

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 #1

Received and published: 15 August 2019

General Comments

This paper presents the use of H_3O^+ reagent ion chemistry on a CI-API-TOF mass spectrometer to detect ammonia, dimethylamine, and iodine oxides in the CLOUD chamber at CERN. The detection of ammonia is pushed further into a quantification technique by performing calibration with a primary standard and intercomparing with a Picarro NH_3 analyzer. The calibration response is characterized for relative humidity dependence since the water cluster ions increase in importance and result in a higher sensitivity. The calibration is then demonstrated to result in a reasonable capability to quantitatively measure NH_3 with the CI-API-TOF in the CLOUD chamber, within the

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expected range of mixing ratios from a set of standard addition experiments. The detection of the other species is presented and their detection limits estimated based on parameterizations with other instrument responses or assumptions on the H_3O^+ ionization efficiency. Overall, this work presents an interesting new method for quantifying experimental NH_3 concentrations that may be possible to translate to atmospheric observations, which is a suitable contribution to Atmospheric Measurement Techniques. However, there are several major issues in the estimated detection limits for dimethylamine and iodic acid and Picarro intercomparison that must be addressed with rigour or removed from the manuscript in order for it to be acceptable for publication.

Major Comments

1. There could be better clarification throughout the manuscript to indicate that the amine and iodine species are detected and that their mixing ratios are estimated semi-quantitatively, as formal calibrations have not been performed with a primary standard. The title should be revised to reflect quantitation of ammonia and detection of DMA and iodine oxide species specifically instead of ‘amines and iodine species’ which is misleading. The discussion clearly states that the DMA and HIO_3 quantities are estimates based off of scaled numbers from H_3O^+ or NO_3^- CI-API-TOF responses to other species (e.g. NH_3 or H_2SO_4). Converting the units from ncps to mixing ratios for those scaled responses leads to values that may be highly inaccurate. The potential for quantification and sensitive detection of these species by H_3O^+ CI-API-TOF can be discussed, but the scaled response estimates should not be used to report mixing ratios, such as in Figures 5 and 8. These should be replaced with signal reported as normalized counts per second (ncps). The authors state in several locations in the discussion potential sources of bias from the assumptions made in converting signal to mixing ratios, which are not fully characterized for the CLOUD chamber and could easily represent a factor of 2 or more error. Based on the presented data, mixing ratios for these compounds should be replaced with ncps units throughout the manuscript. The authors make arguments for the validity of some assumptions throughout the manuscript

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as well, which seem to be undermined by other parts of the discussion. See the technical comments below for instances where this is the case and the discussion should be revisited.

2. Intercomparison with the Picarro NH₃ cavity ring down instrument does not evaluate the measurements correctly and ignores discussion regarding the limitations of the CI-APi-TOF approach (e.g. response times on the order of hours) or the experimental setup of the intercomparison (e.g. the Picarro connected to the exhaust of the CI-APi-TOF). For example, there is a clear background offset in the Picarro measurements from the chamber that is not accounted for, but for which the CI-APi-TOF dataset is corrected accordingly through its independent calibration. There are other important measurement concepts that are missed in the data analysis here such as the aforementioned background offset correction, inlet and instrument surface sorption/desorption effects impact on response times, and detection limits. See the technical comments corresponding to these sections of the manuscript below for several specific comments. It is possible that the intercomparison is technically invalid based on the experimental setup and should be removed from the manuscript, but this cannot be assessed without further data provided by the authors regarding the setup of flows to direct the chamber air to the instruments.

Technical Comments

Page 1, Line 17: Diamines are not presented in the manuscript and are mentioned here. Remove. There seem to be several issues of material that was planned for inclusion in this manuscript that have been removed, but not in all locations. The authors should revisit the manuscript with this in mind to improve clarity throughout.

Page 1, Lines 20-21: The detection limit difference for the amines should be stated as 'at least XX times lower' here to be more specific.

Page 2, Line 33: 2.5 is usually a subscript

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Page 2, Line 36: Use one or the other of 'new particle formation' or 'nucleation' and add 'e.g.' before each example of the ternary and multi-component systems.

Page 2, Lines 40-46: This clarity of this section is not very good because these sentences are discussing too many topics, which should be separate sentences. Delete 'their' and end the sentence after the Dunne et al. reference. In line 42, replace 'show' with 'support this by observing'. On line 44 end the sentence after 'water' and start the next sentence with 'For example' instead of using 'e.g.' in-line.

Page 2, Line 46: It is accurate to state 'enhance nucleation rates'. The 'even stronger' is not necessary and confuses the sentence's evaluation of relative enhancements of amines over ammonia in forming new particles.

Page 2, Line 48: Why have the authors stated 'in principle confirmed' here? Perhaps the specific property assessed (e.g. thermodynamically favored formation) would be a more accurate term to place here.

Page 2, Lines 52-53: The list of references for amine mixing ratios is more comprehensively summarized in a review by Ge et al. in *Atmos. Environ.* (2010) which can replace this list of references[1].

Page 2, Lines 54-57: There is an attempted motivation here that CI-APi-TOF is more versatile than other analytical techniques for atmospheric samples of reduced nitrogen species. However, separation techniques are more selective than CI-APi-TOF, particularly when it comes to the detection of structural isomers. Optical absorption techniques by systems such as cavity ringdown and quantum cascade laser systems are easily as sensitive and with as high time resolution as CI-APi-TOF. The limitation of the prior methods that CI-APi-TOF overcomes should be made with greater clarity here in order to motivate the CI-APi-TOF analytical approach. It would be easiest to remove the first sentence of this paragraph and start the second sentence at 'Chemical ionisation atmospheric pressure interface mass spectrometry...'

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Page 6, Lines 167-171: This is a big stretch in justification for quantifying amines. Strong acids detected by CIMS do not have the same response factors per mixing ratio detected and this is well reported in the literature even though their reaction rates would be predicted to be the same for a given ionisation technique (e.g. 2-16 counts per pptv for strong acids by proton exchange in Roberts et al. in Atmos. Meas. Tech. (2010)) [2]. This detail should be clarified here along with the potential outcome of the assumption for amines likely being up to a factor of 10 error in quantitation as a worst-case outcome. It is likely better to report in this work the measurement of amines only in 'ncps' and to do a ballpark estimation of the mixing ratios in the discussion.

Page 6, Line 186: A sentence should not begin with an acronym. Rephrase.

Page 7, Lines 207-209: This is quite the string of assumptions and underscores the major issue with claimed quantitation in this work. The detection of HIO₃ is, at absolute best, qualitative and units should not be assigned to the measurement in pptv, but 'ncps'.

Page 7, Lines 209-212: This intercomparison is shown in Figure 5, but the axis labels do not communicate this. They should both be reported as normalized counts since the NO₃-CI-API-TOF signal is scaled on the H₂SO₄ response, which does not yield a quantitative calibration factor for HIO₃, but only a relative signal.

Page 8, Lines 223-226: The authors state that the instrument was independently calibrated. This means that they have data to calculate the detection limit of the Picarro NH₃ cavity ringdown system and it should be done here instead of stating the value given from the datasheet.

Page 8, Line 237: The first name of the author should not be given here.

Page 8, Lines 248-251: This comparison of the stability of reagent ion should be made by calculating the change in the calibration slope (ncps vs NH₃ mixing ratio) between high (1-10 ppbv) and low (<1 ppbv) ranges to reach the conclusion that the sensitivity

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is consistent across the full range of experimental mixing ratios used in CLOUD. The authors also state 'sufficient precision' here without defining what the value they use is. The numeric value should be given. It would also be useful here for the authors to comment on the likelihood that this calibration response will hold up under ambient observations where other atmospheric components will compete for H⁺ transfer.

Page 9, Lines 259-261: Here is the HIO₃ intercomparison again. The error in the VMR is estimated based on an applied scalar, which is effectively a guess. It is more transparent, and valuable, to report that the two independent ionisation schemes yields a strong linear response, supporting the sensitive detection of HIO₃ using H₃O⁺ chemistry. Extending this further into estimated mixing ratios is not justified.

Also, for these calibrations, the experiments shown in the remainder of the manuscript are not collecting 20 minute time-resolution data. Averaging at timescales more relevant to the measurement timescale would give a more accurate estimate of calibration response and quantitation accuracy, so long as 20-30 data points are pooled for each calibration mixing ratio.

Page 9, Lines 263-264: The resulting difference in the forced and unforced slopes should be reported with the numeric value of the percent difference.

Page 9, Lines 265-267: 'concentration steps' should be 'calibration mixing ratios' and 'confidence bounds (95 % confidence intervals)' should be '95 % confidence intervals'.

Page 9, Lines 272-274: The response time of the CI-API-TOF to a stable signal following the stepped-down changes in NH₃ VMR should be provided here explicitly. The discussion following this section states that the instrument and line surfaces contribute to background signals observed. Here, the 'diffusion of ammonia from the capillary into the sampling line' should be clarified to indicate that the background observed also has contributions from all surfaces in the calibration system, the instrument inlet, and the instrument walls.

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Pages 9-10, Lines 282-286: The changes in calibration factor should be explicitly given. Are they a factor of 2 different or a factor of 5? This is a measurement technique manuscript and it is VERY important to highlight how small changes in instrument operation and setup can affect the quality of the measurements. Was the CI-API-TOF re-calibrated with these slight changes? How was the calibration factor derived for these CLOUD experiments? Did the response time of the inlet change? All of this information has high value here.

Page 10, Line 294: What does 'including all components' mean?

Page 10, Lines 301-306: This section of discussion is unclear and difficult to follow. Rewrite for clarity since looking at Figure 7, there seems to be disagreement with what is stated here regarding 15 % and 3 % change in signal. Perhaps there is a way to depict this more clearly in a new figure?

Page 10, Lines 308-310: Rewrite this sentence, removing all information in brackets and either placing it explicitly in the sentence or removing it. Also, should the reference to Figure 4 here actually be to Figure 5?

Page 11, Section 3.4: Detection limit calculations require a stable background signal when the instrument is known to be sampling a negative control. Quite a bit of this section discusses contamination issues, which should be made into its own section and kept separate from detection limits.

Page 11, Lines 326-327: These facts should be moved to the calibration section as an addition to the statement about the capillary NH₃ contamination since all of these components can be causing the described time lag in the calibrations and the observations.

Page 11, Lines 334-335: This is a sentence fragment and does not belong in the part of the discussion. It should be moved to the discussion of the RH-dependent sensitivity along with context driven by the data presented in Figure 4.

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Page 11, Lines 336-340: Giving approximated detection limits, along with the assumptions being made for HIO₃ and the amines in the discussion is alright, so long as it is very clear that these are initial guesses. Where these numbers absolutely do not belong is in Table 1, which should be removed from the manuscript. It is highly likely that these numbers will be used out of context and with disregard for the assumptions made here for the estimation (e.g. not everyone will have a NO₃- CI-API-TOF calibrated for H₂SO₄ to scale their measurement against for HIO₃, along with the assumption that the sensitivity is equal on top of that). The authors need to be clear throughout this work that the estimated mixing ratios are consistent with expectations, BUT that a calibration with known quantities of the target analytes should be performed by anyone wanting to make quantitative measurements of these compounds. Again, any figures showing mixing ratios or amines or HIO₃ should be converted back to units of ncps since these estimates are based on tenuous assumptions. Keeping some mention of the potential detection limits in the discussion is alright as it motivates further work in using this instrumental platform for quantitative analysis.

For this reason, the title of the manuscript needs to be revised to reflect what species can be quantified and which can only be detected. Without calibration from a primary standard, HIO₃ and amines are only detected in this work, while NH₃ is quantified and this should be kept clear.

Page 11, Lines 341-347: This part of the discussion is quite unclear. 'E.g.' should be 'For example;'. What is the peak with the highest count rate for the amines and why does this avoid interference for the mentioned fragments? This is not adequately explained. In the final two sentences, the authors undermine their assumptions regarding the detection of amines identically as they detect ammonia, stating that they omit the use of larger product ions, which will skew the sensitivity of detection. Then, this bias is dismissed as negligible because the water cluster signals are smaller for the bases than ammonia. Clearly, this indicates different reagent ion chemistry and product distribution for the amines relative to ammonia, which is inconsistent with assumption that

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they are the same and that the NH₃ calibration factor can be applied to the calculation of amine mixing ratios and detection limits. This is strong evidence against reporting mixing ratios and detection limits for C₂-amines in this work. The strength of this paper lies in the quantitative detection of NH₃ and show focus on that data, with discussion of these additional species kept to a minimum.

Page 12, Line 361: 'Thus, the sensitivity. . .' this sentence is redundant with the preceding discussion and can be removed. This paragraph and the one preceding are nice guides to some of the technical considerations for measuring these target analytes and the controls on signal/noise for each of the ions. The discussion of LOD in these two paragraphs for amines and iodic acid should be changed to discuss signal-to-noise of the instrument.

Page 12, Line 372: 'up to the tetramer (. . .)' could easily be replaced with 'molecules containing 1-4 iodine atoms' and be much more accurate. This should be changed throughout the manuscript, including Figure 6. Calling these species monomers, dimers, etc suggests that the rest of the atoms are part of a fundamental subunit one would typically find in describing a polymer, which does not seem to be the case here? If there are fundamental subunits for these I-containing species and the terminology of monomers, dimers, etc holds, then this should be more clearly written to specify the atoms found in remainder of the subunit.

Page 13, Line 395: The accuracy of the chamber concentrations being much less certain than those from the measurements of NH₃ by the CI-API-TOF should be used earlier on to motivate the need for this instrument being characterized fully.

Page 13, Lines 400-401: Could this difference in response time during NH₃ mixing ratio increases be due to inlet location differences between the instruments inside the chamber? Are the different responses due to concentration gradients as NH₃ mixes throughout the chamber? Or are there very different inlet line lengths? The intercomparison description on Page 7, Lines 219-223 are insufficient to determine if these in-

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strumental measurements are even capable of being properly compared. The authors suggest that in 'some intercomparison measurements' that the Picarro was hooked up to the exhaust of the CI-API-TOF instead of sharing the same sampling line. Surely there are huge losses of NH₃ inside the CI-API-TOF such that it is unreasonable to expect quantitative transfer of NH₃ out of the instrument exhaust? This type of setup would dramatically bias an intercomparison and may invalidate its applicability altogether in this work. The authors should re-evaluate whether the experimental setup was sufficiently robust to expect NH₃ to be transmitted to both instruments in a manner that does not compromise the sample composition. If the conclusion is that this is not possible, then this section of the manuscript needs to be removed as it is likely invalid.

Also, why was a background correction not applied to the Picarro data based on having it sample zero air? The Picarro gas analyzers typically arrive from the factory with a calibration factor and offset applied and can be much more sensitive than the operators' specifications sheets. Given that an independent calibration was done using a permeation device and, presumably an overflow with zero air, the instrument detection limits should have been possible to independently calculate, along with any systematic offset in the instrument response, which could be corrected where this is identified as a factory offset. The calibration of this instrument with external NH₃ would have allowed the LOD for the instrument to be determined the same as it was for the CI-API-TOF (i.e. using S/N=3 from the blank observations and comparing that to the background measurement). Making the intercomparison with more consistent treatment of the calibrations performed on both instruments would strengthen the discussion throughout this portion of the manuscript.

Page 14, Line 417: The material used for the sampling line is not discussed. Part of the discussion from literature line losses (Line 426) talks about stainless steel, but this would be atypical for an NH₃ sampling inlet. The authors need to clarify this material so the context can be properly evaluated. Given the incredibly long decay time constants from the chamber (on the order of days according to Figure 7?), which

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are also not presented for the instrument from the calibrations, it is hard to determine the relative order of the effects here. See comments on the calibration figures for some improvements to the manuscript with additional figures that could be made.

Page 14, Lines 426-434: The water effects on line losses seem to be ignoring an established effect from the literature. Water on inlet surfaces can allow weak acids and bases to dissociate into their conjugate compounds on the surface, increasing the partitioning to the surface. Adsorption on surface sites alone is too simple of an interpretation. Further to this, data is not presented that decouples the effect of the inlet lines from the desorption of NH₃ from the CLOUD chamber walls. The value for inlet desorption is only described as 'it can take a long time'. It would be nice to see some form of time constant determined for the inlet to return to initial conditions and a reflection on whether this waiting period is reasonable compared to replacing the lines between experiments.

Page 14, Line 441: All of Section 3.8 needs to be rewritten in terms of signal instead of mixing ratios, except where estimates are discussed. Figures referred to in this section should all report signal using units of ncps since a direct calibration has not been performed. The comments on how the estimated calibration factor and the observations in the chamber are consistent within the factor of 10-100 uncertainty for DMA put in the chamber can be retained to demonstrate that the assumptions for the CI-API-TOF calibration factor are also likely within this same factor of 10-100. In particular, the line of reasoning on Page 15 from Lines 461-464 is based on biased expectations where an arbitrary correction estimated at a value of 2 would bring the observations 'into even better agreement' with the expected mixing ratios, but this does not have much factual basis since the concentrations shown in Figure 8 span an order of magnitude depending on wall losses and chamber dilution. Perhaps stating that the observations fall within the expected range of values is sufficient for this section and the speculation on correction factors can be removed since a direct calibration of DMA was not actually performed.

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Page 15, Line 473: The specific analytes discussed are ammonia, dimethylamine, and iodic acid and this should be specified here. Depending on the actual chemical species comprising the remaining iodine oxides (or up to tetramers of iodic acid if this is the case), the iodine species detected can be made more chemically specific in the conclusion. Based on Table 2, iodine oxides seems to me to be the best term, and it could be used effectively throughout the manuscript.

Page 15, Line 474: Neither fast time response or time resolution values are given in the manuscript. Indeed, they could yield wonderful proof of the developed technique and should be included. See comments on Figures with some suggestions.

Page 16, Lines 488-491: In addition to having high proton affinity, this perfluorinated amine is also a strong surfactant which promotes its ionisation further.

Page 16, Conclusions: Revise in light of all other changes to the manuscript.

Page 27, Table 1: Remove. The only true detection limit measured is for NH₃ and the rest are estimated based on assumptions that may have significant error. Further to this, the LODs were acquired over 2.5 hours of signal acquisition, while the measurements are reported at 1 minute intervals. A more accurate assessment of detection limits would have been determined at similar timescales, using about 20-30 background measurements.

Page 29, Figure 1: Numeric or alphabetic labeling of the instrument parts with corresponding descriptions in the caption would make this diagram easier to follow as a lot of the text is obscured by color or very small. The 'argon+oxygen+water vapour' could be replaced with 'Ar + O₂ + H₂O'.

Page 31, Figure 3: If a fit is forced through the origin, then a measure of instrument signal while ultra pure zero air should be included as a blank to determine if there is an offset in detection, particularly for NH₃. For the HIO₃ measurement, the x-axis is a scaled value based off of H₂SO₄ detection and not a true measure of HIO₃ and a

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comparison of ncps would be more useful to describe the sensitivity of the H₃O⁺ CI-API-TOF versus the NO₃⁻. For this second plot, was any background value subtracted?

An important component of instrument performance that can be evaluated while doing calibrations such as these is instrument response times (both with increasing and decreasing analyte concentration) from 0-95 % of max signal and 100-5 %. The authors claim that the instrument has a rapid time response with high time resolution, yet no such data is presented in figures and no numeric values reported. This is critical to report as it also helps provide clear context in the interpretation of the chamber observations.

Page 32, Figure 4: Was this sensitivity dependence on RH used to correct the dataset shown from the chamber? With the changes in temperature, if there is water in the chamber, then there will be a change in sensitivity that should be applied and may change the interpretation of the datasets.

Page 33, Figure 5: The x-axis should also be signal-based units. The caption states that there is no RH dependence, yet there is a clear difference within the regressed data that shows this and suggests that it is also statistically significant between 40 to 80 % RH (color suggests that T is constant for these), and consistent with the findings for detection of NH₃ increasing in sensitivity with increasing RH.

Page 34, Figure 6: The logarithmic scale for the marker size should be provided here. The nomenclature replacing 'monomers', etc. should be revised as necessary.

Page 35, Figure 7: The two data components on the y-axis should be separated with a ';' and not with a '/' which implies division. The font size of everything in this figure needs to be made larger. Depending on the outcome of the details of the intercomparison assessment, the Picarro data may need to be removed from this figure, especially if it was connected to the exhaust line of the CI-API-TOF here. Panels a) and b) are not described in the caption and should be. An additional panel that may be of use in the intercomparison is a regression of the CI-API-TOF measurement against that of

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the Picarro when both detection limits are properly accounted for (i.e. properly background corrected based on calibrations that were performed). In the case where one instrument has a higher detection limit than the other (which seem likely to be the case given the sensitivity of the CI-API-TOF), then the higher LOD should be used as the cut-off for the intercomparison.

Page 36, Figure 8: Add a marker where the H₃O⁺ source water was changed on panel a) and make a note of it in the caption. Convert the mixing ratio to ncps and comment on the expected range of values with an assumed calibration constant in the caption. It is surprising that a direct calibration of DMA was not performed since permeation devices for this compound are commercially available, as they are for NH₃.

References

- [1] X. Ge, A.S. Wexler, S.L. Clegg, Atmospheric amines e Part I . A review, *Atmos. Environ.* 45 (2011) 524–546. doi:10.1016/j.atmosenv.2010.10.012.
- [2] J.M. Roberts, P. Veres, C. Warneke, J. a. Neuman, R. a. Washenfelder, S.S. Brown, M. Baasandorj, J.B. Burkholder, I.R. Burling, T.J. Johnson, R.J. Yokelson, J. De Gouw, Measurement of HONO, HNCO, and other inorganic acids by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS): Application to biomass burning emissions, *Atmos. Meas. Tech.* 3 (2010) 981–990. doi:10.5194/amt-3-981-2010.

Interactive comment on *Atmos. Meas. Tech. Discuss.*, doi:10.5194/amt-2019-215, 2019.

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