Author's response letter – amt-2020-357
"Bromine Speciation in Volcanic Plumes: New in-situ Derivatization LC-MS Method for the Determination of Gaseous Hydrogen Bromide by Gas Diffusion Denuder Sampling"
by Gutmann et al.

Report #1 - Response to questions and comments from Reviewer #4

The manuscript has been greatly improved. Only some minor comments should be addressed before publication.

We thank the reviewer for the time to review this manuscript and the suggestions for improvement.

1. Line 24 "HBr concentrations in the range between 0.44 and 2.27 ppb were measured", but as shown in Table 4, this value ranges from 0.44 to 1.97 ppb.

The value in the abstract has been corrected.

The denuder sampling setup was applied in the plume of Masaya (Nicaragua) in 2016. HBr concentrations in the range between 0.44 and 1.97 ppb were measured with limits of detection and quantification below 0.1 and 0.3 ppb respectively.

2. Figure S6 is not mentioned in the manuscript.

A reference to S6 has been added to the manuscript.

Under these conditions, EP eluted at 7.9 min retention time, however, with relatively broad peak widths due to the high concentration of the coating material in the concentrated samples. 5-chloro-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline eluted at retention time 20.5 min. In the field samples, the peak widths increased and retention times changed, probably due to overloading of the column. EPBr eluted at retention time 27.2 min. Depending on the amount of coating material and chloro-derivative, the retention time varied between 25 and 28 min. The internal standard neocuproine eluted at retention time 32.4 min (Fig. S5 and S6).

3. Line 273 Keep the same unit for EPBr with Figure S7.

The units were converted accordingly.

The influence of abundant EP on the EPBr determination was investigated by a test series with 450 mmol/L EP (corresponds to EP concentrations in concentrated denuder samples) and EPBr concentrations in the range of 19 to 263 nmol/ml (n = 6, Fig. S7).

Report #2 - Response to questions and comments from Reviewer #3

The Authors have made substantial changes and these have dramatically raised the quality of this work! Such comprehensive responses and high quality additions to a manuscript certainly required a lot of effort. The extensiveness of the response to the Reviewers is an uncommon demonstration of dedication by these scientists to highly rigorous work. The resulting manuscript is well within the scope of Atmospheric Measurement Techniques and is suitable for publication. Thank you for the pleasure of this!

We thank the reviewer for the interest on our manuscript and for recognizing our efforts.

One extremely small issue remains in the revised manuscript, that would be worth clarifying is:

The authors state that matrix effects do not exist and that is not technically true. There is a matrix effect in the method that impacts the retention of the analytes, but not the ability of the method to quantify the reaction product. This is because the mass spectrometer detects their unique mass fragments and when coupled with the internal standard it makes taking the matrix effects into account possible with very little error. If the authors could rephrase this, it would be more accurate.

That is true. We have improved the wording.

We determined a relative deviation between the two sample types of 2%. We concluded that due to the detection of individual mass fragments by the mass spectrometer and internal standard adjustment, the ability of the method to quantify the reaction product is maintained even with EP-matrix.