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Atmospheric Measurement Techniques Discussions

Interactive comment on "Elemental composition of ambient aerosols measured with high temporal resolution using an online XRF spectrometer" *by* Markus Furger et al.

Anonymous Referee #2

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The aim of the study is evaluating the operation and the data quality of an online XRF spectrometer (namely Xact 625, which allows obtaining 1-h time resolution elemental concentrations). Daily averaged elemental concentrations are compared with ICP analysis of daily samples. Results are of interest as the use of relatively simple online and high time resolution instrumentation for the measurement of PM composition may be very useful in many situations; and it is thus very important to verify the quality of these instruments.

The study is generally scientifically robust and well written. The comparison with ICP data is correctly carried out, showing both elements with good ICP-Xact agreements and elements that are not well quantified by the spectrometer. However, in my opinion, some criticism (on both the use of this instrument and the comparison method) should be more explicitly quoted and discussed.

It is true that synchrotron-XRF or PIXE require expensive and not-easy-to-obtain accelerator time, but at the same time (if the experiment set up is properly optimized) these techniques allow a very accurate elemental analysis of an high number of samples collected in many sampling sites in very short times, while it is difficult to have many online spectrometer to simultaneously collect the PM in different locations.

For the elements of group A (main PM elements), it is true that the Xact-ICP correlation is very good, but it is not sufficient to say that their concentrations are well reproduced by the spectrometer (as stated in the conclusions and in the abstract). Intercepts arrive up to 40% of the average concentrations (as stated in the paper) and, even if they are not so big, I would not say that they are "small" (pag. 7) or negligible. Deviations of slopes from unit, although, again, not very big, are however significant (Xact/ICP ranging from 1 to 1.8, average 1.28). Possible reasons, like sampling and X-ray absorption, are suggested, but, as the authors themselves state, they are not completely supported/demonstrated by this study. Also they are not always convincing. In particular, X-ray absorption would produce underestimation while Xact concentrations are higher than those obtained by ICP; sampling would produce higher deviations for elements in big particles, while also S slope (1.37) significantly deviates from 1; slope of Zn (1.8) is significantly higher than the others. In this situation, it is not possible to conclude that the spectrometer correctly reproduces the concentrations of all elements of group A and that systematic differences have been attributed to specific reasons (as reported in the conclusion section). Looking at obtained results, I would conclude that correlation is very good (for group A), not big but significant differences are however observed (lower than. . .), possible reasons have been investigated but further studies are needed.

(I think it is important to keep Table 2 and all the panels of Figure 2, but fonts should be bigger as it is difficult to read them as they now are).

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Discussion paper

It is also important noting that the comparison is made on daily averages and the accuracy of hourly concentrations has not been directly tested.

Finally, I have some comment on the description of the spectrometer (section 2.3). There are in my opinion important pieces of information that are not reported and that would be very useful: sampling area, irradiated area and X-ray detector used (including entrance window and collimation size). Minimum detection limits reported in Table 1 seam very small for 1-h sampling. Uncertainties are surely much higher that 5% for concentrations close to MDLs.

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