

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

Xu-Cheng He^{1,2}, Jiali Shen¹, Siddharth Iyer³, Paxton Juuti⁴, Jiangyi Zhang¹, Mrisha Koirala⁵, Mikko M. Kytökari⁵, Douglas R. Worsnop^{1,6}, Matti Rissanen^{3,5}, Markku Kulmala^{1,7,8,9}, Norbert M. Maier⁵, Jyri Mikkilä⁴, Mikko Sipilä¹, and Juha Kangasluoma^{1,4}

¹Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, 00014 Helsinki, Finland

²Finnish Meteorological Institute, 00560 Helsinki, Finland

³Aerosol Physics Laboratory, Faculty of Engineering and Natural Sciences, Tampere University, 33014 Tampere, Finland

⁴Karsa Ltd., 00560 Helsinki, Finland

⁵Department of Chemistry, Faculty of Science, University of Helsinki, 00014 Helsinki, Finland

⁶Aerodyne Research, Inc., Billerica, 01821 MA, USA

⁷Helsinki Institute of Physics, University of Helsinki, 00014 Helsinki, Finland

⁸Joint International Research Laboratory of Atmospheric and Earth System Sciences, School of Atmospheric Sciences, Nanjing University, 210023 Nanjing, China

⁹Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, 100029 Beijing, China

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

5 Responses to reviewer1

In "Characterisation of the multi-scheme chemical ionisation inlet-2 and the detection of gaseous iodine species", authors Xu-Cheng He and co-workers describe a new version of an inlet (MION) for chemical ionization mass spectrometry (CIMS) that allows for switching between multiple schemes and reaction times. Overall, they are presenting careful work that employed
10 scientifically sound and appropriate methodology. Its findings will be very interesting for the CIMS community, especially of course if using a MION inlet or similar. Unfortunately, the manuscript itself was not prepared as carefully.

*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
15 addressed below.*

General positive points are the abstract, which I believe provides a good summary (except for some ambiguities noted below), as well as the figures, which are of mostly easy to read and of high quality and well-chosen by their relevance to the presented research.

20

We thank the reviewer for the positive feedback on the abstract.

However, for an AMT paper introducing a new CIMS inlet, its description is confusing and substantially lacking important details, as I try to elaborate in my detailed comments. This deficiency is most apparent in Section 2 (Methods), but found also in some parts of Section 3 ("Results") where additional experimental and analytical methodology are described.

25

We thank the reviewer for this comment. We have tried to incorporate more details about MION2 in the revised manuscript.

In addition, the text will need some proofreading/copy-editing to deal with numerous grammatical errors. Some semantic errors disrupt the reading as well. Nonetheless, the text is in principle understandable.

30

For these reason, I suggest to reconsider the manuscript only after major revisions.

[Disclaimer: I do not feel qualified to judge the various methods used for the DFT calculations (Section 2.4).]

35

We thank the reviewer for the thoughtful reading. We have tried to improve the quality of the writing in the revised version.

Specific comments:

40

Title: Much of this study deals with the Br⁻ ionization scheme, and indeed provides useful insights into that specific scheme in particular, applicable also beyond the MION inlet systems. NO₃⁻, for the most part, is rather used as a reference. Anyway, I would point that out already in the title. E.g., "... using Br⁻ as reagent", or "... using Br⁻ and NO₃⁻ as reagents".

*We thank the reviewer for the constructive comment. We have changed the title to "**Characterisation of the multi-scheme chemical ionisation inlet-2 and the detection of gaseous iodine species using bromide and nitrate chemical ionisation methods**"*

45

Abstract: I suggest disclosing somewhere near the beginning that MION inlets operate (or are at least designed to operate) at atmospheric pressure.

50

Thanks for the comment. We now clearly suggest that MION inlet utilises atmospheric pressure chemical ionisation methods in the abstract.

55 *The revised statement is: **L2: “... using various atmospheric pressure chemical ionisation methods.”***

L4 (abstract): "generally more robust operation" ... please be more specific.

60 *Thank you for the feedback. We have made revisions based on your comments. Instead of using “generally more robust operation”, we have modified the wording to “**a robust operation**”. Additionally, we have included additional information in the Methods section (L146-154) regarding our recent field campaign conducted at a coastal observatory in Finland. During this campaign, the inlet demonstrated stable operation for a minimum duration of two months.*

L20 (abstract): Should specify if the detection limit for H₂SO₄ is achieved via Br⁻ or NO₃⁻ reagents (or both).

65 *We have added that this was measured with the Br⁻ chemical ionisation method.*

*The revised statement is: **L22: “For instance, when using the Br⁻ chemical ionisation method with a 300 ms ionisation time, the estimated detection limit for H₂SO₄ is 2.9×10^4 molec. cm⁻³.”***

70 L22 (abstract): again, "generally more robust" is too vague.

Thanks for the comment. We now deliberately state that humidity has a minor impact on the nitrate chemical ionisation method.

75 *The revised statement is: **L25: “While the NO₃⁻ chemical ionisation method remains stable in the presence of high humidity...”***

80 L95-102: Somewhat confusing description of the MION inlet. Not the only issue, but also: is "reaction time" the same as "ionisation time"? Most critically maybe: how does MION2 allow for two CI methods with same reaction time, and why was that not possible with the MION1? Please clarify.

85 *The response time and ionisation time were previously used interchangeably. We have now replaced all instances of "response time" with "ionisation time" for consistency. The reason MION1 could not accommodate two CI methods with the same ionisation time was due to the geometry of the MION1 tower (the ionisation source), which did not allow for aligning multiple ionisation sources at the same distance from the instrument pinhole. The ionisation source has been*

optimised, enabling us to align three ionisation sources at the same distance from the instrument. We have now added a description of the optimised geometry in the main text (L112-117).

90 After also checking Fig. 1, I think I get it. But now I wonder why only two CI at the same time (and same reaction time) (L101), and not three? (Or even six, if the polarity can be switched quickly as well, which remains unclear. And does "two or more (up to six)" simply mean "up to six" or something more elaborate, possibly including limitations regarding reaction time choice as in MION1?)

95 *The MION2 does allow operating three ionisation methods at the same time. To avoid the confusion, we have deleted the redundant sentence: **Therefore, the new design of MION2 allows it to operate two chemical ionisation methods with the same ionisation time to allow a direct comparison which was not possible with the MION1.***

*The inlet design itself would allow more than 6 ionisation sources to be connected together. (Rissanen et al., 2019) has described the fast reagent ion switching within a second which is not a limitation. Therefore, the MION2 can deploy more ionisation sources if needed. However, since MION2 is a commercial chemical ionisation inlet, the current design considers the need of the majority of customer body. We have now changed the wording from "up to six" to **currently supports up to six ion sources**"*

105 Fig. 1: I suggest to indicate the directions of the various flows, to make the drawing easier to comprehend.

Agreed. We have added red arrows to indicate the directions of the flows in Figure 1.

L108: How was the sample flow provided?

110

The sample flow is sucked into the inlet through a mass flow controller, by a vacuum pump. It is now added in the main text.

*The revised statement is: **L126-128: "The sample flow, which is provided by a mass flow controller connected to a vacuum pump, is set at a rate of 22.5 standard litres per minute (slpm). The target molecules undergo ionisation by reacting with the reagent ions (NO_3^- or Br^-)."***

L110-122: What are typical/required/desired reagent flows, reagent concentrations, and purge flow(s!)?

120 *The typical values for reagent, purge and exhaust flows are 10, 100 and 50 standard cubic centimeter per minute. Therefore, the typical reagent concentration in the ion source is around $2 \times 10^{17} \text{ cm}^{-3}$. This information is added in the*

main text.

125 The revised statement is: **L146: “In MION2, the typical flow rates for the reagent, purge, and exhaust are 10, 100, and 50 sccm, respectively.”**

Also, how are the reagent concentrations facilitated?

130 The reagent gas is provided by passing the reagent flow over liquid CH_2Br_2 . It is now described in the main text.

The revised statement is: **L131-132: “A neutral reagent inflow is introduced, which consists of nitrogen or air enriched with reagent vapour. The reagent vapour is generated by passing nitrogen or air over liquid reagent (nitric acid, HNO_3 , or dibromomethane, CH_2Br_2 , in this study).”**

135 Fig. A1 is missing the "purge flow" (and L119-122).

We have added the purge flow in Figure A1.

140 L124-125: How is that "operational stability" manifest or determined? If elaborated on later, please state so. If not, be more specific.

We have now added detailed description about the stability of MION2. Briefly, we carried out ambient measurement at a coastal observatory in Finland and the MION2 had an uninterrupted operation for more than two months.

145 The revised statement is: **L152-154: “Operational testing during ambient measurements has demonstrated that MION2 exhibits significantly improved stability compared to MION1. For example, recent measurements at a coastal site in Finland involved the uninterrupted operation of MION2 for at least two months.”**

150 L125-127: How have the ion optics been upgraded? I am not expecting much details, but at least some indication of what type of effort was undertaken and required to increase "reagent ion transmission" (by which the authors might actually mean the amount of reagent ions ending up being detected)?

The shape of the last electrode was modified such that there is a shorter distance of zero electric fields, which reduces the ion diffusion losses in that piece thanks to the larger drift velocity and shorter residence time.

155

The revised statement is: **L156-159: “Additionally, the upgraded ion optics inside the ion sources of MION2 have increased the transmission of reagent ions and the observed reagent ion concentration at the mass spectrometer by approximately one order of magnitude compared to MION1. This improvement was achieved by modifying the last electrode within the ion source to minimize ion residence time and reduce diffusion losses of ions.”**

160

Section 2.2.1: What exactly is the "calibration source"? It is referred to multiple times, but never actually specified what it is, except that OH radicals are generated "in it", or how it connects to other parts of the setup. (For example, are the OH radicals actively mixed into that SO₂- and I₂- containing gas mixture, or is the gas mixture going through a region where OH radicals is generated, and the "source" is the sum of something like that?)

165

Similarly, Fig. A2 simply refers to a mysterious "calibration box".

"calibration source" refers to a setup that produces a stable source of H₂SO₄, HOI, and HO₂. It is an aluminum box with a hole that allows a 3-quarter-inch stainless steel tube to go straight through it and connect to the instrument inlet via a Swagelok union. Inside the box, a 3/4 inch quartz tube is connected to the stainless-steel tubes at both ends, which has a high transmission for UV light emitted from the mercury lamp. Adjacent to the quartz tube, the mercury lamp is housed by an aluminum block that has a filter-covered hole. The filter used in the block enables high transmission for 185 nm light emitted from the lamp, which photolyses H₂O to form OH radicals. Prior to the calibration experiment, a mixed flow of N₂, O₂, H₂O, and either SO₂ or I₂ continuously flushes the calibration source. With the lamp on, OH radicals are generated in the mixture

175

*Since the principles of the calibration source is described in detail elsewhere (Kürten et al., 2012), we briefly describe it in section 2.2.1. **L179-184: “The calibration source in the experimental setup was constructed using an aluminum box that encloses a 3-quarter-inch quartz tube. The quartz tube was chosen for its high transmission properties for ultra-violet (UV) light emitted from a mercury lamp. Adjacent to the quartz tube, the mercury lamp is housed in an aluminum block that contains a filter-covered hole. The filter used in the aluminum block allows for high transmission of 185 nm light emitted from the lamp. This specific wavelength of light is effective in photolysing water (H₂O) molecules, generating OH radicals.”***

185

Section 2.2.2: 1st paragraph is a general introduction to the problem that may fit better to the Introduction section.

Agreed. We have moved and incorporated the 1st paragraph into the introduction (L64-69).

Section 2.2.2: Unclear what was done why, and how the I₂ was ultimately supplied during the MION calibration experiments. For example, was the permeation tube output used directly, and the process from dissolution in hexane to quantifying a concentrated solution of the derivative was only to gain knowledge of the I₂ permeation tube output rate? (Which is presented

190

as the conclusion of the main paragraph.)

Agreed. The statement about how we process the I₂ calibration is not clear enough. We have added the following sentences in section 2.2.2. to clarify this.

195

*The revised statement is: **L210-213: “To calibrate the measured signals of I₂·Br⁻ in Br⁻-MION2, we acquired its stable signals by utilising I₂ emitted from a permeation tube, which was regulated at a constant temperature and subjected to a continuous nitrogen stream (50 sccm). The key to this calibration is determining the quantities of I₂ emitted from the permeation tube.”***

200

Eq. 1: Q is not defined.

*Thanks for the comment. We have now defined the Q below equation 1. **L291: “Q is the total flow in the flow reactor”***

205

Table 1, Section 3.1: Detection limits are given for MION2/T1, MION2/T2 and Eisele inlets. But for H₂SO₄, either NO₃⁻ or Br⁻ were used on MION2/T1, so, which reagent ion do the reported detection limits correspond to? And the Eisele inlet presumably used NO₃⁻? If so, is there a reason that the NO₃⁻ scheme with MION2 was not tested for HIO₃, as the Eisele inlet was?

210

*Thanks for the comment. The reported detection limits in Table 1 for MION2 referred to the Br⁻ mode. We have compared these results with different reaction times (Tower1 and Tower2). To avoid confusion, we now specify the reagent ions in Table 1 by adding “**MION2 (Br⁻)**” and “**Eisele inlet (NO₃⁻)**”. It should be noted that HIO₃ has not directly been calibrated, all previous and current studies transferred the calibration factor of H₂SO₄ to HIO₃ because both species are detected at the collision limit. The reported calibration coefficients are only for those species which are directly calibrated. On the other hand, the limit of detection is estimated for species that are not calibrated too, by assuming they are detected at the collision limit. We have now added a note about the LOD estimation in **L559-560: “The species without direct calibration utilise the calibration coefficient of H₂SO₄, thus the LODs for these species generally represent the lower limit.”***

215

Also, it is unclear at this stage what is meant by "APi1" and "APi2".

220

The parts related to APi2 have now been removed from this manuscript since it is much clearer this way.

L344: Is fragmentation at atmospheric pressure (as opposed to only in the ion optics) responsible for the HO₂ cal factors for T1 vs T2 being only a factor of 2.3 apart?

225

The main reason for this is the detection humidity effect. As can be seen in Figure 4, the detection of HO₂ is greater with the Br⁻-MION2-T2 than Br⁻-MION2-T1. This effect reduces the difference in calibration factors between using Br⁻-MION2-T2 and Br⁻-MION2-T1.

230 L360: I am not following the final sentence. As the authors just pointed out, they found (experimentally) that more strongly fragmenting instrument settings reduced sensitivity to HOI, agreeing with somewhat weaker binding between reagent and analyte, compared to the H₂SO₄ case, expected theoretically. So, why would one anyway blame "iodine chemistry schemes" or "differences in experimental conditions"? As those terms are rather vague, I may just misunderstand what is being pointed at. (Oh, is it differences in chemistries between the cited studies and this study?)

235

Thanks for the comments. The original aim of the description is to compare two different factors in our earlier calibration experiments and the current one: 1) the instrument setting and 2) the different iodine chemistry schemes used in the calibration codes. In earlier parts of this paragraph, we have compared the effect of the different iodine chemistry schemes and found that the chemistry schemes introduced minimal differences (0.1 - 0.7%). Therefore, we concluded

240 *that instrument tuning is the reason why we observed different calibration factor ratios of HOI to H₂SO₄ in Wang et al. (2021) and this study. However, we agree with the reviewer that this may complicate the discussion here and we decided to remove the discussion about the effect of chemistry schemes since its effect is minimal.*

L383: Please provide a reference to that "earlier study".

245

*Thanks for the comments. We have changed the "earlier study" to **Wang et al. (2021)**.*

L420: I disagree with the implication of the first half of this sentence. I agree that, for instance, within a typical day, ambient absolute humidity often does not vary by very much. But within, say, a week, one would expect substantial variations. And

250 more so the longer of a time period is being considered...

We agree with the reviewer's concern and have modified the sentence to provide a more accurate recommendation.

*The revised statement is: **L486-488: "Based on our findings, we anticipate that the detection humidity effect of H₂SO₄ would be moderate when the dew point is below approximately 7.6 °C. However, it is important to exercise caution when conducting measurements under higher absolute humidity conditions."***

255

Section 3.4: Figure A9 needs some more explanation, maybe via annotations in the figure (photo). Unclear what is what.

260 *Thanks for the comment. We have replaced Figure A9 with a schematic figure to better demonstrate its functionality. As shown in Figure A9, this core-sampling piece features three ports for the dilution flows, which, when combined with the sample flow, undergo thorough mixing.*

Section 3.5: I appreciate that experiments were carried out using two independent detectors and sample sources. But the
265 discussion of the respective differences is awfully short. (And merely from a statistics point of view, a sample size of two is not that much better than a sample size of one.) Hence, is there anything useful to say about differences between APi1 and APi2 (or APi3 for that matter), beyond time since service? E.g., details on tunings, or purity of gas or calibrant supplies, etc.?

*We thank the reviewer for this constructive comment. We agree with the reviewer that two samples are not that much
270 better than one sample. Therefore, we have removed all the contents about APi2 from the manuscript. In this way, the detection limit section is clearer now. The important message from our exercise with a separate APi-TOF is that our results are repeatable.*

L553: How was DeltaV50 determined? The shapes of the signal-remaining curves (Fig. 6) indicate that for several species
275 the maximum is not obtained at the lowest tested DeltaV. The clearest case is H2O, for which the signal-remaining drops to 50% at 3-4V, but the curve is steep and a higher reference value (signal-remaining = 1) would likely be obtained at yet "softer" settings (e.g., DeltaV < 2V). Correspondingly, if dV50 is simply the 50% point from Fig. 6, I expect several points in Fig. 7 being "too high".

280 *The dv50 is not derived from a simple 50% point from the figure. It is fitted using a sigmoidal shape curve as it was in the original paper (Lopez-Hilfiker et al., 2016). The sigmoidal fit equation we used is:*

*The revised statement is: **L610-614:**"In this study, the dV_{50} is defined by the following equation:"*

$$NSR = \frac{SR}{1 + e^{-k \times (dV - dV_{50})}} + SR_{max,pred}$$

285

where NSR is the normalised signal remaining, SR is the signal remaining, dV_{50} is the desired fitted value as represented in Figure 7 and $SR_{max,pred}$ is the fitted value that represents the maximum SR when a compound does not undergo fragmentation while passing through the ion optics.

290

Fig. 7: It would be very useful if the same color coding was used in Figs. 6 and 7, i.e., same color for same species.

Agreed. We have now changed all the color coding and shape for Figures 6 and 7 to ensure that the color and marker for the same species are consistent.

295

Section 3.7: L568 vs L580 appear to contradict each other, even though using same reference. Is Reaction 4 exo- or endothermic?

300 *Thanks for bringing up this point. The reactions of IO_3^- and I_2O_{2-3} are exothermic while the reaction of IO_3^- and I_2O_4 is endothermic. We now clearly separate the discussions of I_2O_{2-3} with I_2O_4 in the main text. Additionally, we corrected the typo in the current reaction 5 from I_2O_4 to I_2O_3 .*

Section 4 ("Conclusions"): This Section is really a summary of the results and the major discussion points presented in Section 3. With the exception of one or two sentences, it does not provide any new discussion nor actual conclusions. Consequently, it should be named accordingly. (Whereas Section 3 would be more aptly named "Results and Discussion".)

305

We agree with the reviewer and have changed the section titles to "Results and Discussion" and "Summary", respectively.

310 Technical comments:

L14: More correct, I believe, to write "We calibrated for [...]"

We added "for" in the abstract.

315 L34: "spectrometer" -> "spectrometry" (for grammar)

We corrected for this grammar problem.

L38: missing article ("forming a relatively")

320

We corrected for this grammar problem.

[I will stop commenting on grammatical errors (or semantical errors or typos). Some proofreading/copy-editing service will be more suitable.]

325

We thank the reviewer for his careful reading. We have tried to improve the text accordingly.

L81: I assume the authors mean the LOD is higher (hence worse), not lower

330 *The reviewer is correct and we have corrected this error.*

Fig. A2: stain -> stainless

The reviewer is correct and we have corrected this error.

335

L150: "calibrator" or "calibration"?

The reviewer is correct and we have corrected this error.

340 L238-239: I am counting three ways, not two.

The reviewer is correct. We now clearly define the third way as suggested.

Reviewer 2

345

The manuscript "Characterisation of the multi-scheme chemical ionisation inlet-2 and the detection of gaseous iodine species" by He and coworkers presents an upgraded version of the multi-scheme chemical ionization inlet including development of a model for gas kinetic studies related to the characterization of the inlet. In addition, it presents a case study for the measurement of iodine compounds using this new inlet.

350 In general, the topic is well suited for publication in AMT. However, the manuscript in its current form needs some rework prior to this.

There are some parts of the manuscript that are well written, but others are confusing or lack proper descriptions or explanations. The same applies to some figures. The language of the manuscript also needs intensive and proper proof reading in parts. Thus, I have refrained mostly from correcting grammatical errors.

355

We thank the reviewer for carefully evaluating this manuscript and we have tried to improve the quality of writing.

Specific comments:

360 L98-L100: The description of the geometry and the inlet is not represented in Figure 1. For readers unfamiliar with the inlet system of Aerodyne/ToFwerk CIMS instruments it might be difficult to picture what the authors describe (e.g., distance from injection port to pinhole).

Agreed. We have now added information on the distances between the injection port of Tower 1/2 and the pinhole, as well as the inner diameter of the sampling tube.

365

L101ff: How is this achieved? And how do you define reaction time? Please clarify!

The ionisation time (reaction time) is defined by the sample flow rate and the distance from the ion injection port to the instrument pinhole. In the MION2, three ionisation sources can be mounted around the inlet tube, i.e., the injection ports have the same distance to the instrument pinhole. We have now added descriptions about this feature in the Methods part.

370

*The revised statement is: **L125: “Figure A1 illustrates the conceptual schematic of one of the ion sources, depicting the airflow and ion paths.”***

375 L103ff: Is 25cm the standard configuration for the connecting pipe between the two sources, or why was this length used in this work?

The distance is adjustable by using different connection tubes with varying lengths. The 3cm one (T1) has a much shorter ionisation time compared with the Eisele inlet (Jokinen et al., 2012) and we had to use an extension to increase the ionisation time so that a fair comparison could be made. The 25cm one chosen in this study was simply because this was readily available to us during our experiment.

380

L139: Bubblers tend to produce not only gaseous water vapor but also micro droplets, which could act as sink for trace gases. Was there a filter/trap to prevent possible droplets from entering the sample gas stream?

385

Thanks for bringing up this point. We do not have a filter/trap installed after the bubbler to prevent possible droplets. To minimize the possibility of droplets, we utilised two bubblers: one for small flows, with a maximum of 2 slpm passing through, and another one for flows larger than 2 slpm. The latter is a large stainless steel tank connected by a ca. 1.5 m long bended tube to our experiments which prevent droplets from entering our experiments. It should be noted that regular check-ups of the connection pieces were carried out in our experiments and we never observed signs of water deposition. Therefore, we believe that the possibility of droplet formation in this study is extremely low.

390

L212: What was the inner diameter and residence time inside the quartz tube?

395 *The inner diameter of the quartz tube is 24 mm, which is the same as the stainless steel tube. This is essential to ensure a laminar flow without any development of secondary flows due to wall detachment. We now have added this*

statement: **L270: “The residence time inside the quartz tube is 8.5 s.”**

400 L213: What is the wavelength of the used LED(s)?

The main wavelength of the used LED is 528 nm.

405 L263: What is the "It-product"? Please shortly mention the definition for the general reader. In your phrasing the time dependence is completely omitted.

Thanks for the comments. "It-product" refers to the product of UV light intensity at 185 nm and effective illumination time. In this study, we derived the It-product from the N₂O experiment, which was conducted under the same conditions as the H₂SO₄ calibration experiments. The mercury lamp (UVP Pen-Ray) used in the experiments has a potential lifetime of up to 5000 hours when operated correctly. Considering that the experiment time for a H₂SO₄ calibration is only a few
410 *hours, we can assume that the attenuation of the it-product over time in this study is negligible.*

*The revised statement is: **L322-324: “It-product refers to the product of UV light intensity at 185 nm and effective illumination time. In this study, we derived the It-product from the N₂O experiment, which was conducted under the same conditions as the H₂SO₄ calibration experiments. The details of the It-product determination can be***
415 ***found in Kürten et al. (2012).”***

L269: Rephrase "... 1) simulating connected two flow reactors ...".

*Thanks for the comment. We have now edited the sentence to **L338: "... 1) simulating two connected flow reactors***
420 *..."*

Table 1: What is the difference between APi1 and APi2 for Tower 1?

The parts related to APi2 have been removed from the revised manuscript upon reviewer1's request to simplify this
425 *manuscript.*

Table 1: How do reaction times of the towers compare to reaction times typically for an Eisele inlet?

We have included the reaction times for two MION2 towers, as well as the typical Eisele inlet in Table 1.

430 Figure 3: Why is it that the measured values for HOI deviate from the line fit at the lower end, and in every case in the same way (in this figure as well as well as in Figure A7)? Is it because those measurements are close to the LOD?

435 *Thanks for the comment. The main reason for this phenomenon is that HOI detection is more strongly affected by humidity when using the MION2-T2. It is clear from Figure 4 that when using the MION2-T2, HOI detection is more strongly affected than when using MION2-T1. This indicates that we should use the MION2-T1 to measure HOI, which was always the case in our current and previous studies. We have now emphasised this phenomenon in the main text.*

440 *The revised statement is: L491-492: “This phenomenon is the most significant for HOI, i.e., the detection of HOI is more humidity dependent using Br⁻-MION2-T2 than Br⁻-MION2-T1.”*

L344: “. . . will be shown . . .”: Please change wording to point directly to the appropriate section.

We have now changed to L412: “as the humidity effect of HO₂ will be shown to be strong in section 3.3”

445 L355: What is the “signature of HOI”? I guess, what you want to say, is that a fraction of HOI*Br⁻ is de-clustered or loses its charge. Please rephrase.

450 *Thanks for the comments. We have now edited the statement to L419-420: “The preferred fragmentation pathway is HOI·Br⁻ → HOI + Br⁻ (Table 2), and thus a fraction of HOI·Br⁻ dissociates into HOI and Br⁻ after passing the ion optics of the mass spectrometer.”*

L357: “. . . a relatively fragmenting . . .” Relatively fragmenting compared to what? Please rephrase.

455 *Thanks for the comments. We have now edited the statement to L422-424: “As an example, in our earlier studies (Tham et al., 2021; Wang et al., 2021), we used a relatively fragmenting setting compared to the one used in this study in an attempt to reduce (H₂O)_n·Br⁻ clusters and other water-associated clusters.”*

L390: What does “relatively easier” mean?

460 *Unlike H₂SO₄, HO₂, and HOI, both SO₂ and I₂ have their standards, making them much easier to control in RH effect experiments.*

We have now edited the statement: L456-457: “Unlike H₂SO₄, HO₂ and HOI, which require generation from a calibration source, both SO₂ and I₂ have their own standardised sources. This simplifies their control during the

465 ***characterisation of the detection humidity effect.”***

L403: “Despite . . .” please rephrase this sentence, it is difficult to understand.

470 ***We have now edited the statement: L470-472: “Although only five species were characterised and observed for their distinct humidity sensitivity, a general conclusion can be drawn that applies to essentially all of the species: an excessive amount of water content leads to a decrease in detection sensitivity.”***

L406: What do you mean with “humidity tolerance”? Please rephrase.

475 ***We have now edited the statement: L472-474: “The species with stronger binding with Br⁻ exhibits less sensitivity to changes in humidity (e.g, H₂SO₄ and I₂), while the weakly bonded ones (HOI, SO₂ and HO₂) are strongly affected.”***

480 L414: If the H₂SO₄ is lost to the walls it is effectively removed from the gas phase and can as such no longer be detected by any method. I would not call that a systematic error.

We agree with the reviewer and changed the wording about this factor.

485 ***The revised statement is: L481: “This is a universal factor that influences all H₂SO₄ detection techniques with appreciable sampling line residence time.”***

L425ff: Isn't the consequence then to not use Br⁻ for the more distant MION source?

The reviewer is correct. We now added clarification to this in the main text.

490

The revised statement is: L492-494: “Although this effect is difficult to quantify, it practically suggests that the Br⁻ chemical ionisation method should employ a shorter ionisation time (i.e., using the tower 1) when operating MION2 with multiple chemical ionisation methods.”

495 L458ff: How do your findings regarding dilution and the detection of SO₂ fit to your previous statement in L440? Or was that statement exclusively for a low-pressure system?

That statement was specific to species that are detected at the kinetic limit (e.g., I₂, HIO₃ and H₂SO₄. We clarified this statement now.)

500

*The revised statement is: **L527-529: “However, since the detection humidity effect for SO₂ is significantly higher than other species (e.g., H₂SO₄, HOI and I₂), the dilution is still effective for SO₂ measurement. ”***

L491: What does this sentence mean? Can one lower the detection limit by a more thorough analysis of the obtained data, or is it possible to “guess” concentrations of specific compounds even below the LOD? What would be the significance of such an educated “guess”?

Thank you for your comment. We have removed this sentence.

510 L495: What is the “softness” of the tuning of the MS system?

*The ‘softness’ of tuning refers to the optimization of voltage settings for the ion optics. This optimization aims to enhance the transfer of the ions clusters, formed from reactions between analytes and reagent ions, to the detector in the mass spectrometer. We have edited this to **L567: “the fragmentation level (controlled by the tuning of the instrument) of the mass spectrometer”***

515

L496: What significance does a LOD determination at optimum conditions have if the actual measurement conditions deviate strongly from those conditions?

520 *Our statement and data indicate that the determination of LOD for Br⁻ chemical ionisation should take the humidity of the sample air into account. This consideration is crucial for accurately reporting the data. For species that are detected at the collision limit (e.g., I₂, H₂SO₄ and HIO₃), the LODs are indicative for humidity below ca. 40 %. For other weakly-bonded species, providing LODs at a specific humidity can give guidance for controlled laboratory experiments.*

525 L499: The explanation for APi1 and APi2 needs to be given in Table 1 too!

Thanks for the comment. The APi2-related content has been removed from the manuscript.

L511: I do not understand why getting similar LODs from both the MION1 and the MION2 system suggests that the newer one is an improvement over the older one (regarding the LODs). This could also be simply an issue of instrument performance.

530

Thanks for the comment. We have removed related discussions.

L520: Are you making a point that your MS systems were not well performing?

535

Yes, the detector of APi-TOF used in this study had degraded over time. Therefore, it was not under optimal conditions. The LOD estimations in this study may be conservative estimates.

L521ff: “Nevertheless, the achieved...” I believe this sentence is quite questionable.

540

Thanks for the comment. We have re-written this sentence.

*The revised statement is: **L578-580: “Nevertheless, the attained levels of LOD are sufficiently low for atmospheric measurements. The molecules in question typically require concentrations above 10^6 cm^{-3} to exert a significant influence on atmospheric chemistry and aerosol formation.”***

545

L520-L523: I would suggest removing or rewriting this paragraph.

Thanks for the comment. We have re-written this part and integrated it into the previous paragraph.

550

*The revised statement is: **L577-580: “Additionally, the Eisele-type inlet was regularly shown to have a LOD as low as 10^4 cm^{-3} (Jokinen et al., 2012), a well-performing mass spectrometer may further reduce the LOD of MION2. Nevertheless, the attained levels of LOD are sufficiently low for atmospheric measurements. The molecules in question typically require concentrations above 10^6 cm^{-3} to exert a significant influence on atmospheric chemistry and aerosol formation.”***

555

Figure 6: It is somewhat confusing that your diagrams are indicated as a), b), and c), but the labelling is never explained. What adds to the confusion is that you mention three different groups in the text. However, those three groups do not actually correspond to the labelling in Figure 6.

560

Thanks for the comment. We have now changed the groups in Figure 6, which correspond to the groups in the text.

L593: “... for reactions 5 and 6 and they are ...” should read “... for reactions 5 and 6 are ...”

565

Thanks for the comment. We have now changed the statement.

Section 3.7: I find that this section seems to be quite distant from the remaining context of this manuscript. Also, it does not really add to the characterization of the MION2 inlet. For example, would it not possible to do these measurements with the MION1 inlet? The topic is prominently featured in the title but compared to the rest of the manuscript quite weakly presented.
570 Most of the section explains the scientific background and previous measurements, with only the last, short paragraph presenting a laboratory study with some results by the authors.

We would like to express our gratitude to the reviewer for this constructive suggestion. However, we do believe that this paragraph is necessary in our manuscript. A key contribution of MION1-2, employing the bromide chemical ionisation method, is the reliable measurement of iodine-containing compounds (Tham et al., 2021; He et al., 2021; Finkenzeller et al., 2022). This advancement further enhances our understanding of iodine chemistry and particle formation. Nevertheless, recent studies have raised concerns regarding the measurement of species such as HIO_3 . We feel it is obligatory to examine this possibility and provide responses to these inquiries. We consider a characterisation paper to be an ideal platform for presenting discussions and results related to this matter. However, we have improved the integration of this section to ensure a smoother reading.
575
580

Figure A7: Again, both fit lines for HOI do not really seem to represent the data points, hinting at either a linear fit not being the best representation, or at an additional unaccounted factor/bias. Maybe a short discussion would be helpful (See also comment to Figure 1)
585

Thanks for the comment. The main reason for this phenomenon is that HOI detection is more strongly affected by humidity when using the MION2-T2. It is clear from Figure 4 that when using the MION2-T2, HOI detection is more strongly affected than when using MION2-T1. This indicates that we should use the MION2-T1 to measure HOI, which was always the case in our current and previous studies. We have now clarified this phenomenon in the main text.
590

*The revised statement is: **L489-492: “This phenomenon is the most significant for HOI, i.e., the detection of HOI is more humidity dependent using Br^- -MION2-T2 than Br^- -MION2-T1. ”***

- Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin, R. L., Kulmala, M., and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster measurements using CI-API-TOF, *Atmospheric Chemistry and Physics*, 12, 4117–4125, <https://doi.org/10.5194/acp-12-4117-2012>, 2012.
- Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Calibration of a Chemical Ionization Mass Spectrometer for the Measurement of Gaseous Sulfuric Acid, *The Journal of Physical Chemistry A*, 116, 6375–6386, <https://doi.org/10.1021/jp212123n>, 2012.
- Lopez-Hilfiker, F. D., Iyer, S., Mohr, C., Lee, B. H., D'Ambro, E. L., Kurtén, T., and Thornton, J. A.: Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, *Atmospheric Measurement Techniques*, 9, 1505–1512, <https://doi.org/10.5194/amt-9-1505-2016>, 2016.
- Rissanen, M. P., Mikkilä, J., Iyer, S., and Hakala, J.: Multi-scheme chemical ionization inlet (MION) for fast switching of reagent ion chemistry in atmospheric pressure chemical ionization mass spectrometry (CIMS) applications, *Atmospheric Measurement Techniques*, 12, 6635–6646, <https://doi.org/10.5194/amt-12-6635-2019>, 2019.
- Tham, Y. J., He, X.-C., Li, Q., Cuevas, C. A., Shen, J., Kalliokoski, J., Yan, C., Iyer, S., Lehmusjärvi, T., Jang, S., Thakur, R. C., Beck, L., Kemppainen, D., Olin, M., Sarnela, N., Mikkilä, J., Hakala, J., Marbouti, M., Yao, L., Li, H., Huang, W., Wang, Y., Wimmer, D., Zha, Q., Virkanen, J., Spain, T. G., O'Doherty, S., Jokinen, T., Bianchi, F., Petäjä, T., Worsnop, D. R., Mauldin, R. L., Ovadnevaite, J., Ceburnis, D., Maier, N. M., Kulmala, M., O'Dowd, C., Dal Maso, M., Saiz-Lopez, A., and Sipilä, M.: Direct field evidence of autocatalytic iodine release from atmospheric aerosol, *Proceedings of the National Academy of Sciences*, 118, e2009951118, <https://doi.org/10.1073/pnas.2009951118>, 2021.
- Wang, M., He, X.-C., Finkenzeller, H., Iyer, S., Chen, D., Shen, J., Simon, M., Hofbauer, V., Kirkby, J., Curtius, J., Maier, N., Kurtén, T., Worsnop, D. R., Kulmala, M., Rissanen, M., Volkamer, R., Tham, Y. J., Donahue, N. M., and Sipilä, M.: Measurement of iodine species and sulfuric acid using bromide chemical ionization mass spectrometers, *Atmospheric Measurement Techniques*, 14, 4187–4202, <https://doi.org/10.5194/amt-14-4187-2021>, 2021.