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Atmospheric Measurement Techniques
Discussions
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Interactive comment on "Measurement of iodine species and sulfuric acid using bromide chemical ionization mass spectrometers" *by* Mingyi Wang et al.

Anonymous Referee #1

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1 General Comments

The authors present a study on the Bromine-MION CIMS, an impressive new tool to selectively and extremely sensitively measure several relevant iodine species and sulfuric acid at the CLOUD chamber with clearly the same potential for atmospheric measurements. The combination of an extremely clean chemical ionization procedure with a very high-resolution time-of-flight mass spectrometer renders unprecedented selectivity and obviously sensitivity which is shown by means of instrument intercomparisons and employing accurate absolute calibration techniques as well as a rough method based on intercomparisons of measured and ab-initio calculated cluster-ion formation

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and dissociation enthalpies. Overall this is a very relevant study fitting perfectly into the scope of AMT.

However, the way the involved experiments are presented and discussed needs considerable revisions in order to enhance the usefulness to the CIMS community and also be comprehensible for non-specialist readers. I give my general concerns in the following paragraphs and many detailed comments and proposals in the next section.

In general the manuscript is written in a way hard to follow for non-specialists in the CIMS technique. Just as one example the widely used ion signal ratios should be briefly rationalized in terms of ionization reaction rates before being discussed. Although the paper refers to the relevant instrument papers basic procedures and derived quantities etc. used in 'every day live' by the authors must be briefly explained. The reader can not be expected to look up 10 other papers in order to properly follow the basic course of the manuscript.

In places sloppy and unclear formulations are used, e.g. 'uncertainty' instead of clearly stating if accuracy or precision are referred to and if 1 or 2 standard deviations are given. Also details of the experiments need to be much better defined where the relevant parameters have clear influence on the results presented. As an example critical settings of electrical fields employed in the first transfer stages which have strong impact on the relative signals of ion clusters and bare ions in the mass spectra are not even mentioned. Reproducability of the results presented is not given if the reader has to try to isolate such relevant information from the papers cited and can't be sure that they have not been changed. As another example it is not even mentioned which type of mass analyzer is used for the MION-CIMS or also the FIGAERO and what the relevant mass resolutions are. Therefore it needs to be clearly stated in the methodology section 2 in which relevant operational conditions the instrument(s) have been operated. Pressures and flows employed in the IMR and 1^{st} transfer stage and respective reaction times (as well as the electric fields applied in the ion transfer) should be given in the experimental section and not implicitely towards the end of section 3! This is absolutely neccessary for sake of reproducability. A table may do the job here.

In places purely qualitative statements in the discussion should be quantified by giving the relevant parameters such as for relative reaction rates etc. (see in the specific comments).

For the I_2 and Cl_2 permeation devices which have been nicely qualified I am wondering why no parallel gravimetric control has been done as this is a very simple and reliable way of calibrating devices with such compounds and high permeation rates approaching the mg/day regime.

The operations around the permeation devices have been worked out in quite some detail although these procedures are not new but have also been described in earlier publications which are cited. I don't criticize that detail, however, there is a strong misbalance to other experimental details especially since this part has been placed into the results and discussion section 3. Here certainly some restructuring is neccessary.

Two independent approaches for the I_2 calibration have been employed and presented. Both look very good but differ by more than a factor two from the CE-DOAS intercomparison to the permeation tube approach most obvious in Table 3. This is not clearly mentioned nor discussed in the manuscript. On the contrary the summary states that 'different methods result in consistent calibration constants'!? Since both methods used are in principle absolute techniques and individual errors seem much lower there must be some conclusion on this discrepancy seemingly outside the combined error bars. Has the DOAS system been calibrated directly employing the permeation device in order to resolve this? This point clearly needs revision and clarification!

An approach to compare the performance of the MION and FIGAERO instruments especially with respect to surface effects is presented in section 3.4.2 on rise and decay time constants. The tentative interpretation presented seems reasonable, however my feeling here is that the fitting analysis does not give any significant additional information on the signal evolution than obvious already from the pure normalized signals.

MION and FIGAERO agree well for HIO_3 and HOI. Therefore the evolutions probably indicate wall uptake and desorption processes possibly occuring somewhere from the chamber into the IMRs since else certainly much slower decays would be expected. The fitted evolutions just underline the instrument deviations which seem really significant only for IO with the obvious elevated background signals on the FIGAERO. This might also be due to some residual outgassing of the FIGAERO filters after the aerosol measuring phases which just ended before start and end of the photolysis. Another reason for the 'permanent' IO background in the FIGAERO might also be some unrecognized isobaric contaminant on the lower resolution (if I'm not mistaken) FIGAERO analyzer. However, in the current state of analysis I don't see any additional information provided by this analysis technique.

2 Specific Comments

l.116: Here an outline of a typical NPF experiment on the CLOUD chamber should be briefly presented with the operational details of the experiment, like flushing, I2 addition and control, etc as a function of experiment time. See general comments.

l.130: Details of the experiments need to be much better defined, see general comments

l.166: Accuracy is a defined quantity and I'm not aware of 'systematic accuracy'. Is 20$\%$ accuracy or rather precision meant here? For all statements on accuracy or precision it must be clearly mentioned which quantities are given, 1 or 2 standard deviations?

l.171: Isn't 'conformational sampling' the more common term?

l.179: The experimental details on the qualification of the I_2 and Cl_2 permeation devices and HOI calibrator operation from section 3 should be moved to here. Clearly these are methodological details. See general comments.

l.187: ... high mass resolution ... Here the mass analyser type and important specs should be detailed!

l.222: Does the RH range encompass all relevant experiments carried out? Lee et al., 2014, show that for I- ionization the major RH sensitivity of the calibration, especially for small organic acids, is found at quite low RH.

l.228-232: It may be worthwhile to although show the respective plot for the HOI normalization.

l.246: I propose to not present the rather lengthy equation in the text flow but as a separate equation.

l.246: Is there a physical motivation for the inclusion of the quadratic fit? If there is any relevance, apart from the good agreement with the linear relation, it should be clearly discussed. Else it can be neglected.

l.255: For this as well as the Cl_2 device all wetted materials used for the calibration gas generation should be detailed. Especially for the low flow rates used for flushing the permeation devices even compounds like the elemental halogens could be reduced due to surface effects.

l.280: Quantification would clearly help with this statement (e.g. ... agreement within XX$\%$ with ...)

l.290: The calibration constant reported for I_2 from the CE-DOAS intercomparison was $2.7E-10molec/cm^{-3}$, i.e. more than 60$\%$ lower as mentioned earlier. However, were does the ’overall uncertainty’ (is this accuracy?) of 45$\%$ come from while the permeation rate is defined to better than 5$\%$?

l.334: Give the relative reaction rate instead of ' ... relatively slow ...'

l.351: No statements on the accuracy of the H_2SO_4 measurements for the pre-calibrated nitrate-CIMS nor the Br-MION are given in this section. Just the caption of Fig.4 mentions a 'systematic scale uncertainty'. This is very annoying and makes me wonder if this has been left out on purpose ...

l.348: I propose to not present the rather lengthy equation in the text flow but as a separate equation.

l.374: The explanation is hard to comprehend for the non-specialist reader and rather leads to confusion. This should be improved upon e.g. by going step by step from the dissociation enthalpies via reaction rates etc.

l.393ff: Even though the derived calibration constants (and later detection limits) of the species not calibrated directly are quite crude they should be given in a table rather than in the text flow. I propose to include them into Table 3 as a third category c: derived from dissoc. enthalpies (or similar). Table 3 could be extended by another column for the det. limits for all species as well.

l.421: I find the use of 'NPF event' rather annoying since no particle data are shown or discussed, I propose to just refer to the 'photolysis interval' or similar.

l.429: Is there a continuous addition of I_2so to keep it constant over the photolysis causing I_2 to increase when the lamps are off?

3 Figures and captions

Fig.1: I really do like the figure, however, the caption will have to be extended considerably in order to properly inform and guide the reader! First there should be 2

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defined panels (upper and lower, a) and b), ...). Mass defect could be defined in the text so not to extend the caption. More clear identification of the experiment (date, ...) may not be absolutely neccessary here but still enhance transparency. Upper panel: symbol area is proportional to the logarithm of the signal AREA which has a unit of counts/s. However, then the y-axes in the lower panel can not have the same unit! Please, align these details!
Lower panel: The explanations given in the upper left spectrum must be detailed. Although obvious it should be indicated that colors in the panels do match. It might be sensible to use the same x-scaling for all spectra.
What is the averaging time of the spectra shown?

Fig.2: The time series plot shows peak area (not intensity) vs. time.

Fig.3: A different and zoomed color scale has to be selected here in order to better show the range of RH varied from just 40-80$\%$.
Is there an explanation for the slight hockey stick shape visible at high RH and low I_2 concentrations? Is this a consequence of the DOAS det. limit?

Fig.4: The x-axis titles should give the detected ion clusters. The analyte species may be given in the caption.

Fig.1: abc

4 Minor comments, typos, etc.

l.70: I recommend to use ’absorption features’ instead of cross sections.

l.83: The bromide ion ...

l.114: ... the atmospheric oxygen ratio of 0.21 ... (there aren’t 79$\%$ of N2!)

l.186: ... bromide ionS ...

l.247: ... the whole campaign ... THE two curves ...

l.327: ... hydroxyl radicalS ...

l.350: This is a repetition from the equation given before ...

l.414: ... of THE bromide ...

l.423: ... and TO low levels of I_2... (The sentence may otherwise suggests that I_2 had not yet been added to the chamber at this point.)

l.446: ... of THE NPF event ...

l.739, 743: ... with bromide ionS.

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