

# ***Interactive comment on “Measurement of ammonia, amines and iodine species using protonated water cluster chemical ionization mass spectrometry” by Joschka Pfeifer et al.***

## **Anonymous Referee #2**

Received and published: 17 September 2019

The manuscript “Measurement of ammonia, amines and iodine species using protonated water cluster chemical ionization mass spectrometry” describes and discusses a new technique using protonated water clusters ( $\text{H}_3\text{O}^+$ ) with a Chemical Ionization-Atmospheric Pressure interface-Time Of Flight mass spectrometer (CI-APi-TOF) to detect ammonia, dimethylamine, and iodine oxides during experiments performed at the CERN CLOUD chamber. The technique is calibrated for ammonia using a primary bottle standard and dilution system. It is also compared to a commercial cavity-ring down spectrometer measuring ammonia and water vapor manufactured by PICARRO, Inc. No direct calibration is presented for the other species detected, rather the calibration factor for dimethylamine is assumed to be the same as for ammonia and that for

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iodic acid is parameterized from the observations of a nitrate CI-API-TOF instrument making simultaneous measurements in the chamber. Humidity effects on the ammonia sensitivity are investigated. Limit of detection is determined. A characterization of instrument as operated at the CLOUD chamber is presented. The subject matter of the manuscript is appropriate for Atmospheric Measurement Techniques.

Though I do find it exciting that this type of ion source for CIMS instruments is being developed and it shows much promise, I do feel that the manuscript glosses over significant details for evaluation and does not provide enough justification of others to be published without revision.

Major comments: 1. Though powerful, CIMS is not an absolute measurement technique. A good, defensible calibration is necessary. The manuscript should do a better and clearer job indicating that only the ammonia detection is calibrated with a primary standard and that the mixing ratios for the other species are estimated qualitatively. It is too easy for the reader to lose sight of this fact, since no differentiation between calibrated and estimated mixing ratio results is made in the table or the figures.

2. The main product of this work is the development of the ion source. However, details of the ion source are lacking in the text and figures. Figure 1 is more of a cartoon than a schematic. The details that are given in the text (page 5, lines 143 – page 6, 162) are difficult to translate to Figure 1. For example, a counter electrode and capillary are described in the text but not identified in the figure. Dimensions are given in the text that are not shown in the figure. This makes it unnecessarily difficult for the reader to follow how the ion source truly works and evaluate its performance. Also, details such as tubing length and flow rates for the calibration dilution components should also be given.

3. The comparison of the LOD and low background for this water cluster CI-API-TOF instrument to others is not as straight forward as presented here. Here the calculated detection limits are based on a 2.5 hour measurement of synthetic air generated from

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liquid nitrogen and oxygen with a 1 minute average for a single data point (See 2.1 and Table 1). This leads to the question are the values given in Table 1 those after sampling the synthetic air for 2.5 hrs or the values for the full 2.5 hr time period? If is the latter, what was the time required, if any, for the signal to drop to the 3 pptv level after removal of a 5-10 ppbv ammonia calibration addition?

Unfortunately, no data is presented to support the low background and LOD claim. The time series in Figure 7 is not applicable because the effects of the CLOUD chamber cannot be separated from those of the instrument. Here a time series showing the addition of ammonia and the instrument response to its removal in the set-up shown in Figure 1 would be extremely useful. This would also better mimic field measurements, for example, measurements at a ground site when wind shifts from a region with ammonia sources to one without. Then a better comparison could be made to other instruments and their field measurements. Other factors, affecting signal stability, i.e., LOD, include vibrations, for instruments on mobile platforms such as vehicles or aircraft, and heat, for instruments in trailers, on towers, in vehicles, and in aircraft. In many ways the controlled laboratory conditions associated with the CLOUD chamber provide an ideal environment. While the work presented here is impressive, care should be taken comparing the performance there to that reported in a field campaign. This also highlights the necessity of evaluating instrument performance in-situ for every campaign and not relying on spec sheets or one laboratory test.

4. No data is shown to support that this is a fast time resolution measurement either. Similar to my previous comment, a time series showing the signal decay after removal of ammonia would be helpful in evaluating the time response of the instrument. Also, if this is a fast time resolution measurement why does it take at least 20 minutes (Page9, line 254) for the signal to reach the mean value of a steady state measurement used in the calibration curve shown in Figure 3a?

Specific Comments Page 1 line 17, If the authors did not explicitly demonstrate the quantitative measurement of diamines (see page 16 line 504) then they should not be

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mentioned in the abstract. Similarly, amines should be changed to dimethylamine since that is the only amine for which data is shown. Speculative future application should be saved for the discussion in the manuscript not the abstract.

Page 1 line 22, Classifying 10 ppbv ammonia as high is very subjective. What is high for the CLOUD experiment may be typical or even low for many areas as seen in many of the publications cited in this manuscript.

Page 5 line 151, Please show how the reaction time is estimated here.

Page 5, line 158, Are all tubing diameters given in the manuscript representing the outer diameter? The inner diameter should also be given as that affects the flow characteristics.

Page 6, line 180, What is the uncertainty in the mixing ratio of the ammonia bottle and who is the manufacturer? It should be given here with the calibration set-up details not later in the manuscript discussing the calibration results.

Page 7 line 199, What is meant by 'a fairly short equilibration time'? Minutes, hours, seconds? Please show the time series of the ammonia signal as a function of the step changes in ammonia added in addition to the calibration curve shown in Figure 3.

Page 7, line 209-210, How is the assumption given here that both sulfuric and iodic acid are detected with the same efficiency by the nitrate CI-API-TOF justified? Wouldn't this make the estimated iodic mixing ratio a limit in some regard?

Page 7, line 219, The text mentions the PICARRO being connected to the exhaust line of the water cluster CI-API-TOF for comparison. Is this comparison discussed or shown in the manuscript? If not, why? Or am I incorrect that Figure 7 is showing PICARRO measurements being made from its own sampling line on the CLOUD chamber and the comparison is shown in Figure 7? The text also mentions tests when the flow is increased to the PICARRO. When is this used? If used when the PICARRO is sampling the exhaust of the water cluster CI-API-TOF is the flow to the water cluster

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CI-API-TOF increased also? Again, another instance lacking enough detail to evaluate the experiment and experimental results.

Page 9, line 264, I am confused by the use of ppm in this context. Please clarify.

Page 9, lines 282- page10, line 286, This supports my earlier comment that every instrument needs to be evaluated in the in-situ setup employed.

Page 11, line 337-338, This is fairly deep into the manuscript before stating that the calibration factor for ammonia is used for dimethylamine and pyridine. It should be made clear to the reader earlier.

Page 27, Table 1, It should be noted here that only ammonia was directly calibrated and the other calibration factors were assumed or parameterized from other measurements.

Page 29, Figure 1, This figure needs better labeling of the parts, consistent with the description in the text. Include the lengths of tubing. Consider a blow-up insert of the ion source with more detail.

Page 31, Figure 3, Why no x-axis error bars in panel b? Page 9, line 259 seems to suggest that there is a factor of 2 uncertainty in the iodine acid mixing ratio determined by the nitrate CI-API-TOF.

Page 35, Figure 7. Figure 7 is very busy. The agreement between the water cluster CI-API-TOF and the PICARRO is mediocre, especially when noting that the ammonia mixing ratio axis is logarithmic, though for the most part they are trending in the same direction. However, what is causing the deviation observed 29.10 – 30.10 where the water cluster CI-API-TOF shows a significant ammonia drop and then increase that does not correlate with fan cycling or temperature changes?

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