



	Experiment title: X-RAY FLUORESCENCE INVESTIGATIONS ON BREATHABLE ATMOSPHERIC PARTICLES	Experiment number: ME-588
Beamline:	Date of experiment: from: 9/04/2003 (7am) to: 14/04/2003 (7am)	Date of report: 30/08/2003 <i>Received at ESRF:</i>
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Report: Aim of the experiment was to obtain information on chemical and morphological composition of breathable air particulate matter (APM) collected on filters in urban and industrial sites, in order to get insights and useful hints for source identification, hazard assessment and epidemiological studies. Operative conditions useful for the purposes have been screened during the first shifts. Energy of the exciting beam was set at 7.2 KeV in order to be able to record signals from Fe, that are important for powders collected nearby ironworks. The spot size was smaller than $3.1 \mu\text{m} \times 1.6 \mu\text{m}$, while pixel dimensions were $1 \mu\text{m} \times 1 \mu\text{m}$ and the acquisition time \times pixel was 300 ms in preliminar runs and 1000 ms later. For what concerns sample holding, a good choice resulted to be clamping portions of the filters between two polyimide films having a hole in the center, that were placed between two stainless steel support and fixed to the sample holder. Glueing the filters made to appear an artificial signal attributed to Cl. A $\varnothing 500 \mu\text{m}$ zone plate prepared by the TASC/INFM of Trieste ($\Delta r_N = 300 \text{ nm}$ and $f_{7.2 \text{ KeV}} = 89 \text{ cm}$) produced better results than a $\varnothing 100 \mu\text{m}$ TASC INFM 2spot zp (+40 μm , +10 μm), that gave very low signal and allowed poor imaging. Initial measurements have been performed on certified reference material NIST SRM 2783 that contains 2.5 μm nominal size APM on polycarbonate filter. This SRM has 27 certified and reference values for common and toxic elements. Average XRF spectra of four regions of interest (ROI) from the SRM, measuring each $100 \mu\text{m} \times 100 \mu\text{m}$ (r12, r13, r14, r15), are shown in fig. 1a and 1b, reporting the elemental attribution of major peaks.

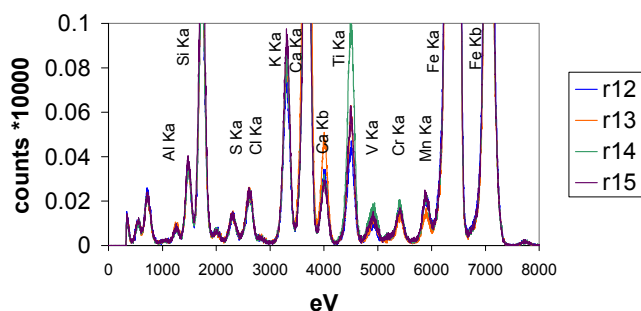
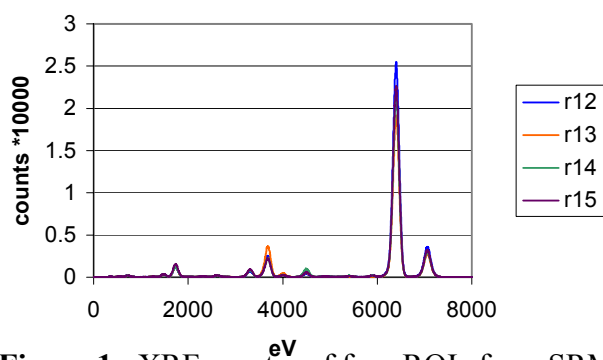


Figure 1a: XRF spectra of four ROIs from SRM 2783

Figure 1b: Identification of major peaks

A further step has been the acquisition of stacks from a blank glass fiber filter similar to the ones used in routine APM monitoring, in order to evaluate the contribution coming from the GFF filters to the XRF signals. Relevant signals of Ba from L_{α} and L_{β} edges were found between 4 and 6 KeV, covering potential presence of interesting K_{α} edges from Ti, V and Cr. This result confirm the opportunity to collect further samples for synchrotron study on quartz filters instead of using GFF. Real samples collected during critical pollution episodes of March 2003 in a urban site close to ironworks (Via Carpineto) and in another one mostly affected by traffic and warming sources (Piazza Goldoni) were then analysed. Ten stacks measured in comparable conditions on ROIs of $100 \mu\text{m} \times 100 \mu\text{m}$ from the available filters form the main data base for drawing environmental considerations from this experiment. The average XRF spectra of the ten ROIs are reported in figure 2. A kernel principal component analysis has been performed on data obtained subtracting to each average spectrum of a ROI the average spectrum of all ROIs, representing the mean contribution to the XRF signal coming from both the filter and background APM.

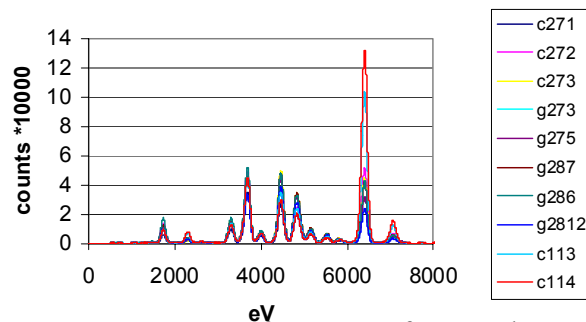


Figure 2: XRF spectra of ten ROIs from real samples

The first two Principal Components are orthogonal linear combinations of the 3000 channels, considered as variables describing the 10 stacks, and they explain respectively 92% and 7% of the total variance of the data set. The first one has high loadings for channels associated to Fe and S, whose presence can be associated reasonably to the ironworks while the second one has high loadings for Si, K, Ca and Ba and it is interpreted as describing the minor variations between the individual glass fiber filters. All the stacks coming from samples collected nearby Carpineto have projections on the first PC higher than those from Piazza Goldoni, showing clearly how they accumulate a pollution component richer in Fe and S. This evidence have not been evidenced yet by means of other analytical techniques. An image analysis has been performed on all available stacks, by means of the image processing toolbox developed by the Delft University for the MatLab environment, focusing preliminarily on Fe maps. Some examples are reported in the following Figure 3. Size distributions were comparable in all cases with the exception of two images from the day when the overall PM amount was the highest and coarser Fe particles appeared (first two Fe maps in the series below).

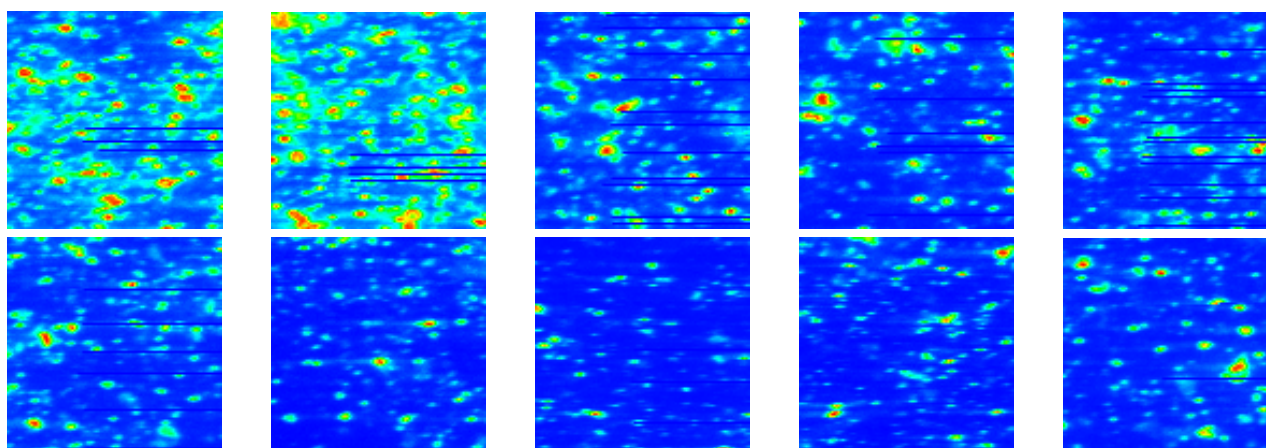


Figure 3: Fe maps from filters sampled on March 2003 (Carpineto site first row, Goldoni site second row).

Technical problems encountered

- During the experiment several beam losses have been experienced.
- A number of dark (blank) lines in the images has been registered.
- The downloadable version of ARTEMIS presents some bugs (grayscale images are not produced and the colorscale cannot be saved as image); the Linux version is arduous to install, requiring a number of libraries for the Python environment, the list of which (with the proper version) is not available. The main proposer has not been able to install Artemis under MS-Windows. Beside all this, Artemis is an excellent software.

Preliminary results from the ME-588 experiment have been presented as oral communication at the International Symposium “Spectroscopy in Theory and Practice”, held in Nova Gorica (Slovenia) from August 27th to 30th.

The obtained results are meaningful, of considerable environmental relevance and a continuation of the experiment would be very profitable in the light of the achieved information. Within next objectives we mention a study on heterogeneity of trace elements on filter surface, useful for validating the quantitation of XRF results obtained on small ROIs, and XANES for Cr particles collected on quartz filters or polycarbonate filters.