

RE: A point-by-point response to referee comments

We thank the reviewer for dedicating time for a diligent review of the manuscript, and for providing valuable comments and detailed suggestions for improvements. We have carefully modified the manuscript to improve the legibility, to clarify critical instrument parameters, and to specify the potential limitation of this method in laboratory and field measurements. Below we provide a point-by-point response to the comments.

Reviewer #2

This is a well written and organized account of the application of a bromide cims instrument for the detection of various iodine containing species as well as sulfuric acid. The authors present nice account with much of the pertinent information related to their experiments. However, I find that there is much to be desired with respect to the errors associated with the methods used here and the various approximation used through-out the analysis. This is significant as the authors are presenting a very optimistic account of the ability of this method to detect extremely low levels of these species in a real-world marine environment. If in fact the authors can provide more details and support their conclusions through the additional information this is a truly remarkable performance and will be of wide interest to the field of atmospheric mass spectrometry. It is my opinion that more detail must be provided to support the publication of this manuscript in AMT and therefore recommend the following minor revisions to the manuscript.

I am having a difficult time understanding the true errors associated with your calibration factors presented throughout the manuscript. In some cases, you are calibrating using external calibration sources and in others you are calibrating using a secondary instrument for comparison. One issue with this whole description is the lack of information provided for exactly how these were performed. What I mean by this is how were the calibrations sources samples, through an inlet or directly into the IMR? Or when two instruments were compared were different inlets used between the two instruments. This is of particular importance when extrapolating the cluster binding energy approximated sensitivities to your instrumentation. I ask all of this because the actual true sensitivity to a given species is a combination of the ionization sensitivity as well as an instrument function which describes any inlet losses or differences in ionization potential between various instruments.

Reply: For the offline calibrations, the calibration sources were directly sampled using the MION inlet after dilution; for the inter-method calibrations, the CLOUD chamber acted as the sources, and the chamber flow was directly sampled using the same MION inlet. In order to make the description clearer, we have now listed the instrument specifications and the operational conditions in Table S1.

The main point of your work is that this method can detect these species with the sensitivity and detection limits sufficient for real world marine environments, so this really matters here. How well do you actually know your sensitivities and detection limits? Are those an upper limits because they represent sensitivities without an inlet present? You have made many assumptions related to the calibration of your instrumentation and that is certainly not reflected in any robust error analysis that is provided to the reader.

Reply: The sensitivity toward a specific compound depends on two factors: 1) whether a compound can be charged by the reagent ion to form a stable ion (cluster); 2) whether the formed ion (cluster) can be guided through the relatively low-pressure regions (by electric fields) and be detected by the APi-TOF. The Br-CIMS is able to detect a compound only when both of these two factors are satisfied. If the compound clusters strongly with the Br⁻ ion, and a minimum delustering occurs in the charging processes and in the low-pressure regions, the compound can be detected at the kinetic limit (e.g., I₂ and H₂SO₄), thus at a high sensitivity.

The detection limit mainly depends on how well we are able to separate the compound signal from background noise (signal to noise ratio). Such signal identification can be compromised by two factors: 1) an undesired peak that covers the compound peak; 2) background signals produced by the electronics, which appear as low-level signals even when there is no compound appearing at that mass to charge ratio (m/z). The first factor is largely overcome by the high mass resolution of our instrument (~10000, Table S1). Thus, the major factor that determines the detection limit is the background noise. Therefore, we define the detection limit in this study by the mean value + three times the standard variation during a two-hour time period in which we know the analyte compound is absent. If a compound peak appears at the concentration as defined by the detection limit, we can easily separate it from the background noise.

All in all, with the instrument calibrations either by offline methods or the inter-instrument methods, we quantify the sensitivity which accounts for the charging processes in the MION and FIGAERO inlets (flow rate, pressure, ion-molecule collision, etc.) and ion transmission in the mass spectrometer. With the analysis on the instrument background, we define conservatively the detection limit toward a compound.

The defined detection limits are all conservative values and rather an upper limit, and often even better detection limits are realized by the instruments (i.e., they are able to measure even lower concentrations). All the detection limits are defined when the inlets are connected to the instrument, thus the detection limits contain the information from the calibration and instrument background.

On the topic of using cluster binding energies for the approximation of sensitivities, the authors suggest that because that sort of analysis has worked for iodide than it naturally works for the Br⁻ ion chemistry, however, there is no evidence that this approach is true. Again this method is also complicated by the differing inlet response functions of the various species and would really only yield an upper limit to the ionization sensitivity not the true detection capabilities of a sampling system. For example, a binding energy does not take into account that sulfuric acid has a different transmission factor than IO which would also vary with sampled ambient humidity on the inlet surfaces.

Reply: Passananti et al. (2019) studied the collision induced fragmentation in the same instrument. It has been concluded that the sensitivity of our instrument largely depends on the cluster formation enthalpies of the analyte-reagent ion cluster and the tuning of a specific instrument. With a specific tuning, a strongly binding cluster has a much lower chance to fragment compared to a less strongly bound cluster. This conclusion applies not only to I⁻ ion chemistry but also to, e.g., NO₃⁻ and Br⁻ ion chemistry.

The reviewer is correct that the binding energy discussion does not consider the different diffusivity of different species. In the revised version, the only calibration factor we transferred is the one for HIO₃. We calculated that the inlet line loss for H₂SO₄ and HIO₃ are 33 % and 36 %, respectively. The calculation was based on a hard sphere

assumption (for the calculation of the diameters of the two molecules), an inlet flow rate of 32 slpm and an inlet length of 1.53 m. As such difference is marginal, we believe that the calibration factor of H_2SO_4 is applicable to HIO_3 . However, to accommodate the reviewer's suggestion, we have deleted our estimation on the exact calibration factor of IO and OIO. And we added a note in the section 3.3.3 that the difference in the diffusivity needs to be considered in transferring the calibration factor.

I think the calibration through instrument comparison method was used in this manuscript to transfer the MION calibrations to the FIGAERO, perhaps I incorrectly understood something. If that is the case, this issue of instrument functions becomes even more of a hindrance to the direct comparison of ambient observations because the two instruments operate at very different pressures with significantly different ionization schemes. These types of issues clearly need to be stated and incorporated into the stated performance of the instruments, preferably through a more robust error analysis. Although that may not be possible as the error in approximated calibration factors may not be available.

Reply: The reviewer is correct that the Br-MION-CIMS and the Br-FIGAERO-CIMS use different inlets and operate at different pressures. These differences would indeed lead to different calibration coefficients in the two instruments for the same analyte. However, it is not the calibration coefficients that we transfer from one to another, we transfer the calibrated absolute concentrations, and only for analytes whose signals from the two instruments are linearly correlated, such as HIO_3 and HOI. Thus, the major error really comes from the calibration sources, e.g. +50/-33 % for HIO_3 and 55 % for HOI.

When two mass spectrometers are compared, there are two minor errors: the statistical error of the signal correlation analysis (e.g. 3.1 % for HIO_3 and 3.2 % for HOI) and the error of small variations in analyte signal caused by reagent ion fluctuation (2.9 % for all analytes). Eventually, the propagated errors are +50/-33 % for HIO_3 and 55 % for HOI. We do agree with the reviewer that a more robust error analysis is important. We have added a statement in Lines 517-519 of the revised manuscript:

“Note that for both HOI and HIO_3 the uncertainties introduced from the correlational analysis are negligible compared to the limited accuracy of the calibration sources (55 % for HOI and +50/-33 % for HIO_3).”

Besides, we have listed the key specifications of the two instruments in Table S1 to clarify the differences.

I would like to know more details on the what the background conditions were during the periods for which the detection limits were calculated. It is well known that when a CIMS instrument samples clean air the background values are continually reduced. In most real world applications conditions are far from clean and as such I would expect a relatively larger H_2SO_4 background than what the authors are stating. I am curious if this discrepancy comes from the fact that this instrument is sampling from what is perhaps the cleanest atmosphere available on earth which allows for unrealistic instrument backgrounds. Yes, that would be the functional instrument detection limits for sampling in the CLOUD chamber, however the results would not be directly translatable to a real-world environment where instrument background are likely significantly higher. If in fact the detection limits are determined from periods of chamber measurements, or even if the instrument is only sampling from the chamber and not room air then the

authors should admit that this is really a best-case scenario for the stated detection limits. This would mean that real-world applications of this method in the marine atmosphere are unlikely to achieve these results. Unless of course the authors can support the idea that these instrument backgrounds are routinely achievable on a standard field deployable CIMS instrument. If this is the case data should be shown describing the various background and operating conditions. Also in general, during the chamber experiments how were zeros performed?

Reply: The reviewer's point is well taken. However, we can justify that these instrument backgrounds are routinely achievable on a standard field deployable CIMS instrument. Other than the CLOUD measurements, in the summer of 2018, we have deployed the same bromide-CIMS for an intensive field measurement at Mace Head, Ireland (for details please refer to our previous publication: Tham et al., 2021). During the campaign, we conducted 4 separate background measurements, by flooding the inlet with excess nitrogen flow (99.999 % of purity) for at least 10 min during the daytime low tide event (typically has significant H_2SO_4 levels, up to 4 pptv). The results show the absence of the iodine species of interest when compared to the ambient spectra, and the calculated detection limit (3σ) for H_2SO_4 , HIO_3 , I_2 and HOI are 7.4×10^5 , 2.2×10^6 , 1.6×10^6 , and 2.1×10^6 , molec cm^{-3} , respectively.

Background levels and detection limits are quite comparable during the CLOUD experiments. We achieve the background conditions by terminating photochemistry and subsequent formation of oxidized iodine species/ H_2SO_4 , while keeping the 330 slpm humidified air constantly flushing the chamber system. In the meantime, we turn up the fan speed to increase the vapor wall-loss rates.

Low background level for HIO_3 and H_2SO_4 can be achieved because they have very low volatility and are irreversibly lost to surfaces, and even 10^7 to 10^8 cm^{-3} HIO_3 or H_2SO_4 (ambient upper limit) would not saturate the sample line walls. For more volatile species such as HOI , partitioning between the gas phase and the wall may increase the background level (although it was not observed in our experiments), which is dominated by vapor concentrations (gas-phase activities). However, the CLOUD experiments run at atmospherically relevant vapor concentrations and conditions, and it is very likely these results are translatable.

The pressure at which these instrument are being run at leads me ask if the authors have identified any issues with the combination of Br- and O3 as it relates to secondary ion chemistry. It is fairly well known that the addition of O3 to an I- CIMS will result in the production of IO-, IO2-, and IO3- which can act as a secondary reagent ion even at low abundances. This presents challenges to interpretation of oxygen rich ions where (HIO2)Br- can actually be the result of a cluster of HOI with BrO-. The pressures used in this study are sufficiently high in an iodide CIMS to result in these reactions at this ozone level and I would encourage the authors to discuss this potential.

Reply: We thank the reviewer for this insightful question. We checked a typical experiment carried out at -10°C and did not find the BrO_3^- in the mass spectrum (or its concentration was below the detection limit). The measured intensities for BrO^- and BrO_2^- were 0.003 and 0.001 ions s^{-1} , respectively, while the Br^- and H_2OBr^- intensities were 129 and 32 ions s^{-1} , respectively. Therefore, the sum of Br^- and H_2OBr^- is 40 000 times larger than the BrO^- and BrO_2^- ; the influence of BrO^- and BrO_2^- on overall detection should be very small.

Additionally, if we assume BrO^- and BrO_2^- have the same sensitivity as the I_2 , the total concentration of BrO^- and BrO_2^- will be 6.7×10^5 molec cm^{-3} . With a residence time of 20 ms in the ion-molecule reaction chamber of the MION

inlet and an ion-molecule collision rate of $2 \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, the first order production rate of the resultant charged clusters (analyte molecule charged by BrO^- or BrO_2^-) is around $2.7 \times 10^{-5} \text{ s}^{-1}$. Therefore, the analyte would need to be at ppbv levels to yield detectable signals in the Br-MION-CIMS, which is orders of magnitude higher than the oxidized iodine species produced in our experiments. Therefore, we conclude that the BrO^- and BrO_2^- (O_3) have a minor effect on the overall detection.

In figure 4 and elsewhere the sensitivities are given as a concentration over signal. This figure should be flipped as the signal in the instrument is dependent on the concentration not the other way around. It would be helpful if values for sensitivity were given in the convention standard for atmospheric mass spectrometry as signal/concentration.

Reply: We have swapped the axis according to the reviewer's suggestion.

I can summarize my main concern with respect to the authors not presenting the errors associated with the work appropriately with one example. There is a large discrepancy between the permeation source derived I_2 sensitivity and the DOAS derived sensitivity 2.7×10 versus 6.3×10 . That is a factor of 2 difference! It seems this is just glossed over and needs to be explained. These are even measured sensitivities with that large of a discrepancy so I am inclined to believe the errors in the approximations are at least as large and likely significantly larger than this difference.

Reply: The reviewer is correct that we describe a difference of a factor of approximately 2.3 for the calibrations of I_2 by CE-DOAS and permeation tube calibrations. However, these two calibrations were carried out with different instruments and slightly different settings, at different times. Due to limitations of available equipment, we were unable to compare the two methods simultaneously. The manuscript was insufficiently clear in this regard. The main take-home message is that in-situ calibration is critical. In this context we regard the agreement within a factor of 2.3 as reasonable; these tuning differences require in-situ calibration but indicate that the instruments are consistent, but the final factor of 2 requires careful calibration. In our case, one of the calibrations (by CE-DOAS) was done onsite at CLOUD while the off-site calibration (by a permeation tube) was carried out in a laboratory at the University of Helsinki. The reviewer is also right that it is misleading to state that the results are consistent. Our initial intention was stating that calibration factors were not inconsistent, since a factor of two difference in two independent calibrations is common in the characterization of the chemical ionization method we use. Three changes are made in the revised version:

1. We have deleted the statement about the consistency in the calibration coefficients;
2. We added discussions about the difference in the inter-method (in-situ) and offline calibrations and highlighted the importance of carrying out calibration experiments at individual experiments;
3. We added a table which lists the key parameters of the Br-MION-CIMS in the inter-method and offline experiments.

Specific comments:

- Section 3.3.4 and 3.3.5 should be flipped as the first sentence of 3.3.4 states the calibration was performed as in 3.3.5

Reply: We have reconstructed the section 3.3, and now the H₂SO₄ calibration appears before HOI calibration.

- *Figure 2 caption doesn't seem to have any proton transfer reaction products as the caption would lead the reader to believe.*

Reply: We only show selected iodine species in Figure 2, as we state in the caption. We therefor deem it sufficient to leave things as is.

- *Figure 6, as sulfuric acid is one of the main foci of this manuscript it really should be included in this figure to show the response time of the measurement.*

Reply: The reviewer makes a good point. However, we do not have H₂SO₄ measurements from the Br-FIGAERO-CIMS – the FIGAERO-CIMS was switched to iodide chemical ionization scheme at that time. We now have removed the Fig 6 and condensed the discussion as per reviewer 1's request.

Table S1: Instrument specifications for Br-MION-CIMS and Br-FIGAERO-CIMS. The values are specific to our instruments, thus can vary according to instrument parameters.

Instrument specifications	Br-MION-CIMS (lab)	Br-MION-CIMS (CLOUD)	Br-FIGAERO-CIMS
Total sample flow (slpm)	20	32	18
IMR pressure (mbar)	1000	1000	150
IMR residence time (ms)	30	20	200
SSQ pressure (mbar)	1.9	2.2	2.0
BSQ pressure (mbar)	0.011	0.012	0.011
^a MION accelerator (V)	-2750	-2800	n/a
^b MION deflector (V)	-210	-290	n/a
Nozzle (V)	11.4	-1.4	0.05
SSQ EP (V)	13.79	-5.13	0.10
SSQ front (V)	20.92	12.45	0.20
SSQ back (V)	-16.94	8.22	-0.30
Lense skimmer (V)	-16.17	-6.16	-0.19
Skimmer (V)	0.59	0.63	4.00
BSQ front (V)	4.78	1.76	5.89
BSQ back (V)	4.93	2.76	5.90
Skimmer 2 (V)	5.77	5.69	5.92
Reference (bias) (V)	124.94	105.87	121.99
Ion-lense (V)	34.076	31.21	39.78
Deflector flange (V)	53.79	75.91	88.31
Deflector (V)	61.77	83.82	95.08
Mass analyzer	microchannel	microchannel	microchannel
	plate detector	plate detector	plate detector
Mass resolution	~ 10000	~ 10000	~ 10000

^a The voltage to accelerate the reagent ions in the ion source (Rissanen et al. 2019).

^b The voltage to deflect the reagent ions to the sample flow (Rissanen et al. 2019).

References

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