Atmos. Meas. Tech. Discuss., 6, C1845–C1849, 2013
www.atmos-meas-tech-discuss.net/6/C1845/2013/

Atmospheric Measurement Techniques Discussions

Interactive comment on "Quantitative measurement of PM_{10} by means of X-ray fluorescence spectra" *by* E. Busetto et al.

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Received and published: 2 August 2013

We want to sincerely thank Referee #2 for his observations, which gave us the opportunity of better highlight details of our experiment. About the remarks on missing information and precisely:

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Interactive Discussion

Discussion Paper

1 instrument layout, working conditions of the XRF tube, pumping speed, size of the deposition area, Minimum Detection Limits as a function of the sampling time, acquisition time of the XRF spectra, etc, etc.

we agree with the referee and we'll include missing information in the revised version of the manuscript.

In the following you'll find an answer to specific remarks:

2 The Introduction reports a short history of PM elemental analysis techniques with a particular attention to the X-ray Fluorescence approach. The Authors miss to quote several articles on ED-XRF, PIXE and SR-XRF measurements and equipments which have been routinely used in the last years being able to detect all elements above Sodium with quite low MDL and fast and simple calibration techniques by thin standard samples (e.g.: Micromatter, NIST - PM2.5 reference material, etc) and with accuracy of a few %.

In the revised manuscript techniques will be quoted and their performances illustrated. We did not considered those techniques since, to our knowledge; they are not suited for use in the field (ie Synchrotron Radiation XRF) or not easily transferable on field (ie PIXE) for their characteristics.

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3 The PM-SMS equipment adopt quartz fiber filters: this choice should be motivated since it's well known that such membranes are poorly suited for XRF analysis: all the light elements (i.e. from Na to K) cannot be quantified or suffer of huge uncertainty, the membranes often present internal contamination by some metals, etc. Best perfor- mance with XRF analysis are obtained using PTFE (as in one of the articles quoted by the Authors and in many other literature examples) and/or Nuclepore or Polycarbonate Membranes. Reasons for using quartz membranes and consequent limitation should be fully discussed.

Quartz filters are the ones routinely used by the partner that helped us to validate PM-SMS equipment, and we wanted to be completely compliant with their procedures. PTFE or Nuclepore or Polycarbonate Membranes have not been tested yet but the equipment can easily support them.

4 In the first validation example the Authors quote a sampling time of 48 hours... this is a very long time. I could not understand the real performance of the PM- SMS: an on-line instrument, in my opinion, should be able to reach reasonable MDLs in much shorter times, let's say a few hours.

The first campaign of measurement was done not in the EPA areas, but was just a test of both the machine and the procedure. For this reason even if the machine operated following realistic conditions we decided to pump material with many different sampling time, in order to verify also the behaviour of the filters and stress the machine (we also sampled for 72 and 96 hour). For this first test we adopted 48 hour because we wanted to collect significant amount of particulate considering that the Elettra Centre is on the top of an hill, with a good quality of the air.

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5 (by the way the agreement with ICP is globally poor and it is shown for Ca and Fe only, why?)

We presented Ca and Fe as to be considered an example of the method application and results, being the ones more frequently present on the filters. Of course, also the other cited elements where present on the filter, and have been measured and compared as well. In the revised manuscript other elements will be shown.

6 Discussing the mass calibration methodology the Authors consider a problem the lack of information on the exact area of the X-Ray spot: I cannot follow their point since with homogeneous samples (and any kind of homogeneous standard) there is no need to know the area of the portion of the filter hit by X- rays

We agree that if the particulate deposited on sample is uniform and homogeneous, concentrations are independent from the dimension of the x-ray spot. But, if for some reason this is not homogeneous, having a x-ray spot size bigger than the dimension of the area covered by the material ensures that the entire amount of it contributes to the fluorescence and there is no need to take care about homogeneity.

7 Fig. 1 and 2 do not show any real information and should be removed

ok.

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8 In urban pollutes sites most of the elements considered in Fig. 3 can be detected with concentration values ranging from 10 to 100 ng/m3 and, at least with Low Volume Sampler (I presume that for its pumping speed the PM-SMS does fall in this category) can easily results with total loading on filter < 1 ug. So the calibration curves show in Fig. 3 should be extended to lower values. In some plots, the fit is extrapolated well below the lowest measured value and this could not be correct.

In the revised manuscript minimum detection limits will be reported and calibration curves will be extended as well in the case it is needed.

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