Atmospheric
Measurement
Techniques

Discussions

Open Access

EGU

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

Anonymous Referee #2

Received and published: 24 February 2021

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 throughout the anaylsis. 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 spectrom-

etry. 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. 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.

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.

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.

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 H2SO4 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

C3

the chamber experiments how were zeros performed?

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.

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.

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 I2 sensitivity and the DOAS derived sensitivity 2.7e10 versus 6.3e10. 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.

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

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

- Figure 6, as sulfuric acid is one of the main foci of this manuscript it really should be

C4

included in this figure to show the response time of the measurement.

C5