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Quantitative measurement of PM$_{10}$ by means of X-ray fluorescence spectra

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Abstract

We developed an automatic device able to sample and analyze in situ and in real time airborne particulate matter (PM) using the X-ray fluorescence of the chemical species layered on a filter, having atomic numbers between 19 (Potassium) and 82 (Lead).

5 Furthermore, we developed a calibration technique, which gives the parameters for real time automatic determination of the absolute mass of the chemical species present on the sample, with a sensitivity varying from 1 to 100 µg per sample.

Our system could represent a simpler alternative to the complex and sophisticated laboratory measurements, such as Inductively Coupled Plasma Mass Spectrometry

10 (ICP-MS) or Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), officially used by environmental agencies. A 6 month in-situ test, carried out in collaboration with the local Regional Environmental Agency, showed that our system gives results comparable with the ones obtained using existing techniques, but with smaller errors. The methodology developed has been submitted for a patent.

15 **1   Introduction**

In many urban agglomerations of developed countries, industrialization pushes people to live near industrial plants, such as cement factories, ironworks, waste disposal of lead, waste incinerators, which can be sources of airborne particulate matter pollution. Epidemiological studies made over the last 10/15 yr (Cupr et al., 2006; WHO, 2000,

20 2005, 2006; Tam and Neumann, 2004; Parry et al., 2008), show that airborne pollution may cause health problems, such as lung cancer (Parodi et al., 2005; Pauk et al., 2005), Alzheimer disease (Calderón-Garcidueñas et al., 2004), and respiratory failure (Kappos et al., 2004). Moreover, it has been demonstrated that the effect of the particulate matter on human health depends on the nature of the particulate (WHO, 2000).

25 For these reasons the World Health Organization has fixed some limits related to the quantities of pollutants that may be present in air (WHO, 2000, 2005, 2006).

To determine the concentration ($\mu g\,m^{-3}$) of each chemical species present in air several methods have been developed (Chow, 1995): Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Microwave Induced Breakdown Spectroscopy, Laser Induced Breakdown Spectroscopy (LIBS), Spark Induced Breakdown Spectroscopy and X-ray fluorescence.

ICP-MS is a mass spectrometry technique which is able to detect metals and several non-metals at concentrations as low as one part in 10^{12} (part per trillion). Here, the sample is ionized with inductively coupled plasma and a mass spectrometer is used to separate and quantify the generated ions (Houk et al., 1980; Date and Gray, 1981).

ICP-AES, also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element (Stefansson et al., 2007; Mermet, 2005). The intensity of this emission is a function of the concentration of the element within the sample. Basic steps in AES are: atomization/vaporization of the sample to produce free atomic species (neutrals and ions), excitation of the atoms, detection of the emitted radiation, calibration of the intensity to concentration, determination of the mass of the elements (Miziolek et al., 2006).

ICP-MS and ICP-AES are the most common techniques used today to perform this type of analysis even if they are designed for laboratory measurements and cannot be applied in-situ.

X-ray fluorescence (XRF) has been used for the quantitative analysis of airborne particulate matter, since the 1970s.

In 1972 Hammerle and Pierson developed a new instrument for in situ automatic determination of the concentration of 9 elements (Ca, Ti, V, Mn, Fe, Ni, Zn, Br, Pb) in PM using the same technique which is generally applied for non-automated laboratory measurements (Hammerle et al., 1975). A few years later Greenwood-Smith patented

a device able to automatically sample and analyze lead in air using XRF (US patent No. 4551848, 1985).

More recently, an automated device has been proposed (Cooper et al., 2009) in which a PTFE (Polytetrafluoroethylene) tape is used to collect airborne particulate matter during sampling, and XRF is used for the automatic quantitative analysis, together with an automatic calibration of the measuring device.

Even for quantitative analysis with XRF instruments several methods have been proposed (Vanhoof et al., 2003; Richard et al., 2010). In 1999 the United States Environmental Protection Agency (US-EPA) developed and released a standard methodology for XRF analysis and absolute mass determination described in Compendium Method IO-3.3 (Kellog and Winberry, 1999). In this description absolute mass values are obtained using thin film standards for mass calibration, since they closely resemble a layer of PM on a filter, and considering film surface densities under the XRF irradiated area. PM values are then calculated comparing film standards peak intensities with those of PM filters.

In 2003, some researchers of the Flemish Institute for Technological Research developed a new technique to calibrate an XRF spectrometer for quantitative analysis (Vanhoof et al., 2003). This method involves the load of a multi-element aerosol on a filter by means of an ultrasonic nebulizer, and the measurement of the corresponding XRF spectrum. Each peak intensity of the XRF spectrum is then associated with the quantity of the corresponding element loaded on the filter determined through the ICP-AES analysis. The mass density ($ng\,cm^{-2}$) could be calculated knowing the XRF irradiated area. Similarly, Richard et al. (2010) developed another method for nanogram element quantification using synchrotron radiation as excitation source for XRF analysis. The samples used for calibration were obtained by depositing picoliter droplets of a customized solution via an ink-jet printer on thin films and subsequently measuring absolute mass with ICP-OES measurements performed off-line.

In this paper we describe an XRF measurement and analysis station using an X-ray tube source with Molybdenum target, pure microfiber quartz discs to collect PM,

and a low cost solid state detector with self-cooling Si-PIN. A software procedure has also been developed to automatically analyze XRF spectra and calculate the absolute mass of the chemical species present on the sample, by considering fluorescence peak intensities and comparing them with the reference measurements previously performed
5 with a new mass calibration method.

2 Instrumentation and measurement technique

In order to sample and analyze in situ and in real time PM using X-ray fluorescence from the chemical species layered on a filter, we developed an automatic sampling and measurement station (PM-SMS) capable of performing measurements outdoors in all
10 weather conditions, transferring measured data to a central server in which they will be stored ready to be used. All sampling and measurement parameters can be remotely changed at any time since the instrument is equipped with several networking modules (Wifi, Ethernet, GPRS).

The PM-SMS consists of a pumping system that samples environmental air and col-
15 lects the particulate matter on high purity quartz-microfiber discs (hereafter called filters) such as those produced by Munktell & FILTRAK GmbH. The sampling parameters are configurable and the system has been designed to comply with atmospheric sample standards set by the EU (Directive 2008/50/EC of the European Parliament). After the sampling, the filter containing PM is exposed to an X-ray tube source with Molybde-
20 num target (produced by Oxford Instruments X-Ray Technology, Inc.) and the emitted fluorescence spectrum is measured using a solid state detector with self-cooling Si-PIN produced by Amptek Inc.

To identify chemical species detectable by the system, the measured XRF spectrum of PM present on the filter has to be compared with the atomic K or L shell emission
25 lines (Janssens, 2005), following the procedure described in the EPA Compendium Method IO-3.3 (Kellog and Winberry, 1999).

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Since atmospheric and environmental conditions could influence the behavior of the multichannel analyzer, an energy calibration is performed by determining the correspondence between the analyzer channels and the emission lines of five pure metallic samples of Ti, Cr, Fe, Ni and Zn (see Fig. 1).

5 Calibrated XRF spectra in the form of count rate vs. energy, as shown in Fig. 2, are automatically processed by the analysis software, using the following algorithm: fit of the spectrum of the particulate via a polynomial regression, the Savitzky–Golay smoothing filter (Savitzky and Golay, 1964; Press et al., 1992); subtraction of the background spectrum (the "white") obtained by measuring the X-ray fluorescence spectrum

10 of a clean filter used as reference; deconvolution of this spectrum and automatic identification of the chemical species through the comparison of detected peaks with the corresponding K or L shell emission lines (Janssens, 2005). The software algorithm rejects possible spurious peaks of intensity lower than 2 sigma of the noise value of the spectrum calculated as the square root of the peak counts rate at any given energy

15 value. The final determination of the absolute value of the mass of each element is made through the correlation parameter calculated in the mass calibration procedure (see Sect. 3).

Finally a calculation of the absolute concentration in air of PM is done through the normalization of absolute mass chemical element quantities to the measured value of

20 pumped air volume during the sampling. This volume is corrected, in agreement with EU standards (Directive 2008/50/EC of the European Parliament), taking into account the air density calculated considering the temperature and the humidity recorded during PM sampling.

After the measurement the sample is carefully stored in a storage-box available for

25 further off-line measurements, even with different techniques (i.e. ICP-MS or ICP-AES).

3 Absolute mass calibration procedure

To calibrate the instrument we measured the fluorescence spectra of several samples in which there is present a single chemical species, with a known mass quantity, different on each sample. The measurement of the intensity of the corresponding peak in the fluorescence spectrum is then directly correlated to this mass quantity, which is assumed to be linear in the range of masses that could be detected by the instrument. A simple linear regression gives the correlation parameter, as the slope of the regression line.

Calibrated samples were prepared by depositing, on a polymeric film, known quantities of water solutions containing a salt of the metal to be calibrated. To assure a homogeneous distribution of the solute on the polymeric surface, we treated its surface with a sandblasting process to obtain a micro structured rough surface. Samples with decreasing quantities of chemical species were obtained by diluting saturated solutions, in order to use the tabulated and certified values of the solubility.

Thanks to the rough surface, after water evaporation, the sample results covered by a salt concretion homogenously distribute in a thin film, with a weight of a few micrograms, faithfully representing the real particulate deposited on the quartz filter. This mass calibration procedure is designed to be periodic, in order to take into account possible variations due to the exposure of the PM-SMS to different weather condition (i.e. humidity, temperature), or simply due to wear.

The calibration method described here is similar to that described by Vanhoof et al. (2003) and Richard et al. (2010) since they use chemically prepared samples for mass calibration. The difference comes from the fact that the masses of chemical elements in the calibrated samples are unknown and the comparison with XRF data is performed by means of an external method such as ICP-AES (Vanhoof et al., 2003) or ICP-OES (Richard et al., 2010). A very similar method has been recently developed by Petterson et al. (2009a,b, 2010a,b) and Cooper et al. (2010). For mass calibration, thin film standards are used as described in the EPA Compendium Method IO-3.3 (Kellog

and Winberry, 1999). However, since the mass of the standard is obtained by multiplying thin film density ($\mu g\,cm^{-2}$) by the area illuminated by the X-ray source, a critical issue is its precise determination. In our approach, this problem is overcome since the X-ray beam has a large illuminated area that covers the entire sample deposited on the filter for mass calibration.

In Fig. 3a and b, the results obtained during mass calibration of elements like Calcium, Vanadium, Iron, Cobalt, Nickel, Lead, is presented. These charts show the relationship between mass and counts per hour for the analyzed chemical species, which, in the typical range for airborne particulate samplings, can be approximated by a straight line.

We also verified that the so called matrix effect (Claisse and Quintin, 1967; Giauque, 1994) is negligible. The calibration curves were re-calculated using samples in which we deposited not only the element under calibration (primary element) but adding one or more elements with a higher atomic number, in order to verify whether their fluorescence photons, with enough energy to excite the fluorescence of the primary element, can produce an increase of the count rate corresponding to the primary element mass. Such an alteration was not observed within the experimental errors.

4   Results and discussion

To test the behavior of PM-SMS in standard operating conditions, we positioned one of our prototypes in the park in front of the Elettra-Sincrotrone Trieste laboratory and we activated the environmental monitoring procedure for a period of 60 days, collecting 30 filters of PM sampled for 48 h following standard sampling rules. We randomly selected a part of those collected filters and analyzed them using ICP-AES method by a certified company, Sangalli Protezioni Ambientali s.r.l. (Italy).

In Table 1, we compare XRF results obtained with the PM-SMS in situ automatic procedure with those obtained professionally analyzing the same samples using ICP-AES. The same results are also reported in Fig. 4. PM-SMS gives comparable results

in term of mass values and can reach a precision typically 5–6 times better than the traditional method.

As an additional test, we entered into an agreement with the local environment agency (ARPA-FVG) to complement the traditional measurement stations with PM-SMS, and using the results obtained by ARPA-FVG as a measure of comparison. Two of the locations commonly used by ARPA-FVG for environmental monitoring and pollution control provided with standard sampling PM devices in the surroundings of Trieste (Italy: 45° 39′ 00′′ N, 13° 46′ 40′′ E) were selected and two PM-SMS calibrated prototypes were positioned. The data were collected in 3 measurement campaigns during a period of 6 months (from July to December 2012).

As a validation of the method presented in this paper we can see, in Fig. 5, that our measurements (hereafter called XRF Elettra) agree with the ICP-MS analysis made by ARPA-FVG (its reference method).

5 Conclusion

We developed an automatic environmental station for in situ PM chemical speciation, measuring the fluorescence spectrum obtained irradiating the sample with an X-ray source The results obtained were compared with those obtained with the conventional Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) methods. We demonstrated that this technique gives results comparable to those of the conventional techniques, with a better precision, adding the availability of real time data analysis. Therefore, PM-SMS can be used not only for the scope described in this paper, but can be a valid tool for environmental safety monitoring and real time alarm systems in places where a risk of heavy metal air contamination could be present.

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Table 1. Comparison between the results obtained by measuring airborne particulate deposited on filters with PM-SMS operating in the park in front of Elettra laboratory and the ICP-AES method by a certified laboratory. The sampling time was 48 h per filter and the average pump flux was 38.33 L min^{-1}.

Samples	Elements	PM-SMS				ICP-AES			
		Mass (μg)	Error (μg)	Concentration (μg m^{-3})	Error (μg m^{-3})	Mass (μg)	Error (μg)	Concentration (μg m^{-3})	Error (μg m^{-3})
Sample 1	Ca	12.0	1.4	0.110	0.013	19.8	6.2	0.181	0.057
	Fe	17.9	0.8	0.163	0.007	21.5	5.5	0.197	0.050
Sample 2	Ca	10.9	1.4	0.099	0.013	8.9	2.8	0.081	0.025
	Fe	10.2	0.6	0.093	0.006	10.4	2.7	0.095	0.024
Sample 3	Ca	34.1	2.6	0.312	0.024	33.1	10.3	0.303	0.094
	Fe	23.1	0.9	0.211	0.008	24.4	6.3	0.223	0.057
Sample 4	Ca	42.2	3.1	0.387	0.029	40.3	12.6	0.369	0.115
	Fe	20.4	0.8	0.186	0.007	22.5	5.8	0.206	0.053
Sample 5	Ca	29.5	2.4	0.270	0.022	23.5	7.3	0.215	0.067
	Fe	17.2	0.7	0.158	0.007	20.1	5.2	0.184	0.047
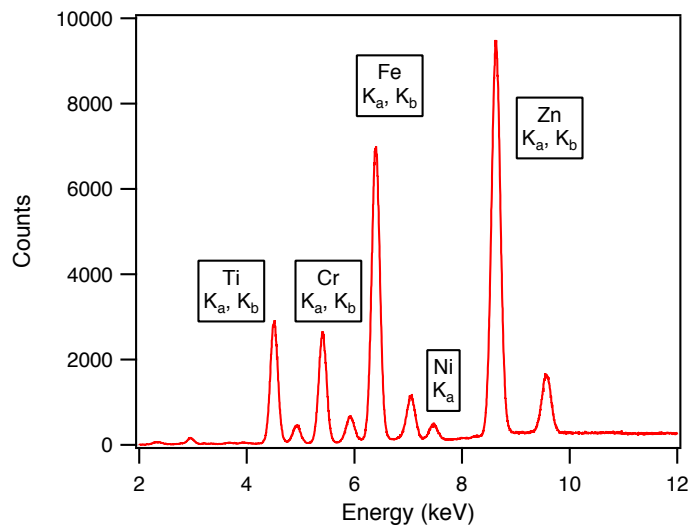
Fig. 1. Spectrum of the energy calibrator. Peak positions of known metals present in the sample are used to calibrate the multichannel analyzer.

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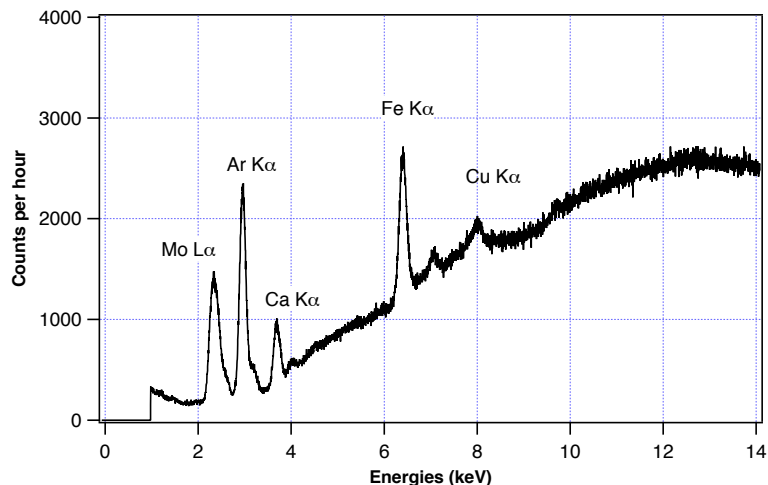
Fig. 2. Fluorescence spectrum obtained during iron mass calibration: molybdenum (Mo Lα) peak comes from the X-ray tube scattered photons; argon (Ar Kα) peak comes from the air, calcium (Ca Kα) and copper (Cu Kα) peaks come from contaminants present in the polymeric filter holder (positioned behind the filter), iron (Fe Kα) peak comes from the element we deposited on the filter.
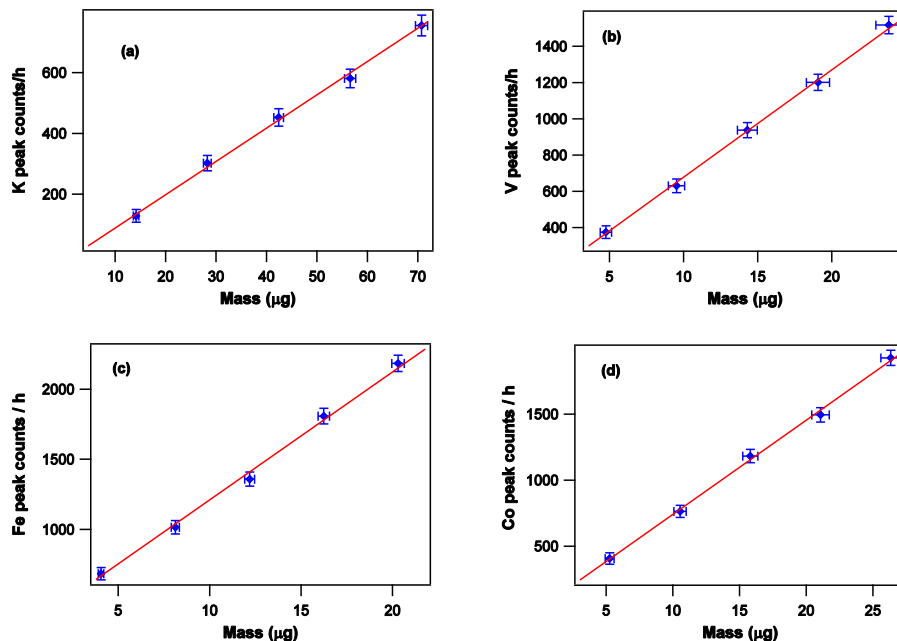
Fig. 3a. Calibration curves obtained for: **(a)** potassium; **(b)** vanadium; **(c)** iron; **(d)** cobalt. In the detection range of PM-SMS, the curves could be approximated by a straight line.

Fig. 3b. Calibration curves obtained for: **(e)** nickel; **(f)** zinc; **(g)** cesium and **(h)** lead. In the detection range of PM-SMS, the curves could be approximated by a straight line.

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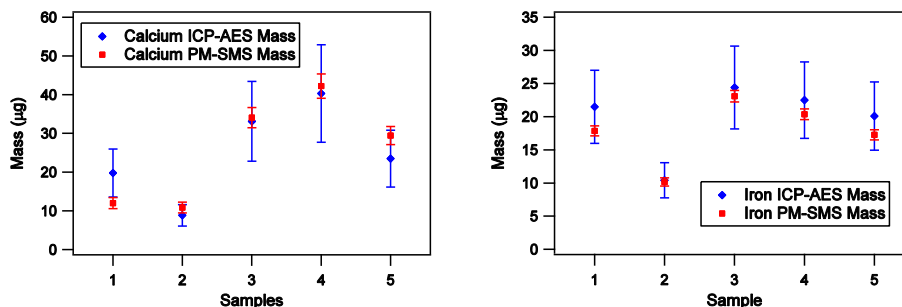
Fig. 4. Comparison between the results obtained by measuring airborne particulate deposited on filters with PM-SMS operating in the park in front of Elettra laboratory and the ICP-AES method by a certified laboratory. The results show that PM-SMS gives comparable results in terms of mass values and can reach a precision typically 5–6 times better than the traditional method.
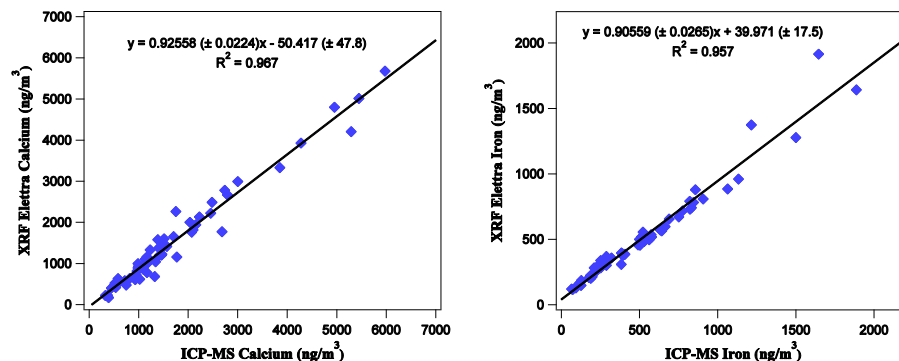
Fig. 5. Comparison between the results obtained measuring airborne particulate at ARPA-FVG sites in Trieste city with PM-SMS and the ICP-MS method (ARPA-FVG reference method) for calcium and iron.