

# Responses to reviewer comments for "Characterisation of the multi-scheme chemical ionisation inlet-2 and the detection of gaseous iodine species using bromide and nitrate chemical ionisation methods"

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In our response to the reviewer, we use *abc* as our response to the reviewer's comments, and **abc** (in bold) represents updated content in the revised manuscript. It should be noted that Table 1 in the tracked change version has formatting issues caused by a latex compiler and the editor and reviewers are referred to Table 1 in the revised manuscript.

## 5 Responses to reviewer1

He et al. present details on the characterization of the MION2 inlet. The design improvements are worthy of being reported. However, the presentation is frustrating.

10 *We thank the reviewer for taking the time to review our manuscript and for their kind words regarding the scientific quality. We also appreciate the reviewer's constructive criticism on the manuscript presentation and the details which are addressed below.*

*It appears that the reviewer might have evaluated the original version of the manuscript, instead of revision 1. We have nevertheless tried to adopt the reviewer's relevant comments and suggestions in revision 2 when possible.*

15 I've never seen anyone choose to define "calibration coefficient" as the opposite of instrument sensitivity. The units of this "calibration factor or coefficient" (pick one, do not interchange) make no sense (molecules cm<sup>-3</sup> cps cps<sup>-1</sup>?).

*We thank the reviewer for the comment. Both the terms 'calibration coefficient' and 'instrument sensitivity' have been employed in this study. The term 'calibration coefficient' is derived by calculating the ratio of actual concentrations and measured signals of the analyte. Additionally, we utilise the calibration factor as an indicator to discern and compare instrument sensitivity across various analytes, assuming constant instrument conditions throughout the comparisons. We have thoroughly reviewed the utilisation of the term 'calibration factor or coefficient' throughout the manuscript. As a result, we have made the decision to uniformly replace all instances with the term 'calibration factor'. The utilisation of the 'calibration factor' unit is sensible for making comparisons between different studies. The utilisation of the "cps cps<sup>-1</sup>" is a measure to highlight the normalisation of analyte signals by the primary ions, which was strongly requested by some of our co-authors in the preceding paper (Wang et al., 2021). However, we removed it as per the reviewer's request throughout the manuscript.*

HOI is confusingly reported as being both not strongly bound to the Br<sup>-</sup> reagent ion and being detected at collision limit.

*We thank the reviewer for the comment. The bounding between the Br<sup>-</sup> reagent ion and HOI is moderate due to their inherent chemical properties. In this context, the detection of HOI depends on the strength of declustering with the instrument settings. In our study, we intentionally fine-tuned our instrument settings to minimise the electric force within the chamber and prevent excessive declustering for HOI·Br<sup>-</sup>. Consequently, HOI is detected at collision limits in this study. This was highlighted in lines 603-613: **A series of iodine oxides and oxoacids is evaluated together with other inorganic species such as H<sub>2</sub>O, HO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> (Figure 6). Based on the results, we categorise the analytes into three categories: 1) analytes which are strongly bonded with Br<sup>-</sup>, 2) analytes which are moderately bonded with Br<sup>-</sup> and 3) analytes which are weakly bonded with Br<sup>-</sup>. The species H<sub>2</sub>SO<sub>4</sub>, HIO<sub>3</sub>, HIO<sub>2</sub>, and I<sub>2</sub>O<sub>4</sub> can be classified into the first category since the initial change in voltage difference does not have a significant impact on the normalised signal. This indicates that these species are detected at the collision limit. It is also apparent that H<sub>2</sub>O, HO<sub>2</sub> and SO<sub>2</sub> belong to the third category, since a small increase in the voltage difference leads to substantially reduced normalised ratios. Finally, IO, OIO, I<sub>2</sub>O<sub>3</sub> and HOI are moderately bonded with Br<sup>-</sup>. These moderately bonded charged clusters can reach a close to collision limit detection if the instrument is softly tuned (the voltage difference is small), but their detection sensitivity can change dramatically if the instrument fragmentation level is high. Lopez-Hilfiker et al. (2016) defined a parameter  $\Delta V_{50}$  (dV<sub>50</sub>, i.e., the dV value at half the maximum of the signal remaining) to describe the analyte and reagent ion binding strength.***

45

The discussion on why Br<sup>-</sup> ionization is more sensitive at shorter reaction time is seriously lacking. Is there loss of reactive species or reagent ions on the MION surface? Is there reagent ion competition with water vapor?

*We thank the reviewer for the comment. The reviewer's observation regarding the irreversible deposition of reactive species and reagent ions onto the walls is indeed valid. Nonetheless, the utilisation of short ionisation times (35 ms and*

50 300 ms) in the MION2 system is unlikely to account for the observed disparities between MION2-T1 and MION2-T2. To illustrate, considering a uniform initial analyte distribution at MION2-T2, only 16 % of  $\text{H}_2\text{SO}_4$  will be lost to the inlet wall before reaching the instrument pinhole at 300 ms ionisation time. Given that the inlet is grounded, the loss of reagent ions onto the inlet tube occurs at a comparable magnitude, disregarding the specific trajectories of these ions. Our working hypothesis to explain the observed phenomenon revolves around the concept that substantially extended ionisation times  
55 facilitate more efficient reactions between reagent ions and water. Consequently, the average value of  $x$  in  $(\text{H}_2\text{O})_x \cdot \text{Br}^-$  becomes larger, implying that the reagent ions within the ion-molecule reaction chamber potentially encompass more than a single  $\text{H}_2\text{O}$  molecule.

For an analyte to be detected, it must undergo ligand exchange reactions with the  $(\text{H}_2\text{O})_x \cdot \text{Br}^-$  entities present in the ion-molecule reaction chamber. Analytes exhibiting lower formation free energies with  $\text{Br}^-$  (indicative of stronger bond  
60 energies) may be more likely to form clusters with  $(\text{H}_2\text{O})_x \cdot \text{Br}^-$ . In scenarios where  $x$  attains a considerable magnitude, the  $\text{Br}^-$  ions could be enveloped by  $\text{H}_2\text{O}$  molecules, effectively masking their permanent dipoles. This eventuality results in none of the analytes becoming charged.

Regrettably, the mechanism outlined above remains a hypothesis at this stage, without substantial theoretical confidence. It is precisely due to this lack of comprehensive support that we refrained from offering explicit explanations. In our  
65 view, further investigative efforts are requisite before a definitive conclusion can be reached. Notwithstanding this, we do provide practical guidelines concerning the utilisation of this inlet (lines 495-497): **Although this effect is difficult to quantify, it practically suggests that the  $\text{Br}^-$  chemical ionisation method should employ a shorter ionisation time (i.e., using the T1) when operating MION2 with multiple chemical ionisation methods.**

70 Table 1, which is crucial to presenting the metrics of MION2, is a mess. Introducing multiple ToF instruments with different signal to noise levels is unnecessary for this table. Present only the sensitivity values (signal per number concentration) at two RH levels at same reaction times, and vice versa. Publication should be considered after major revisions.

*We thank the reviewer for the comment. In the current version of the manuscript, our focus is solely on a single TOF. As suggested by the previous reviewer, we have eliminated one of the multiple TOF instruments, as their presence was caus-  
75 ing confusion. We applied the relevant calibration factor to calculate the LOD for the analytes under specific conditions. Presenting the LOD values in the current format within Table 1 facilitates more effective comparisons with analogous findings in other publications.*

In the abstract and elsewhere, clearly define the sigma level and integration time when presenting LOD.

80 *We thank the reviewer for the comment. In this study, we utilise a sigma level of LOD set at 3, with an integration time of one hour. They have been defined in Equation 3.*

Abstract. When stating it is better than another system, be quantitative. Better by how much?

We thank the reviewer for the comment. We added the details of the performance of the Eisele inlet in lines 22-24: **For instance, when using the  $\text{Br}^-$  chemical ionisation method with a 300 ms ionisation time, the estimated detection limit for  $\text{H}_2\text{SO}_4$  is  $2.9 \times 10^4$  molec.  $\text{cm}^{-3}$ . Notably, this detection limit is even superior to that achieved by the widely-used Eisele-type chemical ionisation inlet ( $7.6 \times 10^4$  molec.  $\text{cm}^{-3}$ ), as revealed by direct comparisons.**

I2 does come into equilibrium with the inlet surface, but what about surface losses? Did you attempt to quantify I2 as a function of tubing/inlet length?

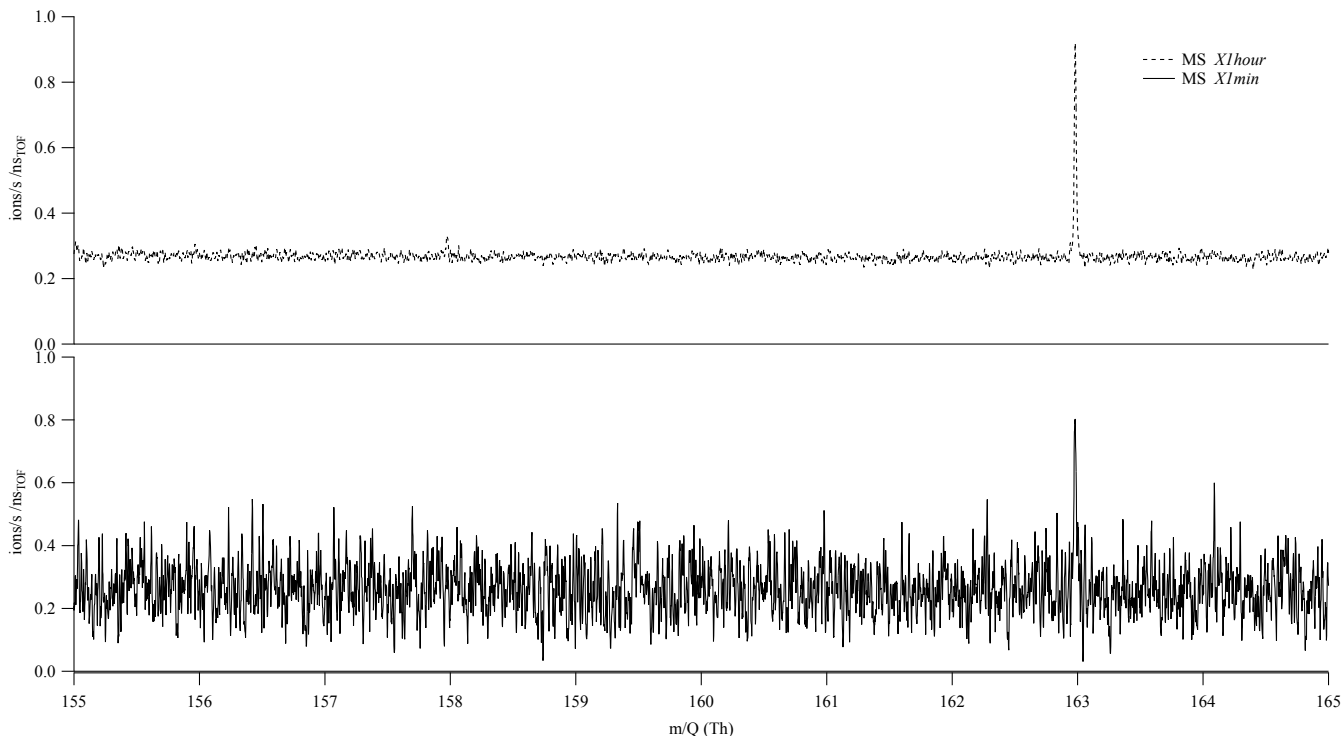
We thank the reviewer for the comment. In this study, we allow  $\text{I}_2$  to reach equilibrium for a duration of approximately 24 hours. During this period, the surface loss and evaporation of  $\text{I}_2$  from the surface reach equilibrium. Furthermore, we employed the same inlet tube for  $\text{I}_2$  calibration; therefore, any surface losses should not impact the accuracy of  $\text{I}_2$  calibration.

95

Equation 3 for defining LOD is vague. Is this a 1-hr LOD or 1-minute LOD? Does the signal-to-noise really continue to improve after 1 hour of averaging? Can we see a comparison of a 1-s spectrum versus 1-hr spectrum? Or an Allan Variance plot?

We thank the reviewer for the comment. It is 1-minute LOD but the standard deviation is estimated for a 1-hr window. We have defined the integration and averaging time for LOD calculation in line 561: '**where  $\mu$  is the mean value of one-hour mass spectrometric data with a one-minute time resolution and  $\sigma$ , is the standard variation of the same data.**'

The signal-to-noise is determined by the signal intensity and noise level. The signal-to-noise increases as the square root of the integration time. Averaging data can improve the background count rate; however, it cannot continue to improve indefinitely, especially after 1-hr average. Therefore, when the interaction time is fixed, the signal-to-noise cannot continue to improve after 1 hour of average. In this study, we averaged the data over 1 minute. Here, we present the 1-minute and 1-hour spectra for the  $m/z$  range from 155 to 165 in Figure 1.

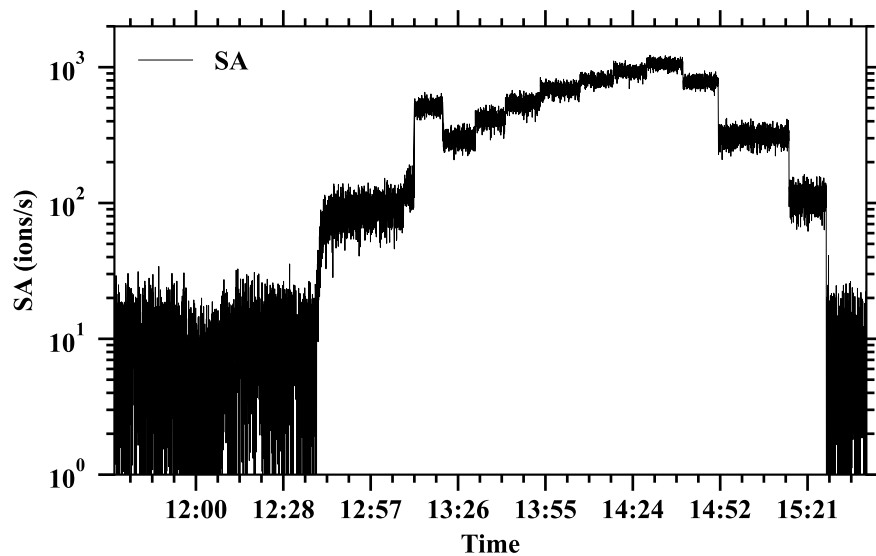


**Figure 1.** Mass spectrum averaged over 1 hour and 1 minute.

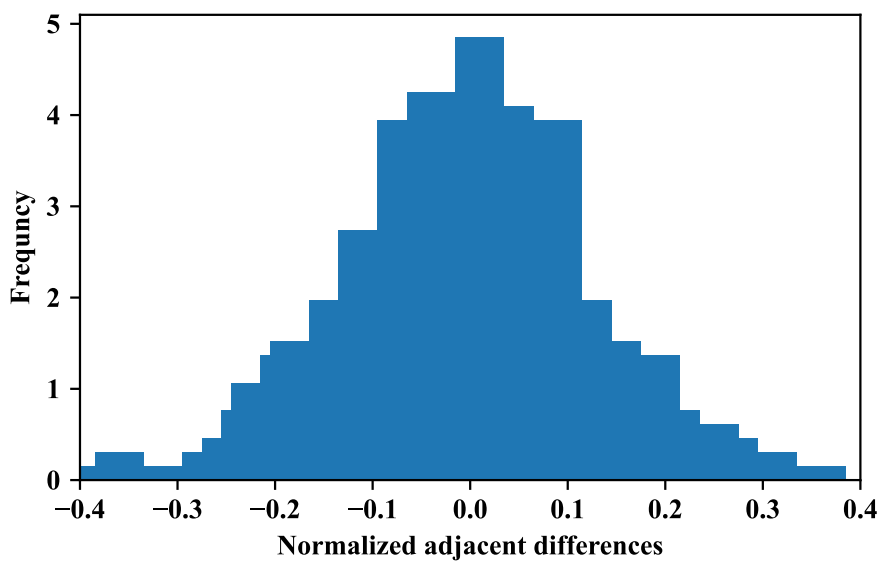
110 What about background counts in the spectra for the species considered here? Consider using equation as in Bertram  
 (www.atmos-meas-tech.net/4/1471/2011/ ). I would like to see a 1-Hz or better time series of a zero procedure for, say, HOI  
 and I2 and H<sub>2</sub>SO<sub>4</sub>. Is there residual signal that linger in the system due to their stickiness, thereby, resulting in higher LOD?

*We thank the reviewer for the comment. We have included background counts and experimental data in Figure 2,  
 which showcases the time series for the H<sub>2</sub>SO<sub>4</sub> signal captured at 1-second intervals. The time intervals between 11:30  
 115 and 12:30 have been identified as the 'background period', with an average background count of 8 ions/s. To evaluate  
 instrumental precision, we analyse the normal distribution of normalised adjacent differences (NAD) for a H<sub>2</sub>SO<sub>4</sub> signal  
 at 500 ions/s for 10 mins, as presented in Figure 3. This analysis yields an instrumental precision ( $1\sigma$ ) value of 0.12. In  
 addition, the rapid response of the H<sub>2</sub>SO<sub>4</sub> signal to the H<sub>2</sub>O flow, both in terms of increase and decrease, indicates the  
 absence of any residual signal. Therefore, we believe that no residual signal is influencing the LOD.*

120



**Figure 2.** Time series of normalised  $\text{H}_2\text{SO}_4$  signal for the calibration experiment, with the data averaged over 1-S intervals.



**Figure 3.** Distribution of normalized adjacent differences, as measured on a  $\text{H}_2\text{SO}_4$  signal of 500 ions/s at 1-S for a  $\text{H}_2\text{SO}_4$  signal at 500 ions/s.

How are you able to define a LOD if you were not able to determine a calibration factor for the IOx species in table 1? Justify the use of the values listed at the bottom of table 1. These are not the calibration factors for  $\text{H}_2\text{SO}_4$ . How did you account for

wall losses of sticky/reactive species such as HOI, HIO<sub>3</sub>, etc. on the surface of MION? How much would their losses affect the calculated calibration factors and LOD.

125 *We thank the reviewer for the comment. For cases where the calibration factors are available, Table 1 utilised the corresponding ones to calculate the LOD for the analyte. However, when the calibration factors are not available for the analyte, we employed the H<sub>2</sub>SO<sub>4</sub> calibration factor instead to estimate the lowest concentration of iodine oxides and the LOD. The losses of H<sub>2</sub>SO<sub>4</sub> and HOI on the surface of the MION inlet have been accounted for in the model and are governed by their diffusion coefficient. The calculated calibration factors and LOD are already loss corrected.*

130

Are you normalizing by total reagent ion counts (sum of Br<sup>-</sup> and water Br<sup>-</sup>)?

*We thank the reviewer for the comment. Yes, we normalised the measure signals to primary ions (the sum of Br<sup>-</sup> and H<sub>2</sub>O·Br<sup>-</sup>).*

135 How did you come up with the -50/+100 % uncertainty? Did you account for the uncertainty in the reaction rates and yields, as well as losses on MION surface?

*We thank the reviewer for the comment. The uncertainty is derived from the H<sub>2</sub>SO<sub>4</sub> calibration system, as reported by Kürten et al. (2012), including the reaction rates and yields (10 %). Furthermore, the model has already accounted for the loss of H<sub>2</sub>SO<sub>4</sub> on the surface through the kinetic simulation. Admittedly, the -50/+100 % uncertainty is more or less an estimation of the error margin. As mentioned, the reaction rate and wall losses are not the primary source of error. The N<sub>2</sub>O calibration experiment is factually the major error source. In this study, the uncertainty in the IT product is around 32 %. To be conservative while considering other minor errors from reaction rates, kinetic simulation, flow meters etc. We give an overall error of -50/+100 %.*

140

145 Figure 7. Use different symbols too.

*Figure 7 has indeed used different symbols; they are the same as those used in Figure 6.*

## Reviewer 2

150 General comments:

This paper describes improvements in the multi-scheme chemical ionization inlet (Rissanen et al., 2019) which apparently have led to detection limits using bromide CIMS comparable to those of the standard Eisele nitrate CIMS inlet. The paper discusses the calibration of the nitrate and bromide chemical ionization units and then investigates the dependence of the bromide method on humidity and instrument settings. Finally, the paper discusses potential ambiguities in the detection of  
155 iodic acid that may be caused by reactions of iodine oxides with the reagent ions in the instrument inlet.

This paper presents valuable research that should be published after mayor revisions are undertaken.

*We thank the reviewer for taking the time to review our manuscript and for their kind words regarding the scientific quality. We also appreciate the reviewer's constructive criticism on the manuscript presentation and details which are addressed below.*

160

I'm struggling to understand what is this paper exactly about in view of the emphasis given in the title to the inlet characterization and the mainly Br CIMS-related material presented. The title states that it deals with the characterization of the MION2 inlet, but throughout the paper the experiments refer to the characterization of a particular (optimized) configuration of this inlet for Br<sup>-</sup> as reagent, using NO<sub>3</sub><sup>-</sup> as a reference. Certain modifications pertaining to the inlet as such, as the new design of the source electrodes and flows, are described in section 2.1, but the actual characterization of the inlet stops there. From this point on, it is the new inlet what it is actually used to characterize and optimize the bromide CIMS method. I think that the authors have done a good job on that and therefore the emphasis should be there. The water dependence of the Br-CIMS signals and the possible strategies to reduce it are relevant for any type of atmospheric pressure ionization inlet, so this is not really a characterization of MION2.

170

*We thank the reviewer for the comment. We agree with the reviewer that we should emphasise the characterisation of the bromide chemical ionisation method. We, therefore, changed the title of the manuscript to **Characterisation of gaseous iodine species detection using the multi-scheme chemical ionisation inlet-2 with bromide and nitrate chemical ionisation methods.***

175

Finally, some material is presented related to the detection of HIO<sub>3</sub> by nitrate and bromide CIMS and potential interferences by IxOy. A significant fraction of this material has already been presented by Finkenzeller et al. 2022 and I don't think it is necessary to repeat it here, especially qualitative or semi-quantitative theoretical discussions. I do feel that this section needs to be reworked to make it fit better into the general context of the paper, e.g. a section about potential interferences in any instrument's inlet. I see a problem with the fact that the interferences are mostly related to the nitrate CIMS system, while the paper is very Br-centered. Nevertheless, the emphasis should be on the new experimental data that have been obtained, which seems to indicate that the nitrate and bromide CIMS signals attributed to HIO<sub>3</sub> are linearly related, which supports the conclusion of the authors about the absence of IxOy interferences under atmospherically relevant conditions.

185 *We thank the reviewer for the comment. We have tried to improve and simplify the referred session. See below.*

Specific comments:

Lines 241-251. Please indicate uncertainties in the iodine output rate of the permeation tube.

190 *We thank the reviewer for the suggestion. The permeation tube utilised in this study is homemade and does not possess the capability to calculate uncertainties. In this study, the instrument settings are kept constant to maintain a stable instrument condition. Consequently, the normalized I<sub>2</sub> signal's three times standard variation over a 10-hour period, with*



1-minute averaging of data, is approximately 1.5 %.

Line 209. Actually section 2.2.2 refers mainly to the development of an iodine source and quantification of its output rate, rather than calibration of the instrument as such, so I would suggest calling this section something in the line of “Development of an iodine source”.

*We thank the reviewer for the suggestion. We have changed the title of the section to **Development of an iodine source**.*

Line 276. There is a statement above saying that to quantify the concentrations of H<sub>2</sub>SO<sub>4</sub>, HOI, and HO<sub>2</sub>, a model was developed (line 192), but there is no description of why such a model may be necessary. I think the authors could have mentioned briefly radial diffusion, wall losses and secondary reactions of the precursor species that may interfere in the determination of the concentration of the analyte.

*We thank the reviewer for the comment. We have edited the statement accordingly.*

205

*The revised statement is: **L276-278: “As described above, calibration of H<sub>2</sub>SO<sub>4</sub>, HO<sub>2</sub>, and HOI requires a numerical model to simulate the radial diffusion, chemical reactions and transport in the calibration source and inlet tube. These processes determine the concentration of the analyte and can be simplified into a two-dimensional convection-diffusion-reaction problem.”***

210

Line 276. The term “chemical dynamics” is confusing in this context and does not represent what the code does, which appears to be chemical kinetics and transport rather than actual reaction dynamics.

*We thank the reviewer for the comment. We have changed the ‘chemical dynamics’ to ‘**chemical reactions and transport**’.*

215

Line 381. Please add an appropriate MESMER reference. I notice that these calculations were already reported by Finkenzeller et al 2022, and hence a reference to that paper should be enough.

*We thank the reviewer for the comment. We have added Finkenzeller et al. (2022) as an additional reference.*

Section 3.1. What is the difference between the H<sub>2</sub>SO<sub>4</sub> concentration calculated directly from initial OH and from the model? Figure 2 suggests that the losses of OH are minimal at the sampling axis. Does the MARFORCE model help to reduce uncertainty significantly? Similarly, the I<sub>2</sub> calibration scheme appears to be well designed to produce full conversion of OH into HOI in a large excess of I<sub>2</sub>. Does the model reveal any significant loss of OH that is worth considering?

*We thank the reviewer for the comment. The direct calculation of H<sub>2</sub>SO<sub>4</sub> concentration from the initial OH does not account for the radial diffusion of the analyte, unlike the model simulation. Apart from accounting for the chemical loss, the model incorporates and simulates the diffusion losses of OH, SO<sub>3</sub> and HSO<sub>3</sub> which reduce the uncertainty significantly.*

225

As an example, in the simulation presented in Figure 2, the initial OH concentration after photolysis is  $2.1 \times 10^8$  while the estimated  $H_2SO_4$  at the outlet is  $1.08 \times 10^8$ .

230 Unlike the  $H_2SO_4$  calibration, which commonly employs  $SO_2$  at levels around 1 ppmv, the HOI calibration utilises a typical  $I_2$  concentration of approximately 100 pptv. This disparity arises from Bromide-CIMS's heightened sensitivity to  $I_2$ , leading to potential reagent ion depletion and quantification challenges with excessive  $I_2$  presence. Consequently, the extended OH lifetime in the HOI calibration accentuates the significance of the MARFORCE model, amplifying its role in mitigating uncertainties associated with the calibration process.

235

Line 397. The readers of this paper will be most likely familiar with these “normalized ratios”, but for a more general audience please explain briefly what is the measured quantity that you are calibrating and why and how you normalize it.

240 *We thank the reviewer for the comment. We have revised the statement in line 397-399: **The actual  $H_2SO_4$  concentrations can be calculated by correlating the count rates, which represent the ratio of the measured  $H_2SO_4$  signals to primary ions. Subsequently, the predicted  $H_2SO_4$  concentrations are compared with the measured normalised signals to derive calibration factors.***

245 Table 1. What is the value in reporting detection limits for iodine oxides if they are based in mere estimated calibration factors as indicated in the table footnote? Where do these calibration factors come from?

250 *We thank the reviewer for the comment. The calibration factors used for the iodine oxides are based on the  $H_2SO_4$  calibration factors derived from two towers. This is because  $H_2SO_4$  is detected at maximum sensitivity, which can be used to estimate the concentration lower limits of iodine oxides. Therefore, the detection limits of iodine oxides can be higher than the predicted values. We have added clear clarification in the footnote of table 1:  **$H_2SO_4$  calibration factor is applied to estimate the detection limits for iodine oxides. Since iodine oxides may not be detected at the kinetic limit, their LODs are mere estimations and can be higher than the reported values in this study. The detection limits are estimated with 1-min data and one-hour data collection time.***

255 Figure 3. Regarding the curvature of the HOI calibration plots, I do not find the response to the previous reviewers or the modifications introduced in the manuscript very helpful. First of all, there is no mention to the curved calibration curves in the modified text. If the authors believe that this is a result of the sensitivity to water of HIO detection by Br- CIMS, they should explain how does this actually reflect in the curvature of the calibrations for Tower 1 and 2. Also, does it make sense to fit straight lines through the HIO log-log data? Why not a quadratic dependence?

260 *We thank the reviewer for the comment. The discussion about the humidity effect of HOI, which is the root of this curvature effect, exists in section 3.3. However, we agree with the reviewer that we should emphasize that the curvature is caused by the humidity effect. Therefore, we modified line 491 to: **Additionally, a longer ionisation time by utilising***

265 *the Br<sup>-</sup>-MION2-T2 results in a stronger detection humidity effect as shown in Figure 4. This phenomenon is the most significant for HOI, i.e., the detection of HOI is more humidity dependent using Br<sup>-</sup>-MION2-T2 than Br<sup>-</sup>-MION2-T1. This phenomenon also elucidates the curvature observed in the HOI calibration when employing the MION2-T2 (Figure 3): the diminished detection sensitivity of HOI counterbalances the augmented HOI production at elevated water content. .*

Line 638. Reaction (5) does not involve breaking multiple I-O and N-O bonds. It simply requires breaking a terminal I-O of I2O3 and forming a new I-O with halogen bonding character with the NO3 moiety, so I am not so sure why this should be less likely than proton transfer. Please rephrase or provide a more compelling argument.

*We thank the reviewer for the comment. We agree with the reviewer and deleted this statement as we believe other evidence is strong enough and a detailed evaluation using quantum chemical methods is not needed. We have modified and simplified the main text accordingly.*

275 Line 647. The main piece of evidence for reactions (5) and (6) is the recurrent observation of the conspicuous IONO<sub>2</sub>.NO<sub>3</sub>- signal (m/z=250.9), which has been reported in all previous field, laboratory and chamber nitrate CIMS work, but is not mentioned in this study. While in field studies (e.g. Baccharini et al. 2020) this signal could be indicative of ambient IONO<sub>2</sub>, in laboratory and chamber experiments it has been observed in the absence of NO<sub>2</sub> (all the works cited by the authors). What is the origin of this ion? This paper deals with a thorough experimental characterization of CIMS instruments, and therefore an investigation of such “measurement artefact” (Finkenzeller et al. 2022) could be expected in this section, not least because this signal could prove useful as a method to detect IONO<sub>2</sub> in the atmosphere. I would be interested in seeing a plot of IONO<sub>2</sub>.NO<sub>3</sub>- vs IO<sub>3</sub>- as those presented in Figure 9. That could shed some light on the origin of that signal (whose IONO<sub>2</sub>.Br- analogue is not observed in the Br- case, according to Finkenzeller et al. 2022).

285 *We thank the reviewer for the comment. The reviewer is right that IONO<sub>2</sub>·IO<sub>3</sub><sup>-</sup> is a measurement artefact in the nitrate chemical ionisation method. This artefact exists both in the ambient measurement and chamber experiments; so we respectfully disagree with the reviewer that Baccharini et al. (2020) indicates the ambient presence of IONO<sub>2</sub> in the high Arctic. The reviewer is also right that the bromide chemical ionisation method does not suffer from this artefact. As per the reviewer's request, we added the IONO<sub>2</sub>·NO<sub>3</sub><sup>-</sup> vs. IO<sub>3</sub><sup>-</sup> in Figure 9. The results show that IONO<sub>2</sub>·NO<sub>3</sub><sup>-</sup> does not come from iodic acid (HIO<sub>3</sub>·NO<sub>3</sub><sup>-</sup> and IO<sub>3</sub><sup>-</sup>), consistent with our conclusion. We added in the main text in line 677-679: Furthermore, if the proposed reaction 5 was to occur at a substantial rate, one would anticipate the IONO<sub>2</sub>·NO<sub>3</sub><sup>-</sup> signal to display a non-linear dependence on IO<sub>3</sub><sup>-</sup> and HIO<sub>3</sub>·Br<sup>-</sup>. However, this is not observed..*

295 Lines 650-653. The molecular parameters employed in this calculation are not provided by the authors, so I cannot reproduce it. Anyway, Finkenzeller et al. 2022 has reported this result already, and therefore I do not think it should be reported here again, specially considering that the uncertain PES does not enable a reliable determination of branching ratios using MESMER. For

saying something meaningful from a theoretical point of view a more in-depth analysis of the PES of this process is needed. I would just ignore this or refer to Finkenzeller et al. 2022.

300 *We thank the reviewer for the comment. We think it is worthwhile to provide this important information in this manuscript especially considering the PES has not been provided in Finkenzeller et al. 2022 and most of the information is buried in the supplementary information which is commonly ignored by most readers. However, we have simplified the referred content to make it concise and coherent to the manuscript.*

Lines 663-665. Finkenzeller et al. 2022 argues that HIO<sub>3</sub> originates from I<sub>2</sub>O<sub>2</sub>+O<sub>3</sub>+H<sub>2</sub>O, so please rephrase to indicate I<sub>2</sub>O<sub>y</sub> with y>2.

305 *We thank the reviewer for the comment. We have changed 'I<sub>2</sub>O<sub>y</sub>' to 'I<sub>2</sub>O<sub>y>2</sub>'.*

Lines 668-670. The authors say that they capitalise on the fact that IO is a good indicator of the intensity of atmospheric iodine activities (please reconsider the term “activities”) and that it influences the ratio of iodine oxides to oxoacids. But then they don't mention IO again. Please clarify. Have you used IO to tune the iodine concentration in the laminar flow tube experiments? Do you have evidence that from a certain IO concentration I<sub>x</sub>O<sub>y</sub> formation starts to dominate the signals? In 310 general, I think the description of the experiments could be better and that more juice could be extracted from the analysis of the data obtained.

315 *We extend our gratitude to the reviewer for their insightful comment. It is indeed accurate that we adjusted the IO concentration in our experiments to ensure comparability with marine boundary layer conditions. While direct IO calibration was not undertaken in our study, we have estimated that the IO concentrations at the lower end fall within the range of 0.66 pptv to 1.2 pptv, based on the H<sub>2</sub>SO<sub>4</sub> calibration. Additionally, drawing from our previous findings as outlined in Finkenzeller et al., 2022, we anticipate that the IO concentrations in our experimental setup remain below the 10 pptv threshold. This substantiates the alignment of our experiments with marine boundary layer conditions in terms of IO concentration.*

320 *In relation to the constituents I<sub>x</sub>O<sub>y</sub>, which encompass IO and OIO, not pertinent to iodine particle formation, it seems that the reviewer's mention pertains to I<sub>2</sub>O<sub>y</sub>. We want to emphasise that our observations do not indicate the prevalence of I<sub>2</sub>O<sub>y</sub> under all ozone concentrations, as illustrated in Figure 9, where I<sub>2</sub>O<sub>4</sub>·NO<sub>3</sub><sup>-</sup> was the dominant signal among the I<sub>2</sub>O<sub>y</sub> species.*

325 *We added in lines 669-670: **The concentrations of IO were carefully controlled to span from levels below to a few parts per trillion by volume levels.***

Figure 9. The top right panel is an important figure that shows a linear dependence between the IO<sub>3</sub><sup>-</sup> signal measured by nitrate CIMS and the HIO<sub>3</sub>.Br<sup>-</sup> signal measured by bromide CIMS. This would indicate in principle that both signals have the same origin and in that sense is very compelling. I would focus the discussion of this section mainly on these measurements.

330 We agree with the reviewer that the linear dependence between the  $\text{IO}_3^-$  signal with  $\text{HIO}_3 \cdot \text{Br}^-$  and  $\text{HIO}_3 \cdot \text{NO}_3^-$  is compelling. We have re-framed this section as **The concentrations of IO were carefully controlled to span from levels below to a few parts per trillion by volume levels. These experiments were replicated for both the  $\text{Br}^-$ -MION2-T1 and  $\text{NO}_3^-$ -MION2-T1, as depicted in Figure 9. The measured  $\text{IO}_3^-$  signal was compared with  $\text{HIO}_3 \cdot \text{NO}_3^-$  and  $\text{IONO}_2 \cdot \text{NO}_3^-$  signals from the  $\text{NO}_3^-$ -MION2-T1, and with  $\text{HIO}_3 \cdot \text{Br}^-$ ,  $\text{I}_2\text{O}_3 \cdot \text{Br}^-$ , and  $\text{I}_2\text{O}_4 \cdot \text{Br}^-$  signals from the  $\text{Br}^-$ -MION2-T1, in order to ascertain the source of  $\text{IO}_3^-$ . It is noteworthy that the gaseous signals of  $\text{HIO}_3$  ( $\text{HIO}_3 \cdot \text{NO}_3^-$  and  $\text{HIO}_3 \cdot \text{Br}^-$ ) exhibit a perfectly linear relationship with the  $\text{IO}_3^-$  signals. However, the signals of  $\text{IONO}_2 \cdot \text{NO}_3^-$ ,  $\text{I}_2\text{O}_3 \cdot \text{Br}^-$ , and  $\text{I}_2\text{O}_4 \cdot \text{Br}^-$  demonstrate a non-linear dependence on  $\text{IO}_3^-$ . This observation implies that the primary source of  $\text{IO}_3^-$  is gaseous  $\text{HIO}_3$ , as a non-linear correlation between  $\text{HIO}_3 \cdot \text{NO}_3^-$ ,  $\text{HIO}_3 \cdot \text{Br}^-$ , and  $\text{IO}_3^-$  would be expected if  $\text{I}_2\text{O}_{y>2}$  significantly contributed to  $\text{IO}_3^-$ . Furthermore, if the proposed reaction 5 were to occur at a substantial rate, one would anticipate the  $\text{IONO}_2 \cdot \text{NO}_3^-$  signal to display a non-linear dependence on  $\text{IO}_3^-$  and  $\text{HIO}_3 \cdot \text{Br}^-$ . However, this is not observed.**

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Why do the bromide CIMS signals stop at Norm.  $\text{IO}_3^-$  signal = 0.015 cps cps<sup>-1</sup>? Where are the bromide CIMS data corresponding to the highest ozone nitrate CIMS data in the top left panel?

345 We thank the reviewer for the comment. The experiments for Nitrate-CIMS and Bromide-CIMS are conducted separately. In the bromide CIMS experiment, the ozone concentration ranges from 2.7 ppb to 539 ppb, which corresponds to the  $\text{IO}_3^-$  signal ranging from 0.002 to 0.015 cps cps<sup>-1</sup>.

Lines 680-683. The water-mediated reactions producing oxoacids may go at a faster rate than the iodine oxide recombination reactions for very low iodine concentrations. But still,  $\text{HIO}_3$  nucleation is not very favourable energetically and the authors have proposed in previous work “a critical role of  $\text{HIO}_2$ ” in stabilizing the  $\text{HIO}_3$  clusters (Zhang et al. 2022).  $\text{HIO}_2$ , which has an uncertain origin in the atmosphere as  $\text{HIO}_3$ , is measured at very low concentrations by CIMS, but of the same order of magnitude than those of  $\text{I}_2\text{O}_3$  and  $\text{I}_2\text{O}_4$ . Can we then rule out that  $\text{I}_2\text{O}_3$  and  $\text{I}_2\text{O}_4$  affect the formation of particles under boundary layer conditions even though they are at low concentrations? Admittedly, this discussion goes beyond the scope of the paper, but I would suggest the authors to smooth their statement if they choose to keep this section.

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We express our appreciation to the reviewer for their insightful input. While it is true that concentration plays a significant role in atmospheric aerosol nucleation, it is not the sole determining factor. An equally, if not more crucial consideration could revolve around the bond energies within dimer clusters, such as  $\text{I}_2\text{O}_4 \cdot \text{HIO}_3$  versus  $\text{HIO}_3 \cdot \text{HIO}_2$ . Addressing the reviewer's observation, we have conducted comprehensive calculations involving the  $\text{HIO}_3 \cdot \text{HIO}_2$  system, which have been thoroughly documented in our recent publication (Zhang et al., 2022). These calculations underscore the noteworthy role that  $\text{HIO}_2$  assumes as a stabilising influence for  $\text{HIO}_3$ .

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While the data have not been presented in this context, we have indeed performed calculations on the bond energy of  $\text{HIO}_3 \cdot \text{I}_2\text{O}_4$ , revealing a notably lower (and hence less stable) energy state when compared to  $\text{HIO}_3 \cdot \text{HIO}_2$  (unpublished, precise figures withheld). This outcome aligns harmoniously with the findings reported in Gómez Martín et al. (2020),

365 which propose a bond energy of  $104 \text{ kJ mol}^{-1}$  for  $\text{HIO}_3 \cdot \text{HIO}_2$  and  $94 \text{ kJ mol}^{-1}$  for  $\text{HIO}_3 \cdot \text{I}_2\text{O}_4$ . Given that a variance of  $1 \text{ kcal mol}^{-1}$  (equivalent to  $4.184 \text{ kJ mol}^{-1}$ ) in bond energy typically corresponds to an order of magnitude alteration in cluster evaporation rate, it is reasonable to anticipate that  $\text{HIO}_3 \cdot \text{HIO}_2$  cluster formation surpasses  $\text{HIO}_3 \cdot \text{I}_2\text{O}_4$  cluster formation, especially when  $\text{HIO}_2$  concentration mirrors that of  $\text{I}_2\text{O}_4$ .

In addition to this theoretical analysis rooted in published outcomes, we are presently engaged in an ongoing investigation  
370 that studies the respective roles of  $\text{I}_2\text{O}_4$  and  $\text{HIO}_2$ , leveraging data from the CLOUD experiments. The results we have thus far agree well with the conclusions within this section, particularly when considering the context of our limited focus on marine boundary layer conditions.

Summary. Rather than changing the name of the section following the comment by a previous reviewer, I think the authors  
375 should try to draw some conclusions from their work. The final summary section is very similar to the abstract.

*We thank the reviewer for the comment. We have edited the Summary thoroughly.*

Table A1. Replace the equal signs by arrows.

*We thank the reviewer for the comment. We have changed the equal signs to arrows.*

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Figure A8. I don't find this figure particularly useful for a paper in AMT. Remove?

*We thank the reviewer for the comment. We have removed Figure A8 from this paper.*

## References

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