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A new method for sample preparation and chemical analysis of athmospheric aerosols

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Abstract

A new method for chemical characterizations of atmospheric aerosols is proposed.
Particulate matter (PM) is routinely collected on filters and following characterized with several analytical techniques. The most common techniques for compositional analysis include atomic absorption spectroscopy (AAS) and inductively coupled plasma spectroscopies (ICP). These analyses requires complete sample digestion, that may be expensive and time-consuming. Moreover sample contamination and material loss may occur.
This sample preparation method consist in sandwiching the filter in two polymeric foils, allowing to protect it from external contamination, to avoid any material loss and to store it for further investigations. After preparation the samples can be directly analyzed by several non-destructive X-ray based techniques. For example micro XRF studies allow chemical mapping and identification of particles composition and micro X-ray diffraction (XRD) allow phase analysis. These kinds of information are useful for determination of emission sources. In this context XRF is considered a preferred technique, however it does not allow trace elements analysis. Total reflection X-ray fluorescence (TXRF) is an energy dispersive XRF with a different geometrical configuration which allows higher elemental intensities and lower limits of detection (Klockenkämper, 1997). In suitable experimental conditions matrix effects can be neglected and TXRF may be competitive with other techniques such as AAS and ICP. TXRF appears particularly promising for environmental analysis, especially when heavy metals must be detected at very low concentrations.
Recently we demonstrated that TXRF measurements of samples prepared with the proposed method, allow the determination of trace elements and quantitative analysis by means of external calibration (Borgese et al., 2012). This method has been successfully applied in a study of Mn environmental pollution assessment due to the presence of Mn–Fe alloy industries in the Brescia province (Borgese et al., 2011), and other studies are still ongoing.

Keywords: Chemical analysis; TXRF; sample preparation; aereosol; particulate matter.

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1. Main text

In this work we propose a new method devoted to the analysis of air particulate matter (PM) collected on filter membranes.

The choice of the method for PM analysis has a big importance in the perspective of sampling for environmental pollution assessment and evaluation of the possible emission sources.

One of the most widespread conventional approach for the chemical analysis of filters is the collection of samples from the sampling system and transportation to the analysis laboratory where elemental analysis is performed by inductively coupled plasma spectroscopies (ICP) or atomic absorption spectroscopy (AAS) after complete solubilization of the sample by microwave acid digestion. This is a completely destructive analysis method. The new approach that we propose is non-destructive. The method includes a step of sample preparation, classification and storage, followed by non-destructive elemental analysis, preferably by total reflection X-Ray fluorescence (TXRF). Nevertheless, the proposed sample preparation procedure does not preclude the possibility to perform the conventional destructive analysis, even in further time (see Fig. 1).
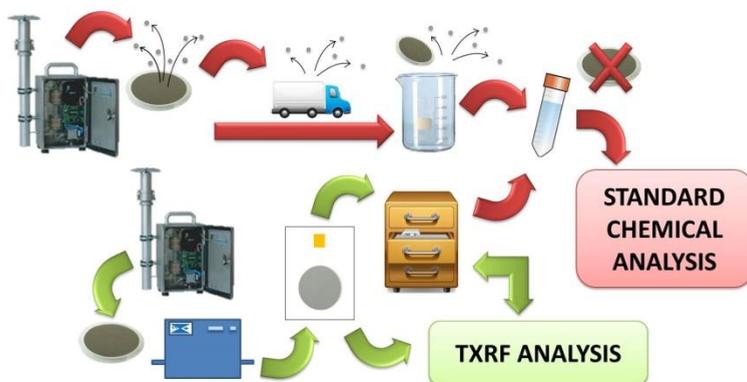

Fig. 1. Comparison between the conventional and novel proposed approach for sample preparation and elemental analysis of PM filters.

Comparing these two described approaches, it is clear that the main drawbacks of the conventional method, such as the possible sample contamination, material loss and damages, mainly during transportation and handling, are completely solved in the novel approach. Indeed, the complete protection of the sample simplify its handling, and the non-destructive analysis technique gives a unique possibility of sample storage and classification.

The preferred non-destructive analysis techniques are based on X-Ray fluorescence (XRF) in the preferable configuration of TXRF, which differs from the conventional energy dispersive XRF only for the instrumental geometry. In TXRF the angle of the incident beam is lower than critical angle for total reflection of X-rays on the sample carrier, and the detector position is a few millimeters above the samples surface maximizing the solid angle for the collection of fluorescence intensity. These features enhanced the detection performance of TXRF making it suitable for trace analysis. Other advantages of TXRF are the detection limits in picograms-nanograms range depending on the atomic number, the few micrograms needed for the analysis, the short measurement time (within 10 minutes)

and the wide dynamic range. The technique is free from matrix effects giving the possibility of quantitative analysis by linear calibration.

The requirements for TXRF analysis are mainly two: a thin film like sample and an X-ray reflector sample carrier. To achieve these requirements the usual sample for TXRF analysis are liquids and slurries. Some microliters of sample, added with internal standard for quantification, are deposited on the carrier and dried to obtain a thin film like residue to be measured.

On this basis, most of the pretreatments methods recently reported in literature for TXRF analysis of air PM filters (De La Calle et al., 2013) involve a destructive step of sample digestion. Only two non-destructive methods, both proposed by us, were considered (Bontempi et al., 2010; Borgese et al., 2011).

The validation of the new method was performed with a standard reference material from NIST composed by a polycarbonate membrane with a known deposited amount of urban PM (NIST SRM 2783). After the employment of the preparation procedure, the sample was measured by TXRF. Quantitative analysis was performed using Cu as internal standard element. The results does not differ significantly from those reported in the reference material certificate (Borgese et al., 2011).
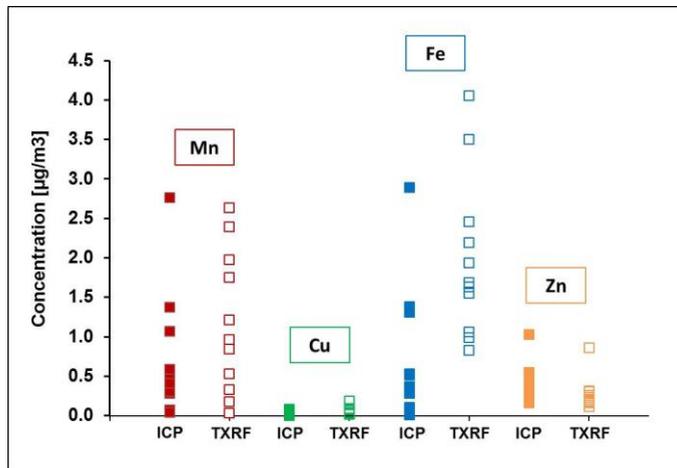

Fig. 2. Analysis of PM filters collected in similar areas during an environmental assessment study and measured by ICP-MS or with the proposed method for sample preparation and TXRF analysis.

Filters collected in similar areas were used to compare the results of the conventional elemental analysis by ICP mass spectroscopy (MS) and those obtained with the proposed sample preparation method and TXRF analysis. The results obtained show similar values with major differences in the case of Fe (see Fig. 2). This difference may be due to the presence of insoluble Fe compounds not measured by ICP-MS analysis.

Usually for air quality monitoring, PM filters are collected by different systems distributed on territory and sent to a unique analysis center where the analytical instrumentation is available (see Fig. 3). For this reason we propose a simple, easy to use and portable kit for the new sample preparation method to be used on site.
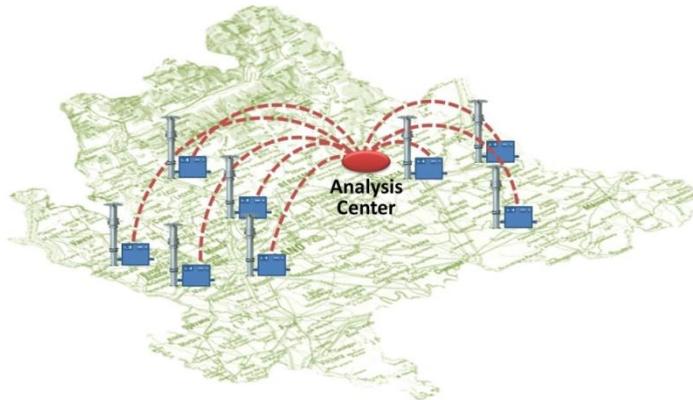
Fig. 3. Schematic view of the geographical delocalization of the sampling systems and
the centralization of the analysis laboratory.

The proposed method simplifies the filter sample preparation procedure, avoiding contamination and material loss, and reducing preparation, measuring time and sample flexibility. The sample treated by this procedure may be analyzed by direct and non-destructive analysis, shaped, stored and classified.
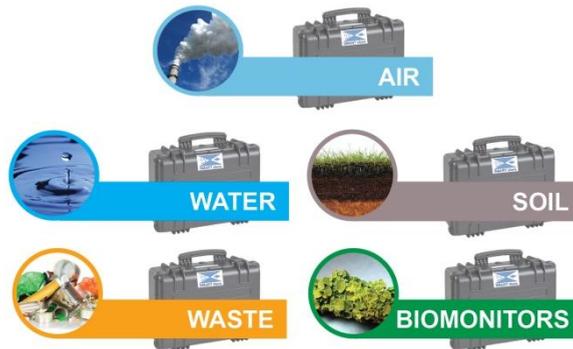

Fig. 4. The main fields of environmental applications of the proposed method for
sample preparation and TXRF analysis.

The proposed method is optimized for XRF based techniques such as XRF, TXRF and µXRF. However, other fields of analysis are under exploration, such as structural and phase analysis by X-ray diffraction and reflectivity, optical microscopy and speciation by means of synchrotron radiation based techniques like X-ray absorption near edge spectroscopy (XANES).

Finally, other dedicated sample preparation methods for other environmental sample such as water, soil, wastes and biomonitors are under development.

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NIST SRM 2783 - Air Particulate on Filter Media.