

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

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(Referee’s statements in italics)

The authors would like to thank the referee for thoughtful reading and critical commenting of the manuscript.

*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.*

We add a statement on other possible sampling techniques and their benefit (see also

remark further down).

We add a reference to Yatkin et al. (2012) and (2016).

“The NABEL network provided the reference for previous data intercomparisons (Hueglin et al., 2005; Lanz et al., 2010), as well as for the intercomparisons of this study. Comparisons between SR-XRF and filter samples analysed with ICP-OES and ICP-MS have been performed previously (Richard et al., 2010). Comparisons of XRF on samples collected on different substrates were performed, e.g., by Yatkin et al. (2012). A recent interlaboratory comparison of PM10 filter analysis methods is presented in Yatkin et al. (2016), where XRF/PIXE and ICP methods were compared for several metrics. Some of these metrics are also applied in this study.”

We added a remark on the regression analyses in Section 3.1:

“The regression intercepts were not forced to be zero to enable examination of potential differences in the measurement accuracy of each of the compared methods, e.g. blank subtraction. The slopes are more relevant and indicate biases between the methods. Orthogonal least squares regressions metrics were calculated which incorporates measurement errors in both quantities being compared. The slopes differed by less than 3.5 % between the two regression methods for the Group A elements. Ba and Pb achieved an almost perfect match with slopes around 1 and negligible intercepts. The other extreme is Zn with a slope of 1.8. Ti is another peculiar case with a slope of 1.13 and the largest intercept/average concentration ratio of 0.37. On average, the Xact 625 yielded approximately 28 % higher elemental concentrations than ICP for the Group A elements.”

We added the statement in the last paragraph of the conclusions:

“Xact streamlines near-real time monitoring of multi-metals despite not being as cost effective relative to conventional samplers that could be deployed in larger numbers at many sites simultaneously, or that could sample several size fractions at once, although

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their actual analysis costs (laboratories, accelerator facilities and staffing needs) are not considered here and they may surmount the instrument costs manifold.”

*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 a 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.*

True. We have added two statements covering these aspects in the introduction:

“Access restrictions limit the number of collected samples to be analysed, and hence field campaigns are predominantly episodic.”

“Instruments of this type can be used for continuous (months, years) monitoring at a site, but their cost restricts the simultaneous deployment of a larger number of devices for different size fractions or at different sites. The benefit of long-term, quasi real time data access, favourable, e.g., for air quality monitoring, contrasts with the possibilities of relatively low cost, multi-site and multi-size samplers used so far in episodic field studies.”

*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 el-*

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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.

Agreed. We have changed our concluding statement to:

“Excellent correlation between Xact 625 and ICP-OES/ICP-MS was observed for 24-h averages of the elements S, K, Ca, Ti, Mn, Fe, Cu, Zn, Ba, and Pb (“Group A”). The daily averages calculated from hourly measurements by Xact were on average 30 % higher (range -4 % to +80 %, dependent on elements) than 24-h integrated filter measurements by ICP. . . . Further research on these issues is 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.*

We have rearranged Table 1 by moving the MDL part to Table 2 and the remainder of Table 1 to the supplement which now only contains statistics of the complete Xact dataset. We have also redrawn Figure 2 completely and have replaced Figure 3 with a new one showing the interference free MDLs of Xact and ICP MDLs as well as the slopes (with standard deviations) and the ratios of the intercept with the average concentrations for each element. In this way, complete information on all intercomparison data is presented in graphical and tabular form for quick reference. See response to referee 2.

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

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It is true that the hourly concentrations have not been compared to ICP data at their original time resolution, since the ICP data are only available with 24-h time resolution, and we included text in the manuscript stating this limitation. Nevertheless, while indeed the emphasis is on the intercomparison of 24-h averages of filters and Xact, hourly S data from Xact have been compared with PM1 SO<sub>4</sub> collected with the ACSM (Figure 5). On the other hand, the estimated mass budget in Section 3.3 is also based on hourly data (2 h interval for the Xact, 3 h interval for the TEOM, to capture the full peak period with high concentrations). Fig. 4 shows hourly resolved time series of Xact, TEOM and ACSM data.

We insert the following statement at line 29 of Section 2.6:

“Comparisons of hourly Xact data were only possible for S with the ACSM data (in the form of PM1 sulphate, assuming that all S occurs in PM1), and between the total Xact element mass and PM10 of the NABEL TEOM instrument, see Sections 3.2 and 3.3.”

And in the conclusions we added:

“The accuracy of hourly values has only been tested for the case of the fireworks peak late on 1 August 2015, where the sum of all elements has been compared to the total mass of the NABEL TEOM. Good agreement between the Xact and TEOM mass was found when corrections derived from the 24-h filter analyses were applied. This was a special case dominated by just three elements, S, K, Cl, and a generalization to all measured elements is not recommended.”

*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).*

True. However, having such proprietary information published is of severe concern for CES due to potential competition with other manufactures. Furthermore, we do believe

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that removal of such information is consistent with discussion of other methodologies (for example, most journal papers focused on ambient data from say, ICP-MS do not provide details of the liquid impingers or cones being used). We checked to ensure that the data interpretation is indeed not impacted by elimination of such details.

*Minimum detection limits reported in Table 1 seem very small for 1-h sampling.*

The reported MDLs are interference-free MDLs at the 1-sigma confidence level for un-sampled tape (see reference Currie 1977 in the manuscript). These MDLs give an estimate on the minimum detectable mass for pure elements, i.e. for single element standards, hence they represent the achievable minimum of detection under ideal conditions. MDLs in a multi-element sample are expected to be higher, depending on sample composition and concentration, but they would have to be reported individually for each measurement. No such routine is presently implemented in the Xact. MDLs decrease with increasing sampling time.

“XRF based MDLs are inversely proportional to the square root of the X-ray analysis time (Currie, 1977), which in the case of Xact is same as the sampling duration. Hence, Xact MDLs are lower for longer sampling durations. Interference free MDLs, while true are idealized lower limits of detection of one single element. As with most analytical methods, matrix effects in ambient samples from interferences between different elements and analyte concentrations could potentially result in MDLs of ambient samples to be higher and vary across samples, which makes them difficult to generalize and report. It is therefore often preferred to report measurement uncertainties to characterize a measurement. ”

*Uncertainties are surely much higher than 5 % for concentrations close to MDLs.*

Agreed. We changed the wording from ‘may be higher’ to ‘are higher’ (p 4, line 14):

“An uncertainty of 5 % or less due to fitting errors and uncertainties in the standards has been derived from laboratory experiments with NIST standards (benchtop XRF,

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filter analyses). Uncertainties are expected to be higher for concentrations close to the MDL; for elements with potential for line interferences in multi-element samples; and, from self absorption effects for lightest elements (Si, S, Cl, K, Ca)."

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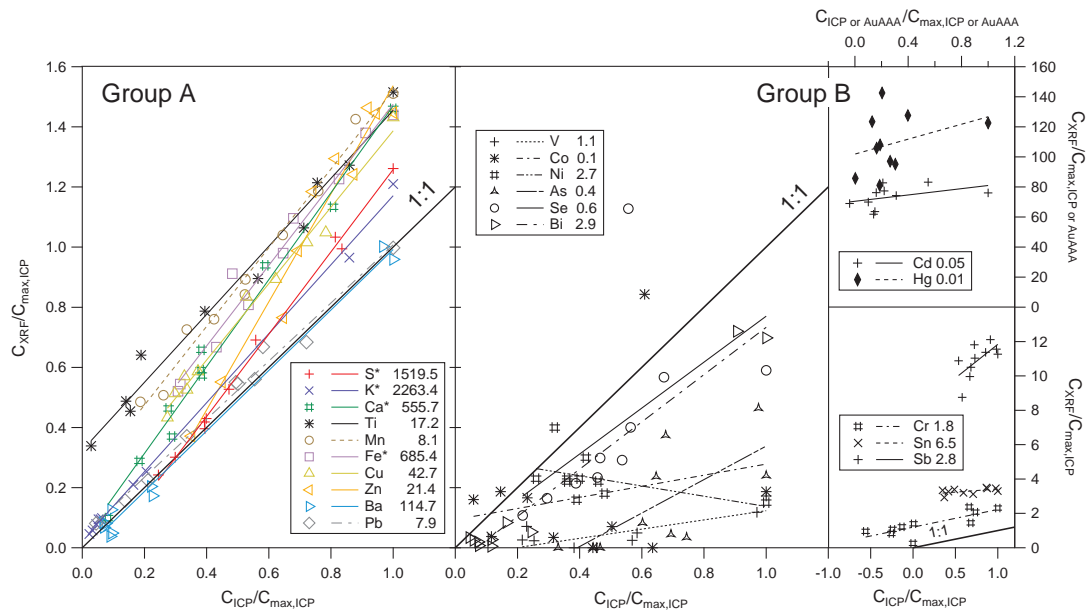


Fig. 1. New Figure 2.

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