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Atmospheric Measurement Techniques Discussions

Interactive comment on "Chromatography related performance of the Monitor for AeRosols and GAses in ambient air (MARGA): laboratory and field based evaluation" *by* Xi Chen et al.

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Response to Anonymous Referee #1

Comment: In this paper accuracy and precision associated with processing of the MARGA instrument chromatograms was studied. The results of the MARGA automated software were compared with the results of the chromatograms corrected using Chromeleon software (Dionex). A systematic bias was found especially at low concentrations. The authors should take into account: 1. Especially the chromatograms of low concentration samples should always be manually checked and reprocessed. The normal procedure is not (or at least shall not be) just trusting the results of automated

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integration. Therefore, I can't find the point, why just the "not-so-well" automatically integrated results (without any other manual peak integration adjustment) were compared with the off-line system. My opinion is that you should use (or at least add) the results found after the best possible off-line MargaTools-correction. Especially, for blank-results, it is questionable to use the chromatograms without checking, because depending on the parameters used, baseline noise can be considered as real peaks.

Response: This is a valid point and warrants clarification of our approach. Our analysis of accuracy in section 3.2 was based on comparison of results generated with the offline MARGA tool (single point LiBr internal standard calibration) to the same chromatograms reprocessed with Chromeleon software (multi-point external standard calibration). For this comparison, periods of instrument malfunction, peaks which were misintegrated, and peaks in which the LiBr internal standard concentration was outside $\pm$10% of the nominal target concentration were excluded from the comparison. This filtering procedure would include low concentrations in which there was an obvious problem with the original peak integration. The results presented in section 3.2 therefore do represent the best possible results from the MARGA tool. The first paragraph of Section 3.2.1, beginning at line 314, has been modified to clarify our analysis. "Chromatograms reprocessed by the MARGA tool were individually examined and concentrations were filtered for periods of instrument malfunction, peak misintegration, and LiBr internal standard outside $\pm$10% of the nominal target concentration. This filtering procedure would include low concentrations in which there was an obvious problem with the original peak integration. Filtered data were not included in the comparison between the MARGA tool and Chromeleon. Table S3 presents the percentage of data excluded from the comparison."

We now also clarify that the laboratory comparison of standards and method detection limits also excludes peaks in which obvious misintegration by the MARGA tool was observed. The following sentence has been added to Section 3.1 line 249: "Peaks that were obviously misintegrated by the MARGA tool were not included in this analysis."

Comment: For measuring low concentrations the LiBr internal standard used in this study is quite high (320 ug/l Li and 3680 ug/l Br) and could be at least half of that. The external standards you used should were much lower. You get more bias, if the concentration of the ITSD is much higher than the measured concentrations.

Response: The LiBr internal standard concentrations (320 ug/L Li+ and 3680 ug/l Br-) are recommended by the MARGA manufacturer. We recommend calibrating with a range of external standards appropriate for ambient concentration levels at a particular sampling site to avoid or reduce the bias that may be introduced by relying solely on the internal LiBr standard.

Comment: For low concentrations it is better to use a concentration column. The loop size used was not mentioned in the text.

Response: The loop size information is now included in the text under section 2.1 line 121.

Comment: p. 6 r. 160 : : : MargaTool: : : peak search sensitivity and peak search smoothing: : :are applied to all chromatograms. – Yes, BUT you can select the chromatograms you want to reprocess and use different parameters to each chromatogram. If you want to use different integrating parameters for the first peaks of one chromatogram and different ones for the last ones, then you have to save them separate files. Like File_A for Chloride and File_B for nitrate and sulphate. That is not so handy and it really is time-consuming, I agree.

Response: We agree. Batch re-integration using the MARGA tool is inflexible and time-consuming.

Comment: p. 9 r. 264 : : : the detection limits: : :evaluated here are large than in Rumsey and Walker (2016): : : I honestly hope that Rumsey and Walker did reanalyze the chromatograms, without doing that the detection limits will be quite high. And the detection limits vary also depending on the purity of the system and the column used.

Response: Yes, the chromatograms were evaluated in Rumsey and Walker (2016) using the MARGA tool with peak search sensitivity and smoothing, similar to what the reviewer described above.

Comment: There would be more benefit of the article for the MARGA community, if you would also tell, what kind of Java script you used for reformatting MARGA raw data.

Response: We now indicate in the acknowledgements that the Java scripts used are available upon request (line 595). We are happy to share them.

Comment: You could also make a list of the changes that could be done to make the MargaTools better.

Response: A list of recommendations for improving MARGA data quality is now included in the conclusions section (from line 577):

"...we make the following recommendations for controlling accuracy: 1. do not rely solely on the LiBr internal standard to ensure accuracy of the chromatographic analysis, 2. calibrate with multi-point curves using external liquid standards, 3. use a range of external standards appropriate for expected ambient concentration levels and for resolving potential non-linearity in detector response at low concentrations."

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