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Atmospheric Measurement Techniques Discussions

Interactive comment on "Technical note: Detection of dimethylamine in the low pptv range using nitrate Chemical Ionization-Atmospheric Pressure interface-Time Of Flight (CI-APi-TOF) mass spectrometry" *by* M. Simon et al.

Anonymous Referee #2

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The authors detail out a chemical ionization scheme to detect gaseous DMA with nitrate as the reagent ion for the CI-APi-ToF. The results are encouraging and the method is potentially useful. The paper is not clearly written, but it can be easily improved. In addition, there are several scientific issues that the authors need to address before this paper can be considered publication.

Major Comments:

Page 13265 line 27: the nitrate trimer was chosen as the normalizing ion signal. This is

a strange choice and it is not very clear why this ion was chosen. The authors write, "it seems likely that this produces more stable cluster ions compared to NO3-(HNO3) due to efficient acid-base stabilization." The normalization ion is chosen based upon which ion is chemically ionizing the neutral molecules/clusters. The rate equations from these chemical ionization reactions (such as those given in reactions R1 and R2) are what produce equations like Equation (4) from this paper. The math can be found in many previous studies ([Berresheim et al., 2000; Eisele and Hanson, 2000] to name two). It would make more sense to add the signals of the nitrate trimer and nitrate dimer to be the normalizing ion signal since both ions could be chemically ionizing neutral entities. The authors are also assuming that clusters do not change upon ionization/entering the mass spectrometer. Each of these assumptions would alter the signal to concentration inversion math (and the predicted transmission efficiency of the clusters ion the mass spec).

It would be useful to know which reagent ion has the highest signal: is it 188 m/z or 125 m/z? From the paper is seems like the nitrate trimer (188 m/z) is the highest, but this is just a guess. This observation would be strange if this is the case. The nitrate trimer is much less stable (lifetime of 4 ms at T=298K) than the nitrate dimer [Hanson and Eisele, 2002; Lovejoy and Bianco, 2000]). As a result, the nitrate dimer ion should have a longer lifetime (not observed to decompose) and should be in higher abundance than the trimer. I wonder if the trimer signal is the highest is because a DMA molecule is actually attached to the cluster and evaporates upon measurement. Obviously, this is difficult to prove but it would be nice for the authors to explore/explain their reagent ion signals better. Page 13264 line 13 The authors report peaks at 170, 233, and 296 m/z in the pure water/DMA environment at T=273 K. This seems to be in contrast to the peaks reported in [Jen et al., 2015]. From their graph Figure S2, I do not see peaks at those masses. They are operating at higher temperatures and with sulfuric acid at about the same concentration as [DMA] in the flow reactor. Can the authors comment on this and add a comparison of their mass spectra to those of [Jen et al., 2015]? I am concerned that if the purpose of this method is to measure [DMA] at the same time as

sulfuric acid and ELVOCs, then the evidence from [Jen et al., 2015] seems to indicate that nitrate+DMA clusters will not be detected in more complex experiments.

Section 3.4 (Page 13271): The Ci-APi-ToF measured DMA mixing ratio is compared to IC measured concentrations. This seems like a rather difficult comparison to make, given differences in sampling and instrument sensitivities. It would be beneficial to compare the nitrate measured [DMA] to [DMA] measured in positive ions using charged water clusters (or something of that sort) with the Ci-APi-ToF. I am not intimately familiar with the instrument but positive ions have been reported with the APi-ToF before so I believe this possible. I bring up this comparison because positive ion quantification of amines (using water clusters or acetone, as the authors wrote in Line 59 and 60) seems to be a more "well established" method.

The comparison with IC (page 13271 Line 10) is off by 5 pptv. Do the authors know if this agreement worsens with decreasing [DMA]? The authors report [DMA] as low as 5.8 pptv from the nitrate measurement. What is the uncertainty associated with this mixing ratio?

Minor Comments:

Page 13259 line 9: "This observation. . ." is an awkward sentence.

Page 13259 line 14-16: Awkward sentence.

Page 13260 Line 7: Comparison with Kurten et al is great, though for readers who do not know what the kinetic limit is, a reference to [Rao and McMurry, 1989]. The authors should note the specific sulfuric acid and DMA concentrations of the experiment in Kurten et al. where the kinetic limit was observed. As written now, the reader thinks sulfuric acid and DMA always proceeds at the kinetic limit which is untrue. This is shown in [Jen et al., 2014] where there are regimes of [DMA] and [sulfuric acid] that lead to the kinetic limit. Also, the kinetic limit refers to the sulfuric acid kinetic limit. DMA likely evaporates from the cluster.

Page 13260 Line 14: "near ground" what does near ground mean?

Page 13260 Line 16: ". . .in how far amines are indeed" the are indeed part makes the sentence sound awkward

Page 13260 Line 17: "This lack of knowledge" is a strange phrase

Page 13260 Line 21: "low enough limit" maybe change to high sensitivity and maybe put a number on it

Page 13261 Line 4-7: "The simultaneous. . ." awkward sentence

Page 13261 Line 14-15 ". . . vessel to study. . ." the to study phrase read awkwardly as the chamber does not study. It is used to study

Page 13261 line 16: "Care is taken. . ." awkward sentence

Page 13261 Line 19: "Results are reported. . ." consider adding "for this study" so the reader knows you are not referring to the previous studies

Page 13262 Line 3: "In order to have..." awkward sentence

Page 13262 Line 9: What is B?

Page 13262 Line 9-10: why mention the by-pass valve if it never used?

Page 13262 Line 15: Since I do not know what B is (or its units), what are the units of A? volumetric flow rate? Molar flow rate?

Page 13262 Line 13-14: standard temperature and pressure can be abbreviated as STP. I believe this is a common abbreviation.

Page 13262 Line 24: a priori should be italicized

Page 13262 Line 24-page 13263 Line 5: these two sentences confused me. Consider shortening the sentences and combining them? Or changing their order.

Page 13263 Line 11: ". . .which is indicating" awkward phrase

Page 13263 Line 17: how low is the condensation sink? What qualifies it as so low? Perhaps put a number on this

Page 13264 Line 3: change recently to previously

Page 13264 Line 10: ELVOCs has already been defined

Page 13264 Line 12: comma after “in the next section”

Page 13264 Line 12: DMA has already been defined

Page 13264 Line 13: The convention is to put a âĂć between the ligands of the cluster. So for 170 m/z, the formula would be NO3-âĂćHNO3âĂćDMA

Page 13264 Line 15: It is not necessary to write the exact mass down for these clusters. It does not provide any additional information than just saying high resolving power of the ToF. I would consider moving the description of resolving power and accuracy of the MS to the first paragraph in this section and masses of the detected ions to section 2.4

Page 13264 Line 22: needs paragraph transition, and “on the contrary to” is an awkward phase and the sentence is rather unclear

Page 13264 Line 22: I could not understand from this paragraph how the CIMS compares to CI-APi-ToF from the experimental setup

Page 13265 Line 9: The newer Cluster CIMS detects sulfuric acid via ligand switching with NO3-âĂćHNO3 [Zhao et al., 2010].

Page 13265 Line 17: The ions detected and their masses are written here. I would then remove the entire paragraph starting Page 13264 Line 15.

Page 13265 Line 15: How long is the ion-molecule reaction time in the CI reaction zone? This number is useful in determining if ion products have time to decompose at atmospheric pressure or if they fragment in MS.

Page 13265 Line 20: “more important reaction” What do you mean by more important? The dominant reaction? Compared to what? R1? This is a confusing sentence.

Page 13266 Equation 4: using T to mean a correction factor is confusing because T is normally used for temperature.

Page 13266 Line 13: If T is losses in the sample line, shouldn’t it have units? A better description of T would be useful.

Page 13267 Line 4: Any hypotheses on why no clusters containing 2 DMA were observed? Also, it would be useful to note the [DEA] of Luts et al. The concentration of base will determine what types of clusters are observed.

Page 13267 Line 8: “Figure 2” The authors switch between writing Fig. and Figure. From the captions of the figures, the appropriate one should be Fig. But, staying consistent is the only important point.

Page 13267 Line 17: Move experimentally to before determine in line 16

Page 13267 Line 21: comma after shut-off

Page 13268 Line 4: “Using the diffusion. . .” awkward sentence from the “one can” part

Page 13268 Line 6: “The fact that” this is a confusing sentence as it makes it sound like DMA and sulfuric acid have the same diffusion coefficients. The last phrase of the sentence is always awkward phrasing as sink and sticks efficiently are the same thing.

Page 13268 Line 18: This one sentence paragraph can be moved into the previous paragraph

Page 13268 Line 23: what is τ? Also the numbers in the parentheses have more significant figures than what the error allows.

Page 13269 Line 8: Even though the CI-APi-ToF uses the same clean air for the sheath as the CLOUD chamber, is it not also possible for DMA molecules to desorb from the

walls (i.e. holdover effects)? This would be a bigger problem at higher [DMA].

Page 13269 Line 10: s after shows, also Figure should be Fig.

Page 13270 Line 1: what is evaporating from this cluster? DMA? Or nitric?

Page 13270 Line 4: Is the APi section the first portion that is below atmospheric pressure?

Page 13270 Line 9: hyphen between ion and molecule

Page 13270 Line 18: the first two sentences of this paragraph read a bit awkwardly

Page 13271 Line 19: “anyhow” read awkwardly

Page 13271 Line 20: no need to write statements after conclusions

Page 13271 Line 22-24: “Applying the correction factor. . .” I do not understand these two sentences. Applying the correction factor would significantly increase the [DMA] reported by Kurten et al. How does this not imply a significant change? (I think I understand the sentences now, but they are confusing.)

Page 13272 Line 2: “at low mixing ratios” what qualifies as low? Maybe put a number on this. Also, this study only shows the DMA can be detected with nitrate CI when no sulfuric acid is present. This detail should be included.

Page 13272 Line 10: “the method introduced . . .” this phrase is a bit misleading. The other chemical ionization methods do not just detect amines. They detect many other compounds too (water clusters can even detect certain types of sulfuric acid clusters).

Page 13272 Line 14-16: “Being capable of measuring...” This sentence implies that nitrate can detect DMA in the presence of sulfuric acid and ELVOCs. This study has not shown this. Also, this sentence is phrased awkwardly.

Page 13272 Lin 19-21: “For this an amine source. . .” Confusing sentence.

Figure 1: MFC1 and MFC3 have DMA that passes through it. Is there any issue with

DMA holdover/other contamination that is introduced by DMA in a MFC?

Figure 2: The y axes show signal in cps but the highest value is 1. This seems like these signals were normalized? It would be useful to instead see raw signals and the signals of the nitrate ions. Also, since the graphs are labeled A-D, it would be helpful to just write the cluster identity for each letter on the graph.

Figure 3: The gray shaded region makes me think that DMA was injected in an integrated time (or something strange like that). It would make more sense to just draw vertical lines with labels that show when DMA was injected/shut off or have the gray region cover the entire vertical dimension.

Figure 5: it is difficult to see the gray area which is the [DMA] set point. Maybe try just a solid line (not red)? Looking at panel A, there appears to be [DMA] carryover from somewhere in the system (seen at 17:00). The set point drops but the signal of the DMA clusters remains more or less constant (about a factor of 2 off). This seems to suggest that this method (not necessarily the nitrate chemical ionization) is not sensitive to quick changes in concentration.

Works cited in this review: Berresheim, H., T. Elste, C. Plass-Dülmer, F. L. Eisele, and D. J. Tanner (2000), Chemical ionization mass spectrometer for long-term measurements of atmospheric OH and H2SO4, International Journal of Mass Spectrometry, 202(1–3), 91-109, doi:10.1016/s1387-3806(00)00233-5.

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