

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 #3

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The paper describes the outcomes of a field test to verify the performance of a quasi on-line XRF system (Xact 625) in the measurement of the elemental composition of PM. The data produced by the Xact system are compared with off-line standard analyses on PM collected on filters sampled by other samplers deployed in the same site. These kind of comparison are always interesting and I think that the paper deserves the publication even if several corrections/improvements are necessary. I have how main issues and a series of punctual comments:

Issue 1: in the discussion of the level of agreement between the Xact 625 results with the other standard techniques, the Authors consider that some differences could be due the use of different sampling devices placed not exactly in the same position. My

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question is: why the substrates used in the Xact625 have not been analyzed off-line by other techniques ? This would have removed any possible ambiguity related to different amount of sampled material...I have not found in the text any comment on this possibility. I consider a detailed discussion on this point absolutely necessary.

Issue2: the Authors discuss quite in deep the differences in the PM composition in the two periods (with and without fireworks) of the campaign. I do not find in such discussion any new or general element which could deserve to stay in the text. I think that this falls outside the main focus of the paper and that most of this discussion should be moved to the on-line supplementary material (or maybe it should find space in some local report). On this point, see the punctual comments below

Punctual comments: Abstract, line 17: the wording “Xact PM10 mass” could be misleading since by ED-XRF just a small fraction of the elements presents in PM10 can be detected. I recommend to use “the total concentration of the elements detected by Xact in PM10” Abstract, line 19: Begin the statement with “Ten” instead of “10” Introduction, line 38: replace “historically required” with “require” Introduction, line 39: This is not true: there are well known methods (e.g.: streaker sampler + PIXE, DRUM impactor + SXRF) which provide hourly or even sub-hourly time resolution with very low MDL. The statement must be changed accordingly. Page 2, line 3: replace “similar X ray facility” with “accelerator facilities” Page 2, line 5: delete “overwhelming” Page 2, line 10: the advantages offered by high time resolution have been discussed in literature well before the “older” reference given in the list. . .to my memory come some papers dating back to the eighties and I think that the Authors should be more precise on this point. Two reference papers are: Annegarn et al., Source profiles by unique ratios (SPUR) analysis: Determination of source profiles from receptor-site streaker samples. Atmos. Env. 26, 1992 D’Alessandro et al., Hourly elemental composition and sources identification of fine and coarse PM10 particulate matter in four Italian towns. JAS 34, 2002

Page 3, line 37-38: a list of element detectable by Xact is reported with the explanation

that the system sensitivity has been determined for each element by a reference sample. Actually, there are in the list couples of elements which interfere in a X-ray analysis (Fe-Co, Pb-As, Ba-Ti) and I really wonder that, for instance, Co and As can be safely detected in ambient aerosol (usually much richer in Fe and Pb). I have not found in the text any comment of this point. I think that the calibration procedure should be better described including a discussion on these possible interferences. This impacts on the data summarized in Table 1 too.

Page 4, first lines: the procedure to determine the MDL takes into account the spectrum collected in a blank portion of the filter. This way the MDL get underestimated since, in each portion of the spectrum, the continuum is not due to the filter only but also to the tails of all the peaks due to the PM elements. Moreover, this method completely not consider the interferences discussed above. More realistic MDL values should be given for each element and a given sampling/analysis time in a dedicated table but should be calculated as an average of PM samples.

Page 8, Par 3.3: the whole section with related figures should move to the supplementary material Pag. 11, line 9-14: the origin of possible discrepancy have not been clearly identified and the wording “are attributed” is not correct and should be replaced by “could be attributed”

Pag. 11, line 25-31: these lines should be removed from the conclusions. . .they are of very local interest and more than a conclusion are just a summary of the findings
Figure 1: the plot in the top panel should be shown in log. Scale: the present picture is not so informative
Figure 2: the number of digits in the value of the a and b coeff. is too high (i.e. show just significant digit). The values of the correlation coeff. Should be added in each plot.
Figure 3: In my opinion the right part of the picture (from V on) does not give any information and should be deleted
Figure 5: the fit of the red points is more or less meaningless. . .please add the R2 values in the plot both for blue and red points
Table 2: should be deleted by inserting the R2 values in the plot of fig. 2

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