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Atmospheric Measurement Techniques
Discussions

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

Anonymous Referee #2

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The manuscript introduces a new instrument for in-situ PM speciation through ED-XRF analysis. As the Authors clarify the same subject is under processing to be patented. I have major concern on the manuscript: I can understand the intention of the Authors to keep confidential details which could damage the patenting procedure however if they want publish a scientific article they must produce all the information which are usually requested in a peer review journal. In my view this is the major problem to be addressed to have a publishable paper. Examples of missing information are: 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.

In addition to the key-comments above I have some further comments/questions:

1)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 %.

2) 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 performance 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.

3) In the first validation example (by the way the agreement with ICP is globally poor and it is shown for Ca and Fe only, why?) 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.

4) 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

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

6) 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 thePM-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.

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