

Interactive comment on “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 Alexandra Gutmann et al.

Anonymous Referee #1

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The paper by Gutmann et al describes the evaluation and field deployment of a new technique to measure HBr in volcanic plumes via denuder sampling and subsequent analysis by LC-MS. Given the current reliance on BrO measurements obtained via remote sensing to characterize halogen chemistry in these plumes, the development of methods to measure HBr represents an important contribution to the field. While the manuscript would be improved greatly by a characterization of the sensitivity and dynamic range of this technique, the authors do demonstrate the technique is selective for HBr and that the fraction of HBr/(Total Bromine) can be obtained as a function

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of distance from the emission source which is a helpful quantity even if substantial uncertainties remain as to the actual amount of HBr measured. While I believe this paper is still a useful contribution to the community, I do want to make clear that I am not convinced the authors have demonstrated an ability to quantitatively measure atmospheric HBr at the mole fractions reported. Below I provide some suggestions for improvement of the manuscript.

Line 91: Why does 250 mL/min provide "ideal" sampling efficiency?

Line 150: While I see the actual temperature programs are given in the supplement, it would be good to give the temperature ranges and total run times for the GC separations in the main text as well.

Line 239: Why this range of values? The highest value you report in Table 2 is 1.90 ppb. Are these high values atmospherically relevant? Does this relationship hold at lower mole fractions such as those you report?

Figure 2: If the goal is to compare the two techniques using the Raschig Tube measurements as an independent variable in a calibration, an orthogonal distance regression of the two sets of measurements would more clearly demonstrate the comparability of the two sets of measurements and give the reader an idea of the sensitivity of the denuder measurements. As I point out above, the calibration should be performed over an atmospherically relevant range of values.

Section 3.5: Move details of the instrument field deployment to the methods. It would be helpful to add information about how the pump was powered during sampling both on the ground and during UAV sampling to give the reader an idea of the logistical requirements. Since UAV sampling is covered, it would also be helpful to provide the approximate weight of the instrument configured for UAV deployment. Was the instrument the only payload for the UAV or was it flown with other instruments? I understand references are provided for the details of UAV campaigns and the answers may exist there, but it would be good to provide the answers to these questions in this paper.

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Line 262-275: The authors haven't actually demonstrated that they can accurately quantify atmospheric HBr at low mole fractions as their laboratory studies only go from 3 to 20 ppb. Even if one assumes these data were quantitative below 3 ppb, the inclusion of actual values below LOD in Table 2 is also not appropriate, it should just be noted that the measurements were below the detection limit.

Line 282: Rephrase "This is in very good agreement with the results obtained with the model's estimations". The point of these comparisons is an evaluation of the model performance, not affirmation of your observations. The model being consistent with your observations reflects favorably on the model, but says nothing about the accuracy of your measurements as you imply here. This sentence as written implies you have doubts about the measurements. I would also add the model prediction to Fig. 5 for ease of comparison by the reader.

Fig. 5: As discussed previously, I think adding the model results referenced in the text would be helpful. The point markers should also be changed. Right now they can be confused with error bars, which is problematic. The author's should also add error bars on the ratio since they are presented in the caption. The y-axis label is not accurate. I believe what is being presented is the ratio of HBr/reactive bromine, not the ratio of HBr/ bromine atoms which is what the label says.

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