values for the XRF spectrometers of Genoa and Milan are in excellent agreement (not shown) for all elements and filter types, as expected, being the two instruments identical. Regarding samples on polycarbonate and cellulose mixed esters, MDL patterns have the same behaviour (for each technique), and MDLs for these two filter types are comparable (not shown), being slightly lower for samples on polycarbonate.

In relation to the purpose of each monitoring campaign, different filters types might be used; thus, the choice of the most suitable technique for analysing aerosol samples should take into account MDLs evaluation for different filter supports. As shown in Fig. 2, for polycarbonate and cellulose mixed esters filters the PIXE MDLs are always better or comparable with those of XRF, in spite of a
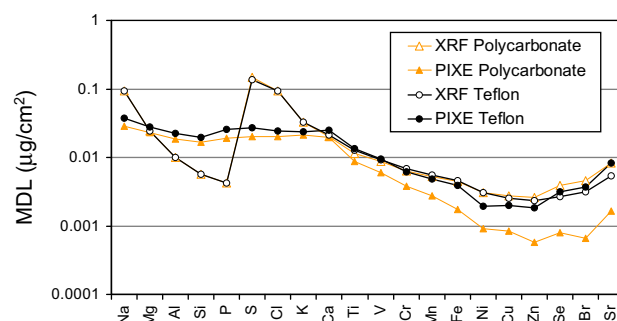

Fig. 2. PIXE and XRF MDLs, for different elements, for samples collected on polycarbonate and Teflon filters.

XRF measuring time of about 7 times greater, except for Al, Si and P; however, Si and Al are normally found in large concentrations in the atmospheric aerosol and higher MDLs do not give problems in the detection of these elements.

In the case of Teflon, for the "low-medium Z" elements the situation is similar to the one found for polycarbonate filters, while for Z > 20 PIXE MDLs increase and become similar to the XRF ones: in fact, the increase of the Compton background intensity in PIXE spectra (due to the γ-rays produced by F [15], a Teflon major component) yields higher PIXE MDLs in the case of Teflon with respect to polycarbonate.

In order to optimise measuring times, in the case of aerosol samples collected on a daily basis it should be advisable to perform:

- One PIXE measurement lasting about 1 min to get the "low-Z" elements concentrations (reducing considerably the beam time at the accelerator).
- One XRF measurement (only the high voltage run) to get the concentrations of the "medium-high Z" elements, with measurement times of the order of
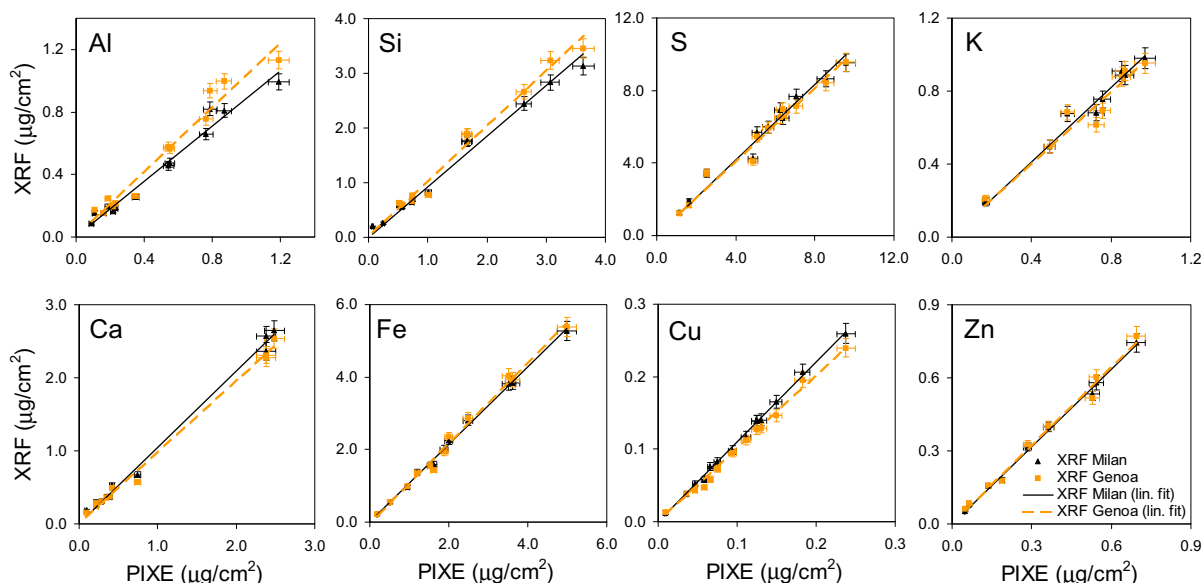

Fig. 1. Linear regression plots for the eight selected elements, namely Al, Si, S, K, Ca, Fe, Cu and Zn.

30–40 min, which is still quite a long measuring time with respect to PIXE, even though the analysis can be done in automatic mode (also during the night).

4. Conclusions

The comparison of PIXE and XRF techniques on fourteen aerosol samples shows a very good agreement among the three laboratories, with discrepancies lying almost always below 10%. No dependence on filter type was observed, and no material loss or volatalisation occurred, except for chlorine, which is known to be subjected to evaporation. The differences in the elemental sensitivity for XRF and PIXE, evidenced by the study on MDLs, are due to intrinsic features of the two techniques, such as different ionisation cross-sections for photons or protons and unlike intensities of the continuous background, which is, moreover, affected by the filter type.

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