

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.

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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 - The paper refers to a very important issue in the characterization of an aerosol

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sampling/analyzing device, namely, its analytical accuracy. Therefore, the work is relevant. There is a careful design of the methods used to validate the quantitative results. They are carefully explained and presented. It is remarkable that several analytical techniques are used to carry out the comparisons. I could find no scientific errors or misleading discussions. The conclusions actually point out to the results obtained in the text. Also, proposals to extend (and improve) the results are given. In short, I consider the paper should be accepted for publication. Nevertheless, I would like to suggest a few (minor) corrections and additions.

Author's response: We would like to thank the anonymous referee for the very positive feedback and the suggestions to our manuscript. Please find the answers to the individual comments below. The original comments are written in black and the author's reply and changes to the manuscript are coloured in blue/green, respectively.

RC - 1. In section 2.1, I recommend adding a few lines mentioning the x-ray source and its operating conditions employed, as well as the detector type and characteristics (resolution, in particular). This may help the reader to better understand the results given in this manuscript. Also, the software and atomic databases used to analyze the x-ray spectra.

Author's response: The authors have added further information on the XRF analysis to section 2.1. to help the reader understand the results.

The section has changed from: "The instrument measures 24 elements between Silicon and Uranium at a time resolution between 15 minutes and four hours using ED-XRF. The size fraction of the PM sample collected onto the Teflon filter tape depends on the size selective inlet chosen. The instrument samples with a volumetric flow rate of 1 m³ h⁻¹ through an inlet tube heated to 45 °C when the ambient relative humidity (RH) exceeds 45% to avoid water depositing on the tape. Sampling and analysis is performed continuously and simultaneously, except for the time required to advance the filter tape (≈20 s) from the sample to the analysis position. Daily automated qual-

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ity assurance checks are performed every night at midnight and consist of an energy alignment (an energy calibration using a copper rod, inserted into the analysis area); and upscale measurement to monitor the stability of the instrument response (for Cd, Cr and Pb); and a flow check through an independent mass flow sensor. Additional quality assurance checks employed here included flow calibrations, regular external standard checks, field blanks performed using a HEPA filter as well as tape blanks before and after each tape change.”

It now reads (added text is underlined, P4L30 onwards): “The instrument measures 24 elements between Silicon and Uranium at a time resolution between 15 minutes and four hours using ED-XRF. The size fraction of the PM sample collected onto the Teflon filter tape depends on the size selective inlet chosen. The instrument samples with a volumetric flow rate of 1 m³ h⁻¹ through an inlet tube heated to 45 °C when the ambient relative humidity (RH) exceeds 45% to avoid water depositing on the tape. Sampling and analysis is performed continuously and simultaneously, except for the time required to advance the filter tape (approximately 20 s) from the sample to the analysis position. During the analysis, the sample is excited using an x-ray source (Rhodium anode, 50 kV, 50 Watt) in three successive energy conditions, which target three different suites of elements. The resulting x-ray fluorescence is measured with a silicon drift detector and the spectra are analysed using a proprietary spectral analysis package which takes into account all peaks associated with a given element. Daily automated quality assurance checks are performed every night at midnight and consist of an energy alignment (an energy calibration using a copper rod, inserted into the analysis area); and upscale measurement to monitor the stability of the instrument response (for Cd, Cr and Pb); and a flow check through an independent mass flow sensor. Additional quality assurance checks employed here included flow calibrations, regular external standard checks, field blanks performed using a HEPA filter as well as tape blanks before and after each tape change.”

RC - 2. The aforementioned information might be useful to understand several of the

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apparently incorrect results, like the As overestimation. For instance, the As Kalpha x-ray peak overlaps the Pb Lalpha peak. Therefore, it is very important to carefully integrate and correct both peaks using the corresponding beta lines. This may be the reason of the extremely high overestimation in the measured As concentrations. Although it is not explained in depth, Se is another element with possible problems in quantification (see Fig. S7).

Author's response: The authors added text relating to the spectral peak fitting process, which takes into account all peaks associated with a given element, in the answer to the comment above. Further the equipment supplier has made us aware of a US-EPA verification report (US-EPA, 2012) which analysed Se and found an excellent agreement ($R^2 = 0.926$) and a brief summary of this has been added to the introduction Thus the paragraph was changed from: "Despite these limitations, the XACT is unique in measuring elements automatically using energy dispersive XRF (ED-XRF) and has been successfully evaluated in a number of field studies (Furger et al., 2017; Park et al., 2014). Park et al. (2014) found..."

It now reads (P3L33 onwards): "Despite these limitations, the XACT is unique in measuring elements automatically using energy dispersive XRF (ED-XRF) and has been successfully evaluated in a number of field studies (Furger et al., 2017; Park et al., 2014; US-EPA, 2012). In a verification test carried out by the US-EPA (2012) measurements of Ca, Cu, Mn, Pb, Se and Zn by the XACT were compared to filter based measurements (filters analysed using ICP-MS). This verification test showed that the daily average Xact 625 results were highly correlated and in close quantitative agreement with ICP-MS analysis results for the six metals, except Cu, which was close to the detection limit in many cases. Park et al. (2014) found..." The reference was added to the reference list: "US-EPA: Environmental Technology Verification Report. Cooper Environmental Services LLC Xact 625 Particulate Metals Monitor, Report no. EPA/600/R-12/680. Agency, U. S. E. P. A. (Ed.), U.S. Environmental Protection Agency, Cincinnati, OH 45268, 2012."

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RC - 3. The plots in Figs. 2 and 6 need a larger lettering to facilitate reading. Moreover, instead of using thousands of nanograms, possibly using micrograms is easier.

Author's response: Increased the overall figure size of Figs. 2 and 6 to facilitate reading as increasing the font size of the equations would have interfered with the lines/graph, especially in Fig.6. For consistency throughout the manuscript it was decided to keep m-3 for all graphs and tables.

RC - 4. Only as minor but important corrections in writing style, expressions like the one given in page 6, line 13, "75-650 nm" must be written as "75 nm to 650 nm," according to the International System style rules (please, read the official document in the IBPM web site). This must be corrected in all the manuscript. Similar changes must be made when writing quantities (like those in page 6, lines 35 and 38), where a space between the numerical value and unit symbol is missing.

Author's response: Changed the manuscripts according to the International System of Units rules.

RC - 5. Also referring to the official document of the SI, the units "ppb" must be avoided, because of the different meaning of "billion" in diverse countries and languages.

Author's response: Changed "(18.2 M Ω , TOC < 5 ppb, PURELAB[®] Ultra Analytic, ELGA (Veolia Water Technologies))" to (P5L16): "(18.2 M Ω , TOC < 5 μ g L-1, PURELAB[®] Ultra Analytic, ELGA (Veolia Water Technologies))."

Please also note the supplement to this comment:

<https://www.atmos-meas-tech-discuss.net/amt-2017-363/amt-2017-363-AC2-supplement.pdf>

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

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