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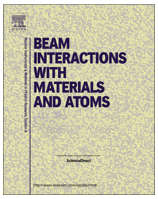

Comparison of PIXE and XRF analysis of airborne particulate matter samples collected on Teflon and quartz fibre filters

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ABSTRACT

Within the framework of research projects focusing on the sampling and analysis of airborne particulate matter, Particle Induced X-ray Emission (PIXE) and Energy Dispersive X-ray Fluorescence (ED-XRF) techniques are routinely used in many laboratories throughout the world to determine the elemental concentration of the particulate matter samples. In this work an inter-laboratory comparison of the results obtained from analysing several samples (collected on both Teflon and quartz fibre filters) using both techniques is presented. The samples were analysed by PIXE (in Florence, at the 3 MV Tandetron accelerator of INFN-LABEC laboratory) and by XRF (in Elche, using the ARL Quant'X EDXRF spectrometer with specific conditions optimized for specific groups of elements). The results from the two sets of measurements are in good agreement for all the analysed samples, thus validating the use of the ARL Quant'X EDXRF spectrometer and the selected measurement protocol for the analysis of aerosol samples.

Moreover, thanks to the comparison of PIXE and XRF results on Teflon and quartz fibre filters, possible self-absorption effects due to the penetration of the aerosol particles inside the quartz fibre-filters were quantified.

1. Introduction

Particulate matter suspended in the air with an aerodynamic diameter of less than 10 μm (PM_{10}) is regularly sampled around the world in order to evaluate the degree of pollution caused by aerosols in a specific location. In Europe, the PM_{10} mass concentrations should be determined according to the European reference method EN 1234, 2015 [1]. The type of substrate used to filter the air and hence collect particles can be made of either glass fibre, quartz fibre, PTFE or PTFE-bonded glass fibre. If the objective of the sampling is merely to determine the PM_{10} mass concentration the best choice would be the use of Teflon filters [2,3]. However if a complete chemical characterization of the aerosol is required the choice of filter will depend on the analytical technique to be used. While the ionic and element content is usually better quantified on Teflon filters due to the lower concentration of the analysed species in blank filters, the evaluation of the organic and elemental carbon can typically only be determined on quartz fibre filters [4]. Therefore, to get a comprehensive chemical characterization (including ions, metals and carbonaceous components), the use of two different samplers in parallel (equipped with Teflon and quartz fibre filters, respectively) allows for the best analytical performances; nonetheless, when such approach cannot be followed, quartz fibre filters should be chosen.

Two common techniques used to determine the elemental composition of aerosol samples on filters are XRF (X-Rays Fluorescence) and PIXE (Proton-Induced-X ray-Emission) [[5–7] (and therein references)]. The advantages of these techniques are well known for the following reasons: they are multi-elemental, non-destructive, do not need any sample preparation, and have good precision and accuracy. The disadvantages are mainly related with the absorption of low energy X-rays (emitted by low Z elements) inside the sample itself, that is inside the aerosol particle itself and, depending on the penetration of the particles through the sampling substrate, inside the filter. Some studies have compared the results obtained by both techniques on substrates like Teflon, cellulose or polycarbonate [8–11]. However, to our knowledge,

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there has been relatively little reported about these comparisons on quartz fibre filters [12].

The main objective of this work is to evaluate the performance of both techniques on quartz fibre filters and on Teflon filters; furthermore, the attenuation of low-energy X-rays depending on the type of filter will be determined by comparing the results obtained on samples simultaneously collected on quartz fibre and on Teflon filters.

2. Experimental

2.1. Sampling site

The sampling campaign was carried out in the urban centre of Elche, a medium-sized city (~190,000 inhabitants) located in south-eastern Spain, ~12 km from the Mediterranean Sea. The typical climate in the region is dry Mediterranean, with soft winters and long droughts in the summer season. The sampling site was at 3 m above ground level, in the first floor of a municipal office block. More information about the sampling location can be found in [13,14].

2.2. Sample collection

Twenty-four hour PM_{10} samples were collected simultaneously onto quartz fibre (Whatman QMA, 47 mm diameter) and Teflon (Whatman PTFE, 2 μm porosity, 46.2 mm diameter, PP ring supported) filters using Derenda 3.1 low-volume samplers ($2.3\ m^3\ h^{-1}$). The campaign was performed during the months of October and November of 2013. Sampling started at 0:00 h local time each day. The total number of valid samples was 40. Before weighing, all filters were conditioned for at least 24 h at a relative humidity of 50 ± 5% and temperature of 20 ± 1 °C; PM gravimetric masses were subsequently divided by the sampled air volume to calculate average daily PM_{10} mass concentrations. After weighing, the filters were stored in the fridge at 4 °C until chemical analyses.

3. Methods

3.1. XRF measurements

XRF measurements were carried out at the Atmospheric Pollution Laboratory of the Miguel Hernández University in Elche, Spain using the ARL Quant'X (Thermo Scientific Inc, USA) EDXRF spectrometer. Excitations rays are produced by an air cooled X-ray tube (Rh anode, 40 W maximum power, 4–50 kV anode voltage, 0.02–1.98 mA anode current) and the emitted X-rays are detected by means of a Peltier cooled Si(Li) detector (15 mm^2 crystal area, 3.5 mm crystal depth and 155 eV FWHM energy resolution at the 5.9 keV Mn K_α line).

Different primary beam filters can be placed in front of the X-ray beam in order to decrease the X-ray energy to the correct excitation bandwidth of the elements to be analysed. Five different conditions (Table 1) were fixed to optimize the sensitivity for groups of elements choosing different filters and voltage of the tube. All the samples were analysed in vacuum.

Table 1
Measuring conditions for XRF.

Filter	Voltage (kV)	Live time (s)	Elements
No filter	4	250	Na, Mg
Cellulose	10	300	Al, Si, S, Cl, K, Ca
Pd thin	30	300	Ti, V, Cr, Mn, Fe, Ni, Cu, Zn
Pd thick	50	250	Br, Sr, Pb
Cu thin	50	250	Sb, Ba

The instrument was calibrated using pure thin film standards (Micromatter– XRF Calibration standards, 50 μg/cm^2, N – Nuclepore® polycarbonate aerosol membranes, USA). A check of the calibration results was periodically performed analysing the NIST standard SRM2783 (Air Particulate on Filter Media). XRF spectra were fitted using the WinTrace software package (Thermo Electron Corp.). Detection limits for the instrument, calculated as in [15] are reported in Fig. 1 for samples collected on different substrata, namely Teflon and quartz fibre filters.

3.2. PIXE measurements

PIXE measurements were performed at the LABEC laboratory using the external beam line fully dedicated to aerosol analysis by IBA techniques. The set-up is extensively described elsewhere [16]. Briefly, samples are positioned at about 1 cm of distance from a 500 nm Si_3N_4 beam extraction window; a collimator at the end of the beam line sets the beam spot to 1 × 2 mm^2 and the charge flow during the measurement is measured by means of a graphite Faraday cup positioned just behind the samples. At the moment of this analysis, the detection system counted on two Silicon Drift Detectors (SDD), optimized for the detection of low-Z and medium-high-Z elements, in order to take into account the differences in the X-ray emission cross sections (an upgraded 3-detector system is used at present, as described in [17]). The detector dedicated to low-Z elements was a 280 μm thick, 10 mm^2 Ketek GmbH SDD (collimated to 7 mm^2 by a Ta–Cr–Ti–Al multilayer collimator, to shield the outer part of the area, where incomplete charge collection may happen [17,18]), having 145 eV FWHM energy resolution at the 5.9 keV Mn K_α line with 1 μs shaping time. The detector, positioned at 45° with respect to the beam line, was shielded from backscattered protons by means of a magnetic deflector and the volume between its entrance window and the sample is saturated by helium. The detection of the medium–high Z elements was accomplished by a 450 μm thick, 113 mm^2 (collimated to 80 mm^2) Ketek GmbH SDD, with 165 eV FWHM energy resolution at the 5.9 keV Mn K_α line with 1 μs shaping time. This SDD was positioned at 135° with respect to the beam direction. It has a 25 μm thick Be entrance window; absorbers (450 μm Mylar foils) are mounted in front of it to attenuate the low energy X-rays.

Samples were bombarded with a 3.0 MeV proton beam on the target (about 3.2 MeV in vacuum), which is the optimum beam energy for the analysis of Teflon filters and is also adequate for quartz fibre filters [19–21], with a 40 nA current for 180 s and with 10 nA for 300 s, respectively, for Teflon and quartz. Using a scanning system, most of the area of the sample was analysed, to average over possible non-homogeneous deposits.

PIXE spectra were analysed with the GUPIXWin software [22] and elemental concentrations were obtained by comparing the sample yields with a sensitivity curve obtained measuring in the same experimental conditions a set of thin Micromatter standards (with a 5% uncertainty). PIXE detection limits are widely discussed elsewhere [16,17,8,11].

4. Results

Results of the measurements performed with XRF and PIXE on the two series of samples simultaneously collected onto Teflon and quartz fibre filters were compared for all the elements with concentration higher than the detection limits for both techniques in all the samples. Slopes and offsets of the calculated regression lines are reported in Table 2, together with the r^2 correlation values. The results are presented as described next: column (a) comparison of PIXE and XRF results for the same set of samples collected on Teflon filters; column (b) comparison of PIXE and

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