Atmos. Meas. Tech. Discuss., 3, C739–C751, 2010
www.atmos-meas-tech-discuss.net/3/C739/2010/


Atmospheric Measurement Techniques Discussions



# *Interactive comment on* "Chemical ionization mass spectrometer (CIMS) for ambient measurements of ammonia" *by* D. R. Benson et al.

**D. R. Benson et al.**

slee19@kent.edu

Received and published: 21 June 2010

Response to Anonymous Referee #2

Summary Response: We appreciate the reviewer's comments and helpful suggestions. Below, we addressed each comment in detail. The major revisions based on the review include: (1) addressed if volatile ammonium aerosol could bias our data, (2) clarified variability of the instrument performance, especially variability in sensitivity, (3) added a calibration curve, (4) added discussion of past aerosol measurements which could explain why ammonia concentrations are low in this region, and (5) included several current references on ammonia detection techniques.

Comment: This manuscript describes the deployment of a CIMS for the measurement

of atmospheric ammonia in three different seasons. The technique appears promising for the provision of high time response data, with sufficient sensitivity to make measurements at sub-ppb mixing ratios. The value of the season-to-season comparisons is questionable, because the configuration of the sampling assembly seems to have been altered for each period of deployment, which may introduce biases.

Response: We agree that some degree of bias may exist due to variations of the inlet setup from season to season and have reflected this in the manuscript (Page 21, Section 6, Conclusions: L470 – 472).

Comment: Additionally, there appears to be a large degree of variability in the accuracy and precision of the technique, which the authors have not adequately explained.

Response: There were certain degrees of variations both in background signals and sensitivity. Background signals usually had the same trends as ambient NH3 levels, indicating that there were some effects of adsorption and desorption of NH3 on surfaces inside inlet, but such effects were taken into account by using background measurements. Sensitivity also varied day to day, but the measured [NH3] levels did not vary over time as sensitivity did. In the present study, we did not make intercomparison tests with other NH3 instruments. Being subject to some degree of variability in the accuracy and precision of the current technique, however, the intercomparison made during the Summer of 2009 in the Michigan forest using our CIMS technique and a wet scrubbing method coupled with long-path absorbance photometry (employed by Dr. Xianliang Zhou from State University of New York - Albany) further showed that this CIMS technique provides reliable NH3 measurements. For example, the [NH3] measured over an 8 day period showed similar results with these two independent methods within experimental uncertainties. A detailed description of these intercomparison results is discussed in (Kanawade et al., in preparation). (Page 18, Section 5, Discussion: L399 – 413)

Comment: In order to be publishable in AMT, this manuscript must present the char-



AMTD
3, C739–C751, 2010





acterization of the instrument performance in a more consistent and understandable way. For example, the analysis of the time response provides some parameters from a single fit, but presumably several experiments were carried out.

Response: In this revision, we have tried to make more consistent explanations of the instrument performance. In the ACPD manuscript, we had revised Figure 3 to only include the fitting to the given equation. In the submitted manuscript, we originally included two fittings to show that they were similar even though the sensitivities were different (25 and 37 Hz/pptv), for example. The pre-factors were within 12% between different fittings (the first pre-factor was identical within standard deviation) and the second time constant was within 50% (the first was identical within standard deviation). (Page 12, Section 3.1, Time Response: L255 – 257).

Comment: The authors should more clearly address whether the presence of volatile ammonium aerosol could bias their signal.

Response: Agree. There is also the possibility that volatilization of ammonium nitrate from various surfaces of the instrument can contribute to the measured NH3 ion signals, but the volatilization is usually negligible for temperatures under 50 °C and residence times less than 2.3 s (Neuman et al., 2003). Because our temperature (35 °C) and inlet residence time (0.068 s) were lower than this, there should not be any bias in the signal due to volatile ammonium aerosol. Another study (Fehsenfeld et al., 2002) also confirmed that volatilization in mass spectrometer systems [the system used for that study is similar to (Huey et al., 2004), (Nowak et al., 2006) and our CIMS] is limited for time scales less than one second. As discussed in Sections 3.2 and 3.3, we also did not see any temperature dependences of the instrument background and sensitivity, and this proves that NH3 artifacts from vaporization of ammonium decomposition from the aerosol phases were negligible in our instrument. While we tried to minimize the effects of volatilization of ammonium nitrate from surfaces by heating the inlet system, we have also made frequent background measurements, which ultimately reduces the effects of these artifact signals. (Page 6, Section 2, Instrument: L121 –



AMTD

3, C739–C751, 2010





133).

Comment: The interpretation of the ambient measurements is limited by the lack of supporting measurements (e.g. aerosol composition or at least mass loading, SO2, HNO3), but nevertheless the implication that mixing ratios are low because emissions are low is overly simplistic. Have past aerosol composition measurements been made in the region that could at least suggest whether aerosol is generally acidic?

Response: This is a valuable point. During the ICARTT experiments, (Sorooshian et al., 2006) showed that when flying the Cleveland area, SO2 emitted from power plant plumes were as high as 69.5 ppbv and that the ammonium-to-sulfate ratio also indicated insufficient amounts of ammonia present so the high levels of sulfuric acid would not be neutralized. It is also true that SO2 emission in Ohio ranks amongst the top in the nation (http://www.epa.gov/air/sulfurdioxide/) because of the strong SO2 emission from large size coal-burning power plants in this region (http://www.epa.gov/cgi-bin/broker?_service=airdata&_program=progs.webprogs.emisumry.scl&_debug=2&geotype=st&geocode=OH&geoname=
typically, the reported SO2 concentrations were nearly at the ppbv or tens of ppbv range year around in Akron and Cleveland in recent years. Data taken from the Ozone Monitoring Instrument on the NASA EOS Aura platform (Krotkov et al., 2006) gave the average SO2 concentration ($\pm 1\sigma$) as 0.7 $\pm$ 1.3 Dobson units (DU) for the winter, 0.3 $\pm$ 0.13 DU for the spring, and 0.5 $\pm$ 0.52 DU for the fall in the planetary boundary layer in Kent, Ohio. These values were anti correlated with the median [NH3] ($\pm 1\sigma$) values (60$\pm$75 pptv for winter, 200$\pm$120 pptv for spring, and 150$\pm$80 pptv for fall) and show that when [SO2] was higher that [NH3] was lower. This could be explained by removal of NH3 through uptake by sulfuric acid aerosols. From these reasons, it is possible that ammonia concentrations are low this area due to the high emission of SO2 and thus the high acidity of aerosols (Sorooshian et al., 2006). (Page 19 – 20, Section 5, Discussion: L431 – 448)

Comment: I provide more specific comments below: Abstract – the discussion of the sensitivity, uncertainty and detection limits is a bit ambiguous. What averaging time is



AMTD
3, C739–C751, 2010





used to calculate a detection limit of 60 pptv and is that for a 3 sigma detection limit?

Response: The sensitivity has a 30% uncertainty based on variability in calibration signals. The detection limit is based on 3 sigma deviation and the averaging time was 1 minute. (Page 1, Abstract: L16 – 17).

Comment: Introduction – is citric acid denuder really a technique on its own? Don't you need to specify the analysis technique used after the denuder collection? For what sampling period and analysis technique is the 25 pptv detection limit given?

Response: The actual analysis technique used once the extract is removed from the denuder is ion chromatography (Fehsenfeld et al., 2002). The sampling period is two hours and the detection limit is 25 pptv for the chromatographic system (Fehsenfeld et al., 2002). (Page 3, Introduction: L62 – 64).

Comment: There are many more recent discussions of ammonia measurement techniques (in AMT alone: Wolff et al., 2010; von Bobrutzki et al., 2010; Ellis et al., 2010; and in ACP Norman et al., 2009) Given that you heated the inlet to 35 _C (at least during the fall), how confident are you that no ammonium-containing particles volatilized prior to the ion-molecule reaction region? P1135 L 27, Sentence should start 'Amongst these" P1137 L7, The sentence "Below, we only describe the inlet and flow tube regions (Sects. 2.2 and 2.3)." should be moved to the end of the paragraph it is part of.

Response: We added one of the reviewer's references (von Bobrutzki et al., 2010) for comparison of the different CIMS techniques and (Thomas et al., 2009; Ellis et al., 2010) to describe more ammonia measurement techniques in introduction. As mentioned above, ammonium nitrate volatilization was found to be negligible for temperatures under 50 °C and residence times under 2.9 s (Neuman et al., 2003). Because our temperature (35 °C) and inlet residence time (0.068 s) were lower than this, there should not be any bias in the signal due to volatile ammonium aerosol. Another study (Fehsenfeld et al., 2002) also confirmed that volatilization in mass spectrometer systems [the system used for that study is similar to (Huey et al., 2004), (Nowak et al.,



AMTD
3, C739–C751, 2010

2006) and our CIMS) is limited for time scales less than one second. (Page 6, Section 2, Instrument: L121 – 127). This decomposition is also expected to be temperature dependent. However, we did not see any dependence of the ammonia data on temperature (including background, sensitivity and calculated ammonia mixing ratios) and this proves that desorption/decomposition of ammonium to ammonia was negligible at our measurement conditions (Page 13, Section 3.2 (Background and Uncertainty): L290 – 292; Page 14, Section 3.3 (Sensitivity and Uncertainty): L314 – 315). We have reworded the appropriate sections in the text according to the reviewer's comments (Page 3, Section 1, Introduction: L62; Page 5, Section 2, Instrument: L112 – 113).

Comment: P1137 L23 – km and miles in same sentence

Response: This part has been reworded. (Page 7, Section 2.1 (Measurement Site): L141 – 142).

Comment: Figure 1b – Was any attempt made to characterize sampling losses of ambient ammonia in the inlet before PFA tee 1?

Response: As mentioned in section 3.1, calibration gases were added directly to CIMS inlet for calibration measurements (PFA tee 1, C1 – C3 in figure 4a). However, we also added cal gases to our flow tube with the CIMS inlet attached (the flow tube was attached to the very beginning of the inlet) (C4 in Figure 4a). The response to this addition shows that there were minimal losses when compared with the other measurements, indicating the losses in the inlet before PFA Tee 1 are minimal. (Page 12, Section 3.1: L266 – 271). In C1 – C3 the ammonia mixing ratio based on dilution was 800 pptv and for C4 it was 400 pptv; and, the signal change for C4 was also about $\frac{1}{2}$ of the change for C1 – C3 ($\Delta$Hz $\sim$ 20000 for 800 pptv and $\Delta$Hz $\sim$ 10000 for 400 pptv) (Page 12, Section 3.1, L264 – 266).

Comment: Figure 2 – It's extremely difficult for the reader to see the various colours meant to differentiate between the ambient, cal, and zero.



AMTD
3, C739–C751, 2010





Response: Changed the style of lines to help differentiate between the different types of measurements. (Page 35, Figure 2)

Comment: Section 2.3 – How constant were the relative proportions of the reagent ion? Did you perform any tests to confirm that normalizing to their sum was the most appropriate approach? Is there evidence that they all react with ammonia to produce m/z = 64 amu with the same efficiency?

Response: The relative proportions of the reagent ions were usually within 10% of each other. No tests were performed to confirm that normalizing the sum was the correct approach. But in order to account for the possible fluctuations in reagent ion signals which were caused by the fluctuation of pressure in the ion-molecule reaction region (<10%), we also monitored these primary reagent ions and normalized them when calculating [NH3]. It was seen that when the reagent ion peaks would change all the product ion peaks would change accordingly. For normalization, the mean value of the sum of the three major reagent ion signals for a day was taken as a standard value (100% normalization) for that day. Then the sum of the three major reagent ions at each time was compared with this mean value and the ratio of the each sum value and the mean value was taken into account into ammonia mixing ratios. If the ratio is 1 then the normalization factor would be 1 for ammonia mixing ratio calculations; if the ratio is 1.1 then the normalization factor would be 1/1.1. For proton-transfer chemical ionization reactions, cluster formation is very common and in order to avoid the complexity of ion clusters, CDC is used to make spectra much cleaner. Reaction rates of these proton transfer ion molecule reactions (for example, all these three reagent ions with ammonia) are very similar to each other; these are collision limited reactions and their reaction rates are nearly 2×10-9 cm3 s-1. So this simplifies normalization of these different reagent ion signals. (Page 10, Section 2.3 (Ion Molecule Reaction Region): L221-226)

Comment: The authors state that the use of the CDC prevents them from detecting clusters of water and reagent ion, but can they be sure they don't exist in the ion-



AMTD

3, C739–C751, 2010



molecule reaction region. Could the humidity-dependence of calibrations offer any indication as to whether this might be significant?

Response: The CDC comes after the ion-molecule reaction region (Figure 1a), so it would remove any clusters that are formed prior to there. As stated in Section 3.3, there was no clear RH dependence for the sensitivity which means there was no humidity dependence of calibrations (Page 14, Section 3.3, Sensitivity and Uncertainty: L314 – 315).

Comment: Section 3 P1141 – Equation 1 – this looks like an equation for a bi-exponential fit, and the 1/e2 time depends both on the time constants and each terms pre-factors. Why does Equation 1 provide parameters for one specific fit, when the time decay experiments were carried out several times – as shown in Figure 3? The authors should present a more representative value with some indication of uncertainties. Given that the shorter time constant is on the order of 2 sec, a data collection rate of 1 Hz may not be sufficient to describe the decay rate of the signal.

Response: In the ACPD manuscript, we have altered figure 3 to only include the fitting to the given equation. We originally included two fittings to show graphically that they were similar even though the sensitivities were different (25 and 37 Hz/pptv). The pre-factors were within 12% between different fittings (the first pre-factor was identical within standard deviation) and the second time constant was within 50% (the first was identical within standard deviation). 1 Hz data was what the CIMS was setup to collect. Averaged data (say 2, 5, 10 s etc.) may have given better fittings and a better detection limit, but some of the time resolution would have been lost. (Page 12, Section 3.1, Time Response: L255 – 257).

Figure 4a – why was the time response so much worse in calibration addition C4 than for addition C3, which both had the same nitrogen flow? P1141 – L25 why was the instrument response to the addition of 400 pptv as expected for the addition of 800 pptv? Section 3.2 P1142 If some of the signal during the background is from desorbing



AMTD

3, C739–C751, 2010

ammonia from the inlet, wouldn't it be most appropriate to normalize the signal to the reagent ions (i.e. use the sensitivity to calculate it as a mixing ratio)?

Response: As mentioned above, the calibration addition for C3 was added directly to the CIMS inlet while the calibration for C4 was added to a flow tube connected to the CIMS inlet. Because the flow tube had a larger diameter ($\sim$ 3 cm) it took time for the ammonia to diffuse through our flow tube and reach the CIMS inlet. In C1 – C3 the ammonia mixing ratio based on dilution was 800 pptv and for C4 it was 400 pptv; and, the signal change for C4 was also about $\frac{1}{2}$ of the change for C1 – C3 ($\Delta$Hz $\sim$ 20000 for 800 pptv and $\Delta$Hz $\sim$ 10000 for 400 pptv). (Page 12, Section 3.1, L264 – 266). Signals during the background mode from possible desorbing ammonia in the inlet have nothing to do with reagent ions (which is caused by pressure fluctuations in the ionization region) or their normalization. Also, the effects from desorbing ammonia in the inlet are minimal, as mentioned above.

Comment: Fig 5a: If the inlet design and time response were optimized for the fall measurements, why are the counts so much higher during the background in this season?

Response: This is due to the fact that the sensitivity was higher during this time as well. So while the counts are in fact higher, the background (calculated in ppbv) is still similar because the sensitivity is higher during this period.

Comment: Fig 5b – I don't think this is the appropriate use of 'calibration curve' in the caption. Section 3.3 What accounted for the wide range in sensitivity? Was the concentration of the NH3 cylinder confirmed by another method?

Response: The caption was changed to "calibration measurement". For the winter and spring, the sensitivity range was much smaller compared to the fall. This may be due to the fact that when we set up in the fall, the instrument had been transported from Michigan for long distance and once it was set up, it took time for the instrument to stabilize (this is why you see the sensitivity constantly increasing). Also, the ethanol liquid which was used to produce the reagent ions had to be replenished every day.



AMTD

3, C739–C751, 2010

Because of this daily maintenance and having to shut off flows to refill the bottle, it was possible that this changed the signal variability, resulting in the differences in sensitivity on a day to day basis. While we don't understand which factors affect the stability of sensitivity, it is also clear that even though the sensitivity did vary, this changing sensitivity did not affect the measurements; for example, the calculated ammonia mixing ratios did not follow the same pattern as the sensitivity varied and during the fall, the ammonia mixing ratios were always in the sub-ppbv level (Figure 6). (Page 14, Section 3.3 (Sensitivity and Uncertainty): L311 – 314). The concentration of the NH3 cylinder was not confirmed by another method but the uncertainty given by the manufacturer (Linde) was 5 % (Page 8, Section 2.2 (Inlet: Background, Ambient, and Calibration Mode): L179 – 180). We have now added a calibration curve (Figure 4b).

Comment: P1145 L 11 – extra period before reference

Response: Corrected.

Comment: Discussion In your comparison of the different CIMS ionization schemes, you indicate that the different reagent ions lead to different background measurements. Can you be sure that this difference wouldn't be more appropriately attributed to the inlet configuration used by each instrument?

Response: Different ion-molecule reaction schemes will produce various results as far as what the instrument background will be due to different chemical species being used. However, inlet configurations can also affect signals, as condensation in the tubing can lead to NH3 losses (Norman et al., 2009). The sampling line effects, such as RH and ammonia concentrations, can also play a role in background measurements (Ellis et al., 2010), although in our case the background signals did not have a clear dependence on RH, but varied with the sampled NH3 level. (Section 5, Discussion: L375 – 379).

Comment: Why would a curved inlet lead to the loss of a gas phase species?



AMTD
3, C739–C751, 2010

Response: One reason to reduce curvature in the tubing is that we want to use the shortest amount of tubing possible so that the residence time is kept at a minimum. Also, curvature in the tubing can lead to kinks which may alter or disrupt the flow and would lead to losses on the sides of the tubing.

Comment: P 1146 L26 – The lower levels in Kent may be attributed to lower vehicle emissions, but one should also consider the role of aerosol uptake. Could the presence of high levels of aerosol sulphate act as a strong condensational sink where your measurements are made?

Response: Agree. During the ICARTT experiments, (Sorooshian et al., 2006) showed that when flying the Cleveland area, SO2 concentrations from power plant plumes were as high as 69.5 ppbv and that the ammonium-to-sulfate ratio also indicated insufficient amounts of ammonia present so the high levels of sulfuric acid would not be neutralized. It is also true that SO2 emission in Ohio ranks amongst the top in the nation (http://www.epa.gov/air/sulfurdioxide/) because of the strong SO2 emission from large size coal-burning power plants in this region (http://www.epa.gov/cgi-bin/broker?_service=airdata&_program=progs.webprogs.emisumry.scl&_debug=2&geotype=st&geocode=OH&geoname= typically, the reported SO2 concentrations were nearly at the ppbv or tens of ppbv range year around in Akron and Cleveland in recent years. Data taken from the Ozone Monitoring Instrument on the NASA EOS Aura platform (Krotkov et al., 2006) gave the average SO2 concentration ($\pm 1\sigma$) as 0.7 $\pm$ 1.3 Dobson units (DU) for the winter, 0.3 $\pm$ 0.13 DU for the spring, and 0.5 $\pm$ 0.52 DU for the fall in the planetary boundary layer in Kent, Ohio. These values were anti correlated with the median [NH3] ($\pm 1\sigma$) values (60$\pm$75 pptv for winter, 200$\pm$120 pptv for spring, and 150$\pm$80 pptv for fall) and show that when [SO2] was higher that [NH3] was lower. This could be explained by removal of NH3 through uptake by sulfuric acid aerosols. From these reasons, it is possible that ammonia concentrations are low this area due to the high emission of SO2 and thus the high acidity of aerosols (Sorooshian et al., 2006). (Page 19 – 20, Section 5, Discussion: L431 – 448).



AMTD
3, C739–C751, 2010





Additional References: Ellis R. A., Murphy J. G., Pattey E., van Haarlem R., O'Brien J. M., Herndon S. C.: Characterizing a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) for measurments of atmospheric ammonia, Atmospheric Measurement Techniques, 3, 397-406, 2010.

Fehsenfeld F. C., Huey L. G., Leibrock E., Dissley R., Williams E., Ryerson T. B., Norton R., Sueper D. T., Hartsell B.: Results from an informal intercomparison of ammonia measurement techniques J. Geophys. Res., 107, 4812-4819, doi:4810.1029/2001JD001327, 2002.

Huey L. G., Tanner D. J., Slusher D. L., Dibb J. E., Arimoto R., Chen G., Davis D., Buhr M. P., Nowak J. B., Mauldin III R. L., Eisele F. L., Kosciuch E.: CIMS measurements of HNO3 and SO2 at the South Pole during ISCAT 2000, Atmospheric Environment, 38, 5411-5421, 2004.

Krotkov N. A., Carn S. A., Krueger A. J., Bhartia P. K., Yang K.: Band Residual Difference Algorithm for Retrieval of SO2 From the Aura Ozone Monitoring Instrument (OMI), IEEE Transactions on Geoscience and Remote Sensing, 44(5), 1259-1266, 2006. Norman M., Spirig C., Wolff V., Trebs I., Flechard C., Wisthaler A., Schnitzhofer R., Hansel A., Neftel A.: Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland), Atmospheric Chemistry and Physics, 9, 2635-2645, 2009.

Nowak J. B., Huey L. G., Russell A. G., Tian D., Neuman J. A., Orsini D., Sjostedt S. J., Sullivan A. P., Tanner D. J., Weber R. J., Nenes A., Edgerton E., Fehsenfeld F. C.: Analysis of urban gas phase ammonia measurements from the 2002 Atlanta Aerosol Nucleation and Real-Time Characterization Experiment (ANARChE), J. Geophys. Res., 111, D17308, doi:17310.11029/12006JD007113, 2006.

Sorooshian A., Varutbangkul V., Brechtel F. J., Ervens B., Feingold G., Bahreini R., Murphy S. M., Holloway J. S., Atlas E. L., Buzorius G., Jonsson H., Flagan R. C., Seinfeld J. H.: Oxalic acid in clear and cloudy atmospheres: Analysis of data from



AMTD

3, C739–C751, 2010

International Consortium for Atmospheric Research on Transport and Transformation 2004, Journal of Geophysical Research, 111, D23S45, 2006.

Thomas R. M., Trebs I., Otjes R., Jongejan P. A. C., Brink H. T., Phillips G., Kortner M., Meixner F. X., Nemitz E.: An Automated Analyzer to Measure Surface-Atmosphere Exchange Fluxes of Water Soluble Inorganic Aerosol Compounds and Reactive Trace Gases, Environmental Science and Technology, 43, 1412-1418, 2009.

von Bobrutzki K., Braban C. F., Famulari D., Jones S. K., Blackhall T., Smith T. E. L., Blom M., Coe H., Gallagher M., Ghalaieny M., McGillin M. R., Percival C. J., Whitehead J. D., Ellis R., Murphy J., Mohacsi A., Pogany A., Junninen H., Rantanen S., Sutton M. A., Nemitz E.: Field inter-comparison of eleven atmospheric ammonia measurement techniques, Atmospheric Measurement Techniques, 3, 91-112, 2010.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 1133, 2010.