

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 #3

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General Comments

In this work, the authors present a series of synthesized epoxides to produce a selective gaseous diffusion denuder coating for the collection of HBr, specifically applied to volcanic plumes. Significant synthesis effort has been input to the production of the molecular probes, followed by laboratory and field tests for selectivity, robustness, reproducibility and suitable quality assurance and control metrics. The authors find that their best performing probe is capable of collecting HBr from groundsite locations, but not when deployed on a UAV. They compare their results to a chemical plume

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model for volcano emission chemistry and find reasonable agreement to validate their methodology. Overall, the work performed here is suitable and of interest towards publication in Atmospheric Measurement Techniques pending major revisions. Foremost, the writing style of the manuscript is in dire need of improvement. The writing feels incredibly rushed and requires a significant additional time investment. It is abrupt, can be logically disorganized at times, and outright impossible to follow at others. There is an over-reliance on short paragraphs, and under-reliance on grounding in the literature, amongst other issues (see Major and Technical comments below). In addition, important aspects of the methodological work have been completed, but are missing. This include fundamental separation performance metrics for the molecular probes and reaction products, instrument detection limits, accuracy and precision assessments, range of linearity, spike and recovery summation statistics and so on. The work has already been performed to provide this critical information and the performance of the method does not appear to have critical flaws based on what is provided in the current version of the manuscript. The revised work should be re-evaluated through peer review to ensure this remains the case.

Major Comments

1. The abstract clearly demonstrates the overall symptom of unclear writing style present throughout the manuscript. The work is presented topic by topic in short paragraphs with abrupt changes. The abstract should succinctly summarize the findings of the work with clear connection between the topics. Further to this, the abstract is nearly as long as the introduction, which is the best written aspect of this work. In locations where specific changes to organization or technical language are required, they are specifically noted in the Technical Comments below. Where the authors need to independently improve clarity, a statement of 'revise for clarity' is indicated as the intention of the writing is not easily determined and/or the authors have the freedom to re-organize according to their preference.

There is a heavy reliance on conjunctive adverbs (e.g. however, therefore) in the writing

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of the manuscript. In some cases, their use undermines the findings of the experiments by suggesting contrast when there is complementarity. The authors should take specific care to use these terms sparingly and accurately. Specific removal of such terms and identification of conflicting use are noted in the Technical Comments below.

2. Technical details of the methodologies from preparation of denuders, extraction and recovery of analytes, through to separation of target products, and quality assurance and quality control all have major oversights. These are numerous and critical for this work to be published in a journal focused on measurement techniques. It appears that all the necessary work has already been performed, so additional experiments are not likely required to address the Technical Comments presented in detail below.

3. A large section of the field observations needs to be moved to the methods section. The intercomparison with the DOAS data is mentioned but results are not presented. The model-measurement comparison needs to be expanded and generally rewritten for clarity.

Technical Comments

Page 1, Abstract: Rewrite after addressing all revisions to the manuscript. Focus on a concise summary of the most important achievements of this work.

Page 2, Line 45: 'are among the not negligible constituents of volcanic emissions'. Revise for clarity.

Page 2, Line 46: 'Monitoring of halogens' should specify some landmark examples.

Page 2, Line 46: 'Already' is not needed here. Delete.

Page 2, Lines 50-51: This thought is incomplete 'made BrO/SO₂ a promising monitoring tool'. Why? Is it because BrO can be monitored from space? This is what the following sentence seems to imply, but it is not clear. This paragraph should also finish with a summary statement such as 'if HBr emissions decrease like those observed previously for Cl, then it may be possible to provide greater forewarning regarding vol-

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canic eruptions through the use of remote sensing instruments. It is therefore important to have methods to determine if such reductions in HBr do, in fact, also occur'. The link between HBr and BrO in plumes monitored from space do not materialize without providing this connection.

Further instances of this type of oversight are noted below only as 'requires connecting sentence' below so the authors may provide their own context over the reviewer's assumed intention in their writing.

Page 2, Lines 59-60: The last sentence of this paragraph is not required. Add the reference after 'hypothetical (Gutmann et al., 2018 and references therein)'.

This paragraph also requires a connecting sentence.

Page 3, Lines 69-72: Revise for clarity. The short statement 'as products bromohydrins are formed' does not stand on its own.

Page 3, Line 75: HPLC-MS should be defined at first use. Seeing as the authors deem the inclusion of ESI in the abbreviation below, a consistent term should be used throughout the manuscript.

At the end of the introduction it is fairly common to see the structure of the presented work laid out in a short list of points. It would be highly beneficial to ensure the structure of the manuscript flows as the authors desire by outlining the order in which content is going to be presented at the end of the introduction and then maintaining that structure throughout the manuscript.

Page 3, Line 79: HPLC-MS or HPLC-ESI-MS should already have been defined in the abstract or introduction above and should be used to replace all instances of 'high-performance. . .' henceforth.

Page 3, Lines 86-87: 'The vials containing the analytes were weighed regularly to determine output rates'. This assumes that emissions are made in the same proportion as the mixture contained in the vial, yet HCl, HBr, and H₂O will all have differing per-

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meabilities out of the vial in these mixed aqueous solutions. Was consistency between the active molecule determined by mass loss from the vial confirmed by an independent quantitative method after scrubbing the gas flow into a collection solution (e.g. ion chromatography)?

Page 3, Line 92: should 'realized' by 'made of'?

Page 3, Line 93: 'is the sampling' should be 'is sampling'

Page 4, Line 95: No comma is required after both. Delete it.

Page 4, Lines 97-100: These three sentences can be greatly simplified because the setup is clearly depicted in Figure 1. The last two sentences can be removed and the first two combined into a more concise description.

Page 4, Lines 100-106: 'Apparently', 'However', and 'Therefore' are not needed at all in this section and can be removed. The last sentence is not needed as adding '(Fig. 1b)' after 'both vessels' at Line 98 is all that is required to direct the reader to this schematic.

There is a sentence fragment of 'indicate inaccurate gas flows or fluctuate' that seems to be left over from something else that doesn't belong here either. It is worth noting here as well, that losses of strong acids to such experimental surfaces from the gas phase is well established and expected. The literature is particularly deep on this consideration for measurements of HNO₃ in atmospheric chemistry field and lab setups. This work should reference such pre-existing knowledge.

Finally, the sentence currently beginning with 'Therefore' should be the first sentence in this block of information. Followed by, the sentence currently starting with 'However' and then the one with 'Apparently'. This presents the experiments much more clearly as: i) we took care to connect things in the following way, ii) this ensures comparability, and iii) is critical in order to account for losses of strong acids to experiments surfaces.

Page 4, Figure 1: The figure caption does not meet the journal guidelines. The panels do not get described on separate lines. Please refer to other manuscripts published in

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AMT to ensure correct formatting of figure and table captions. It is also difficult to see where panel (a) ends and panel (b) begins. Consider placing these in a frame or at least dividing them with a solid vertical line. Typically, the lettering for panels is placed in the upper left corner of the respective panel.

Page 4, Line 112: The use of 'treatment' is not very specific. Consider revising to 'denuder preparation, extraction, and analysis'.

Page 4, Line 114: 'to avoid photochemical reactions' of what? HBr? Or photolabile HBr precursor gases, such as BrO? Or are your molecular probes susceptible to photodegradation? Please revise for clarify.

Page 4, Lines 116: Please revise for clarity. Were the '6 times of 0.5 mL' applied all at once? After each aliquot was dried? Is the drying system a custom creation or a commercial device? The use of 'therefore installed' is confusing word choice here. If it is a custom creation, a photo of the setup and a few more specific details in the Supporting Information may be of interest to others who wish to reproduce this technique or apply it to other denuder coating setups.

Page 5, Line 123: While 'educt' technically makes sense to use here, it is fairly uncommon to encounter in this field. Consider replacing.

Page 5, Lines 129-133: The use of 'elute' here is not quite correct. This term refers to the exiting of a compound from a packed column of a compound retained on a stationary phase by a mobile phase. The methodology being used here is a solvent extraction of the denuder coating and the writing should state 'extraction' instead of 'elution'.

What does 'five steps each with 2 mL of solvent' mean? Five sequential extractions, each with a volume of 2 mL for a given solvent? Was the denuder capped and inverted to ensure solvent contact with all surfaces or was the surface simply rinsed. Please clarify.

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For the extraction efficiency assessment, how was the amount of 0.01 mmol EPBr applied to the denuder? It is not clear if the recovered amount from the extraction method was compared to a standard solution containing the same quantity of EPBr or if it was quantified via a calibrated instrumental technique. This should be specified.

Lastly, is the 'second elution step' being performed on a previously extracted denuder? Please clarify. Technically, this is an assessment of residual EPBr recovered in a second 5x2 mL extraction.

Page 5, Line 134: 'Eluates' should be 'extracts'

Page 5, Lines 134-139: This paragraph needs reorganization for clarity. The use of formic acid appears without any motivation or reasoning, flasks are mentioned for the first time and cannot be related to prior parts of the method. The internal standards used seem to have abbreviations later in the manuscript, which are not defined here. Typically, for a concentration and recovery methodology the procedure is presented as: i) internal standard identity and quantity added, ii) conditions of the concentration step, iii) analysis. This can then be followed by the obtained recovery results without the use of formic acid, then providing the rationale for its use, and finishing with the perfect recovery results obtained.

Page 5, Table 1: This belongs in Section 3.1. It would be valuable to add the chemical structures of each epoxide molecular probe, and the HBr-specific reaction product, as new columns in this table. In addition, the 'result' for EP states 'suitable', but like the 9,10-epoxystearic acid a chlorine side product is mentioned in the manuscript, but not noted here. Should that not be listed here? Perhaps the column heading should be 'Observations' instead of 'Result'?

Page 6, Lines 146-147: State that this derivatization converts to carboxylate functionality to a trimethylsilyl derivative, reducing polarity and increasing volatility. Is the second sentence here supposed to be the details of the derivatization(70 C for 90 min)? It states 'sample storage'. Suggest revising for clarity.

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Page 6, Lines 151-152: Unit notation here is incorrect and inconsistent with unit presentation requirements of this journal (use a space between values and units). The separation programs in Tables S2-S3 can be combined into a single table with sub-headings for the different analytes to reduce repetition of the headers.

Page 6, Lines 165-169: No sample chromatograms of the molecular probe, the reaction product, a sample collected under contrived laboratory conditions sampling HBr, nor actual samples are shown. The tables in the SI also suggest that a reference compound only noted as 'TBA' was used in these samples. What is this and why was it necessary to use? Where matrix effects were encountered, why were dilutions not performed on the samples to attempt reducing the noted effects of: shifting retention time and broad peak widths? Were the areas of the sample peaks within the linear calibrated range of the instrumentation? The described observations suggest that the column and/or detector may have been overloaded or saturated, respectively. The mass spectra for clean standard solutions of the probe and product, as well as mass spectra obtained from the field samples to confirm these molecules despite the altered retention times are necessary to include in the supporting information.

One crucial chromatography metric missing from the assessment of all the methods tested is the calculated resolution between the probe molecule, the reaction produce, side products, the injection standard (presumably this is what 'TBA' is in Table S4), and the internal standard for recovery corrections.

The instrument linear range, detection limits, accuracy, and precision measured over the course of this work should all be presented in this section of the methodology for the quantified molecules noted in the preceding paragraph. It is not possible to ascertain from the current manuscript if samples were analyzed under reliable analytical conditions for quantitative analysis.

Page 7, Line 173: 'a significant loss of the compound was observed during sampling' How? Was this quantified by an instrumental method? What was the exact amount

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lost? Everything? How was 'significance' determined statistically?

Page 7, Line 174: 'Obviously, 2,3-... Is too volatile.' is redundant. Delete.

Page 7, Lines 174-177: Provide quantitative information to support your conclusion. There are too many ideas in a single sentence here and the authors should attempt to separate these for clarity.

Page 7, Line 178-179: 'massively' and 'however' are not needed. Delete.

Page 7, Line 183: Should 'causes low volatility' be 'reduces volatility'?

Page 7, Lines 187-188: 'Although derivatized HBr...'. Table S4 states that these molecules had different retention times, but resolutions between the peaks are not given. What is the actual analytical issue here? And if the analytes could be quantified, what does it matter if the products all have the same m/z ion in EI if you can identify the product by injecting an authentic standard? Presumably, if there are matrix effects a spike of the product through standard addition would be a viable option, but would be more labour intensive. This discussion should be expanded and be more thorough.

Page 7, Lines 189-190: Certainly more discussion and the criteria for meeting the designation 'suitable' are warranted here!

Page 7, Line 190: 'chapters' should be 'sections'.

Page 7, Section 3.2: There are many different topics within this section that would greatly benefit from separate subheadings (e.g. Coating Breakthrough Experiments, QA/QC and Matrix Effects, Coating Stability, and Interferences and Cross Reactions). It would help organize the section and reduce the number of places where connecting sentences would otherwise be required to make the discussion contents easier to follow.

Page 7, Line 196: 'Therefore, the' can be 'We tested'. The rest of this sentence requires further clarification. One can eventually discern that the point is to apply an upper limit

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of HBr mixing ratio to the denuder, based on prior ambient observations of plumes. Suggest revision for clarity.

Page 7, Line 199: How was the coating quantity on the denuders determined? Was this quantified using the instrumental methods presented or was this determined by calculation? From the description of the denuder coating section, it does not seem likely that all of the analyte solution applied to the denuder surface is retained and that likely a large amount of the applied solution exits the denuder when it is rotating on the 10 degree sloped setup with gas flowing over it. This contrast between theoretical amount of probe applied compared to the practical result of the method would be valuable to discuss here if the applied amount was not quantified.

Page 8, Line 200: 'clearly' is not required. Delete.

Page 8, Line 201: 'was below 1 %' in which denuder? The third one? For all field samples collected were both denuders extracted to ensure accurate quantitative collection of the targeted HBr? The following use of 'however' can be deleted.

Page 8, Line 202: Given the issues encountered with peak width and shape in the HPLC separation, perhaps such aggressive concentration steps were not required to retain suitable detection limits for the method? It would be worthwhile to comment on such findings here. The use of 'finally' at the end of this sentence does not really work. Consider using 'We determine that use of 15 mmol/L EP coating solution was ideal to coat denuders with 45 umol EP.'

Page 8, Lines 204-206: 'The influence of EP' due to what? Its much higher concentration relative to EPBr? What are the 450 mmol/L 'concentrations'? Are these standard solutions? Were the mixtures done at equal amounts of EP compared to EPBr? A retention effect of EP on EPBr is likely to be muted under equimolar mass loadings on the analytical column and observed more realistically by simulating ratios you'd expect to find in real samples. What does the 'n=6' refer to here? Six standard mixtures of equimolar concentration between the upper and lower bounds stated? Six injections of

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the two concentrations? Does the upper limit of this range correspond to the maximum concentration of EP that could be extracted from a denuder? None of these important details are discussed, but they have surely been considered. Please expand the discussion to improve clarity and communicate the care and detail considered in this work.

What values were the standard deviation percentages determined from? Some metrics are very useful (e.g. accuracy and precision in quantitation) while others are not (e.g. retention time). This is critical to specify and justify why the metric you selected has utility in concluding that no matrix effects exist in the separation technique from the probe and product molecules.

Page 8, Line 207: 'Constricted' should be 'concentrated'. What are the 'samples' mentioned here? Contrived samples made from pure compounds, field samples, lab samples, or all of the above? How many times was the sample reanalysis performed and at what temporal frequency (e.g. monthly, weekly)? A plot of the data and clear indication of the identity of the samples is required to ascertain whether the stated stability of the probe is a sound conclusion. The trend of sample stability/degradation quantified should be presented with a figure in the Supporting Information.

Page 8, Lines 211-215: The authors present method detection and quantitation limits, but instrument performance metrics are missing from the methods section (as well as how they were determined). Since the molecular probes are novel analytes without pre-existing methods published in the literature, such QA/QC is critical to present here. Please add, so that the results presented here can be evaluated with that information in mind.

Were there detectable peaks for the reaction product in the field blanks that set the method detection limits higher than the instrument detection limits? How many field blanks were analyzed to calculate these values? What was the variance between the blanks, if any? Were there detectable reaction product peaks in a denuder that was

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extracted immediately after drying? How did these compare and what does this tell you about the potential for contamination of denuders during transport? This helps clearly set up the reasoning behind the assessment of interferences and cross-reactivity that follows.

Page 8, Line 217: 'would be at least conceivable as a' is very confusing. Consider 'is the most likely' instead. 'However' at the end of this line is, again, unnecessary.

Page 8, Lines 217-218: What mixing ratios of Br₂ were used, what other gases were present with the Br₂? This sentence requires revision for clarity and justification for the representativeness of the Br₂ quantities investigated.

Page 8, Lines 219-221: Since methyl bromide was not explicitly tested, has not been detected in volcano plumes, and will not produce the same product as HBr, it is not worth discussing. Delete.

Page 8, Line 228-230: Reorganize and clarify.

Page 8, Lines 230-231: How long as the 4 ppm HCl exposure performed for? A comparable duration to field sampling volume and duration? What about integrated exposure with some approximated limits based on the literature?

Page 9, Lines 238-240: The alkaline traps are the established techniques and the new EP probe should be compared against them. Here, the comparison is made the other way around.

Page 9, Figure 3: This should be converted to a table with the +/- values given and statistical tests for similarity performed to demonstrate that both methods are measuring the same quantity of HBr. This is a more robust validation of the developed EP molecular probe. The last sentence in the caption is a repetition of text already presented in the discussion. Delete.

Page 9, Section 3.5: Much of the information presented here should be relocated to the methods section to describe the sampling site and sampling approach. Only results

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and discussion of the new denuder method should be presented here.

Page 9, Lines 251 and 256-257: The UAV system needs to be briefly summarized here. Referring to prior reports alone is not adequate.

Page 9, Line 255: The NOVAC station is not defined anywhere? What does this stand for? Figure 4 does not denote it specifically. In the subsequent discussion, there is no comparison made to the DOAS measurements noted here. This is a highly valuable field intercomparison. What were the results or why was it not possible to get usable data? Ideally, this should be expanded.

Page 10, Figure 4: Color code the ground versus UAV locations. Place distances from the HBr emission source to the sampling locations on the map and remove from Table 2.

Page 10, Line 262: The range is from '< LOD' to 1.97 ppb. A reference to Table 2 should be made at the end of this sentence and the last sentence of this paragraph deleted.

Page 10, Lines 264-265: This information belongs in the caption for Table 2. Relocate.

Page 10, Line 268: The 2x2 information in brackets should be deleted and a column for the number of samples collected at each location added to Table 2.

Page 10, Line 268-270: are these mixing ratios statistically the same or different? Can the precision of the method be approximated despite the small number of replicate samples? This is an example of where determination of the method precision for the laboratory experiments can bolster the robustness of the method when applied in the field and the discussion here can bridge those findings together.

Page 10, Line 270: A deviation of a deviation is not very meaningful and a good reason for calculating it is not given. Justify or remove.

Page 10, Line 276-282: The model-measurement comparison is too brief and needs

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to be expanded to clearly demonstrate the quality of the field measurements. For example, the loss of HBr in the model is stated as a percentage, but the loss of HBr observed is discussed in the same context. One has to hope they identify the correct information in Table 2 and then calculate this independently to ascertain the statement of 'very good agreement' is true. Overall, I cannot follow the logic of this section and it weakens the manuscript when it should be strengthening it. Please revise.

Page 11, Table 2: Samples with HBr quantities below the method detection limits should be reported as '<LOD' or as '<XX' for the corresponding detection limit of a given sample. A column for the number of samples at each location and date needs to be added, as well as for the sampling method (ground vs UAV). Is the Br/S in the table measured or modeled? This needs to be stated in the figure caption and in the discussion.

Page 11, Figure 5: Can the fraction of HBr/Br from the model be added to the figure for comparison? Based on the discussion this should be possible and compare well.

Conclusions: Rewrite based on revised manuscript and in light of all comments above.

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