

Interactive comment on “Field and laboratory evaluation of a high time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols” by Anja H. Tremper et al.

Anja H. Tremper et al.

anja.tremper@kcl.ac.uk

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Please find below the author's response to the interactive discussion comments from the anonymous referee.

Referee comments: RC

Author's response given below individual referee comments

RC - General The manuscript presents a comprehensive lab and field evaluation of the

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CES Xact 625 XRF spectrometer. Various alternative methods with different time resolutions and particle sizes are compared with the XRF measurements, with generally good agreement to XRF and between methods. Explanations for deviations are given. The manuscript adds to the literature on quality assessment of the Xact online spectrometer, an instrument with great potential for monitoring environmental metals and other elements in airborne particles. The study is more comprehensive than previous studies that compare those methods, although some questions with Xact data quality remain. The structure of the manuscript, the results and the presentation of the material are good. The data has been analyzed and presented with care. The language is impeccable. The topic is relevant and well worth publication in AMT.

Author's response: We would like to thank the anonymous referee for the positive feedback and the suggestions to our manuscript. Please find the answers to the individual comments below.

RC - Major comments The study describes intercomparisons of time series of metal concentrations measured with the Xact and with other techniques. The statistical work horse is Deming regression which assigns individual measurement uncertainties to each technique. This approach is straightforward and has been applied in other studies. Comparisons are made between Xact and ICP-MS (with different digestions), ACSM, URG, and XRF (measuring filters with the Xact itself). Data were collected in field studies and in laboratory experiments. The field studies show good regressions with a slightly positive bias of the Xact vs. ICP-MS, in agreement with previous studies. It is nicely demonstrated that the slope depends on the digestion method used for ICP-MS, and an overestimation of the XRF values compared to the ICP-MS values may turn into an underestimation when using the other digestion method. This makes a generalization of regression results (which technique is best or better?) rather difficult. Comparisons with ACSM and URG suffer from the different size classes sampled (PM_{2.5}, PM₁) and the different particle characteristics (non-sea salt, non-refractory). A comparison then requires additional assumptions to bring the values into closer agree-

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ment. This is discussed by the authors, but it also makes the comparisons more qualitative than quantitative. Interesting is the comparison between Xact measurements and filters analyzed with the Xact (Table S1). Slopes ranging from 0.8 to 1.85 with R^2 values > 0.9 (excluding the extreme cases of As and Se) might indicate more serious issues with the calibration of the Xact or with the spectral deconvolution algorithm, even though the number of samples is only 12, and slopes of 1.31 (Ba) and 1.62 (V) are not significantly different from unity, according to the authors. Here I would like some comment from the authors.

Author's response: The authors do not believe that the differences in slope indicate an issue with the calibration of the XACT. The reasons for the discrepancies can more likely be found due to the small sample size of this pilot study, the authors feel that the analysis method, including filter substrate and punching technique could be optimized. Nevertheless, every effort was made to make this as robust as possible - blank filters were analysed and used to correct for the filter background and to calculate the limit of detection when the XACT was used with filters on a 15 min analysis cycle. In comparison to the online XACT measurements which were made on an hourly basis, the LOD of the filter method was much higher. This was likely due to the shorter analysis time, the different area of deposit on a filter sample and the filter material (Zeflour has a density of around 16 mg cm⁻² whereas our filter tape has a density of about 2 mg cm⁻²; the mass density of the filter material will impact the XRF detection limit by the ratio of the square root of the mass density. Further the fitting routine in the deconvolution software is optimised for the filter tape used and is another potential area of optimisation if this approach were to be pursued.

To make this clearer in the manuscript we have added the following to the "Materials and Methods" section 2.4 (P7L30):

"For quality assurance purposes, field and laboratory filter blanks were analysed and used to correct for the filter background. The blank measurements were also used to calculate the limit of detection for this method."

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We have also expanded the results section 3.3 (P12L18) to include the above discussion:

"Reasons for the discrepancies in the slopes may be caused by the difference between the filter material and analysis time used for the filter samples (Zeflour, 15 min) in comparison to the online method (proprietary PTFE tape, 1 hr). Additionally the fitting routine used in the deconvolution software is optimised for the filter tape used and might also contribute to the observed differences."

We have further added a comment in the conclusions section 4 (13L18): "Further, to develop the filter analysis method using the XACT and piloted in this study, different filter materials should be tested and the deconvolution approach optimised if necessary."

RC - The laboratory experiment regressions in Fig. S2 show very good agreement between Xact and TEOM, except for some outliers for S. The concentration maxima are extremely high compared to typical ambient concentrations. Except Zn, all elements should be prone to self-absorption effects in XRF analysis when the deposited layer becomes too thick, but no such effect can be seen in the regressions. Are self-absorption effects so well compensated by the Xact software? It would be helpful to add information on particle sizes (as measured with the SMPS) and/or deposit thickness to understand why XRF self-absorption effects do not show up in the graphs.

Author's response: Sample self absorption depends mostly on the thickness of the deposit and its composition and even at these high concentration levels sample absorption effects contribute a relatively small amount to the overall analysis result. Sample self absorption was calculated for S and even at the highest concentration self absorption effects are less than 1%. Please also see response to referee 5.

Nevertheless the authors have changed the sentence in section 3.1: "All calibrations resulted in a linear relationship between the mass calculated using TEOM mass concentrations and measured by the XACT for the standard range used."

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It now reads (P8L32): “All calibrations resulted in a linear relationship between the mass calculated using TEOM mass concentrations and measured by the XACT for the standard range used. Sample self absorption effects were calculated to be <1% for the maximum concentration of S (the lightest element used) and therefore insignificant in the use of this instrument.”

Minor comments RC - P7L1: Middlebrook instead of Middlebook

Author's response: The spelling of “Middlebrook” has been corrected on P7L4: “The collection efficiency was calculated using the Middlebrook parameterisation (Middlebrook et al., 2012). . .”

RC - P7L34-36: Strange sentence.

Author's response: Changed the sentence “Including values below the LOD had the advantage of being able to include daily XACT mean concentration was calculated from hourly concentrations that might have been lost if data below LOD was excluded and the daily data capture was not met.”

to (P8L3) “By including values below the LOD it was possible to calculate daily XACT mean concentrations, which might have been lost if data below the LOD had been excluded and the daily data capture had not been met.”

RC - P8L11: remove one ‘.’ after Table 3.

Author's response: Removed the duplicated “.” On P8L18 “. . .; these are shown in Table 3. For the ACSM. . .”

RC - P12L7: remove one ‘.’ after filter measurements.

Author's response: Removed the duplicated “.” On P12L18 “. . .resulted in higher results than off-line filter measurements.”

RC - P21 Table 7: Check the arrangement of rows carefully.

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Author's response: Formatted Table 7 on P22 using Font “Times New Roman” and Font Size 8 as used in the other tables; this corrected the formatting problem.

RC - P17 Fig. 7 and Figs. S3-S5: It might make the graphs more consistent when the coloring of all figures were in agreement. I suggest to color the dots in the Figures S3-S5 in red (HF/HClO₄), and blue (HNO₃/H₂O₂), to correspond to the colors in Fig. 7.

Author's response: To avoid confusion with the different colouring, the authors decided to keep the colouring of Fig. 7 as it is, but change Figs. S3-S5 and S7 to use black dots for all graphs.

Please also note the supplement to this comment:

<https://www.atmos-meas-tech-discuss.net/amt-2017-363/amt-2017-363-AC1-supplement.pdf>

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-363, 2017.

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