

## ***Interactive comment on “Field inter-comparison of eleven atmospheric ammonia measurement techniques” by K. von Bobruzki et al.***

**K. von Bobruzki et al.**

kvbobruzki@web.de

Received and published: 6 December 2009

### General Comments

Anonymus Referee #2: I found the instrument descriptions to be uneven, in particular the level and applicability of citations.

Reply: This un-evenness partially reflected the fact that some of these instruments are research instruments, which are well documented in the peer reviewed literature, while others are commercial instruments, for which only few publications are available. In the revision, we have made an attempt to even out the descriptions as much as possible to provide an improved balance.

Anonymus Referee #2: One piece of information not provided was an estimated of the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



accuracy uncertainty for each instrument, i.e., how well does each instrument think it can measure NH<sub>3</sub>.

Reply: Information about precision provided by the manufacturers could already be found in Table 1, and we have added a column listing the accuracy stated by the manufacturers, where an a priori estimate was available. Unfortunately, most manufacturers do not provide information on accuracy. For many instruments, the accuracy is likely to be dominated by the implementation of the technique, i.e. inlet lines, temperature control, accuracy of calibration standards. As such, for most instruments, establishing a feel for the accuracy is an outcome of this study not an input.

Anonymus Referee #2: For instruments that calibrate using permeation devices, there is an uncertainty associated with the permeation rate that directly ties in with calculating the concentration of the calibration standard. For the absorption techniques, there is an uncertainty associated with the available cross sections. While the manuscript attempts to evaluate instrument A vs. instrument B, it does not address whether either A or B accurately reflects the ambient concentration. I think this is important information in evaluating the overall state of NH<sub>3</sub> measurements. The authors should look at the NASA TAbMEP project (<http://www.air.larc.nasa.gov/TAbMEP.html>) for further examples of comparison analysis.

Reply: While the comparisons within the TAbMEP project aimed at harmonising the datasets so that meaningful concentration differences can be derived, this is not the subject of the current study and the data are not feeding into further analysis. However, it is clearly beneficial to make a judgement on what the best estimate of the concentration would have been. For the reasons stated by this reviewer, we believe that the wet chemistry instrument currently have an implicit advantage in that they do not rely on an accurate gas-phase standard or any absorption cross sections. They also provide a more robust approach to separating gas and aerosol phase. However, they could potentially suffer artefacts from interfering compounds. The associated discussion has been expanded in the revised manuscript.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Anonymus Referee #2: In addition, the abstract ends by stating three factors affecting measurement precision: inlet design, state of inlet filters, and quality of gas-phase standards. Yet, only the inlet filter issues are thoroughly discussed in the text. No place in the text discusses inlet design or gas standards in depth enough to support the conclusion implied in the abstract.

Reply: All three factors are discussed in the text. We regret that the investigation into each was not as detailed as the reviewer would like to have seen, but we feel it is still discussed in sufficient detail to warrant the mention in the abstract.

Anonymus Referee #2: There are, also, a number of very general statements concerning certain instruments, in particular in section 4.2 that are not supported with any data presented here.

Reply: In section 4.2 we refer to the data presented in Tables 1, 2, 5 and Fig. 4f. We have modified some of the text to reduce speculations.

Anonymus Referee #2: Furthermore, I agree with the other referee that relative humidity could have a significant influence, especially to inlet response.

Reply: A more detailed analysis of this will be subject of a second paper. See reply to Reviewer 1.

Anonymus Referee #2: I also agree that describing the quality of the instruments with a correlation coefficient to an ensemble average (NH<sub>3</sub>-ref) could mask systematic differences. I think this can be seen in some of the Table 8 correlation plots.

Reply: That is why we present both, the comparison against the ensemble average and the comparison of the instruments against each other. See reply to Reviewer 1. We used the ensemble measurement as a reference as we felt that it would not have been fair or justifiable to single out a single instrument as the gold standard, as each approach has limitations.

Anonymus Referee #2: Finally, I'm not sure what the take home message of this

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

manuscript is. Is this paper making correction recommendations or is it showing that, compared to trace gas measurements of CO and NO, NH<sub>3</sub> measurements have a long way to go?

Reply: We certainly agree that NH<sub>3</sub> measurement technology is intrinsically more difficult and less advanced than measurement approaches for CO and NO for the reasons discussed in the text. We cannot make correction recommendations as the exact magnitude of the correction will depend on the individual setups, calibration systems etc. The message of the paper is to reflect the limitations of the state-of-the-art in measurement technology, and to highlight the key issues that need to be considered when making measurements of NH<sub>3</sub> in the future. Finally, we provide some guidance as to what approach may be suited for which applications, which we have expanded in the revised manuscript.

#### Specific Comment

Anonymus Referee #2: 2.1 Site description and Figures 1 and 2: This section states the inlet heights of all instruments but does not give an indication of the horizontal spacing between inlets. From figure 1 it is difficult to see the actual inlets. At first look one could assume all the inlets are located on the scaffolding but I do not think that is the case. Labelling the location of the inlets in figure 1 or describing the distance between gives stronger support to the claim made later that some difference between instruments is due to natural variability of sampling different air.

Reply: The inlets have now been marked on Fig. 1 and the distances have been indicated.

Anonymus Referee #2: If they are all at the same location then I question that any instrument is sampling different air. For future experiments the investigators should consider having all the inlets at the same location as in the nitric acid comparison described in Arnold et al., Atmospheric Environment [2007].

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive  
Comment

Reply: Some of the instruments are bulky and it would have been difficult to sample from the same location at the same time as using inlets as typically used by the different groups (one of the objectives of the study). The study presented here is not a replacement of laboratory comparisons under controlled conditions, but a complement.

Anonymus Referee #2: The wind panel on Figure 2 does not convey much useful information. There is no scale or direction information. Am I correct in assuming the top of the page is North? There are two typos with the aerosol data. The legend and caption should read NH<sub>4</sub><sup>+</sup>.

Reply: The wind panel shows both magnitude and direction. We have added a scale for the wind speed as depicted by the arrow length and explain the direction in the revised caption. The formatting of NH<sub>4</sub><sup>+</sup> has been corrected.

Anonymus Referee #2: 2.3 Measurement techniques: P1791 Line 13: The described inlets were made of what material?

Reply: The inlet material is HDPE (High Density Polyethylene) as explained in the revised version of the manuscript.

Anonymus Referee #2: P1793 Line 12: Starting here and throughout the measurement technique descriptions the authors switch between metric and American units. I find this distracting and confusing and recommend they choose metric throughout.

Reply: We changed to metric units.

Anonymus Referee #2: P1794 Dual-QCLAS: Here the instrumental background is determined by the addition of NH<sub>3</sub> free air generated by a catalyst heated to 300°C. However, not only does this remove NH<sub>3</sub> but changes the RH of the air. Neither here nor in the Whitehead reference given do the authors show that the change in RH has no effect on the inlet characteristics and no impact on the determined background.

Reply: We agree that changes in RH (and temperature) can change the inlet characteristics and e.g. cause desorption from the inlet lines. This is exactly the reason for

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

using the catalyst as this actually attempts to minimise the effect on RH. By contrast, using zero air or N<sub>2</sub> from a cylinder would cause a large difference between the RH during sampling and zero determination. The Pd/AL<sub>2</sub>O<sub>3</sub> catalyst has been shown to have a negligible affect on the water concentration of the background air (Wert et al., 2002). We have clarified this in the revised manuscript.

Anonymus Referee #2: P1794 Compact QCLAS: I am intrigued by the use of the virtual impactor but am disappointed that there is no reference or data to support that it works and has no effect on ambient NH<sub>3</sub> concentrations, i.e. possible additional losses. Also, as mentioned in the general comments section, no information about how the permeation rate is determined (i.e., weight loss, optically (see Neuman et al. Environmental Science & Technology [2003]) or its uncertainty is given.

Reply: The inlet we use was designed by Scott Herndon at Aerodyne Research Inc. We have changed the text in order to better describe its design. The best evidence that the impactor has little or no effect on the NH<sub>3</sub> is to show time response to a perm tube addition with and without the impactor. We do not have any published data on this response comparison at this time, but it will be further addressed in the AMT paper to be submitted in a few weeks. The permeation rate was determined gravimetrically by the manufacturer (Kin-Tek) as 100 ng min<sup>-1</sup> at 40°C. The rate was confirmed as 100 ±5 ng min<sup>-1</sup> at 40°C by passing a flow of permeation tube standard through citric acid filters for 24 hours, followed by extraction with deionized water and analysis using ion chromatography, as described in the revised manuscript.

Anonymus Referee #2: P1796 Ntirolux-100: During what part of the 6 month calibration cycle was the instrument deployed? What is the uncertainty associated with that calibration?

Reply: The Nitrolux-100 was calibrated just before the beginning of the inter-comparison(8th August 2008). The uncertainty: zero intercept: -0.006 ppbv; Linearity check: R<sub>2</sub> = 0.999, System response time (under dry conditions): 90% in 2 minutes.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Anonymus Referee #2: P1797 CRDS: How often does the manufacturer calibrate the instrument? When was it most recently calibrated? What is the uncertainty?

Reply: The instrument used in the inter-comparison was a test instrument which had been on the road for a couple of months. It was ~2 months subsequent to its most recent calibration.

Anonymus Referee #2: P1797 CIMS: I'm unclear why Marcy et al is referenced in relation to the  $\text{H}^+(\text{C}_3\text{H}_6\text{O})_2$  ion chemistry when it describes, as stated in the title of the reference, measurements of  $\text{HNO}_3$ ,  $\text{HOI}$ , and  $\text{ClONO}_2$  using  $\text{SF}_5^-$  ion chemistry. The references used to describe the CIMS configuration actually describe some conflicting configurations (i.e., flow tube vs perpendicular ionization configuration, collisional dissociation chamber vs no dissociation). It is difficult to know what was used. The authors should improve their instrument description or more thoroughly vet the references given.

Reply: The referee is correct and we have removed the references to Hagg and Szabo (1986), Crounse et al. (2006) and the review of Huey et al. (2006) to eradicate any confusion. The CIMS instrument is identical to the one used by Kim and co-workers. That is to say that we use flow tube for ionisation and have collisional dissociation chamber and now the cited references only refer to CIMS instruments that have the same configuration. However it should be noted that this does not reflect changes in the ion molecule chemistry as this only requires a change in gases and not a change in the configuration of the CIMS. Standard addition calibrations were performed at least hourly with the output of an  $\text{NH}_3$  permeation device (Kin-tek, La Marque, TX). The permeation device is housed in a temperature controlled PFA sleeve at  $40^\circ\text{C}$ . Nitrogen ( $\text{N}_2$ ) continuously flows (10 sccm) over the permeation device and through the PFA sleeve in order to ensure stable output of  $\text{NH}_3$ . The output from the permeation device connects to a PFA tee located at the inlet. A vacuum line connects through a solenoid valve to the third leg of the tee. Calibration gas and some ambient air are removed in a 100 sccm flow through the vacuum line. This prevents the continuously flowing

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



calibration gas from being introduced into the inlet when the solenoid is open during ambient measurements. When the solenoid valve closes, the calibration gas is added to the inlet. The resulting signal enhancement from a known amount of NH<sub>3</sub> is used to determine instrument sensitivity.

Anonymus Referee #2: P1799 Line 22: More information about the common NH<sub>3</sub> gas cylinder is needed, specifically, its manufacturer, concentration, and uncertainty on the concentration. I think the importance of this test is glossed over in the text. Table 2 shows that only one of the six instruments for which this test was performed was within 13% of 'known' independent standard. If the standard is only believed to be good to 20% this is not bad. If the standard is believed to the 5% level then there may be more problems.

Reply: The cylinder is nominally 21 ppmv NH<sub>3</sub> in N<sub>2</sub>. (Manufacturer BOC). For supporting material for previous analysis of the cylinder see Thomas et al., (2009). In Thomas et al., (2009) the cylinder concentration yielded  $18.97 \pm 0.05$  ppmv. During the experiment presented here the cylinder concentration was established as  $20.2 \pm 1.4$  ppmv (2SD). Then at the 2 SD level the error is  $\pm 9\%$  to one decimal place. The conditions under which the calibration was carried out were rain and strong winds, therefore not ideal conditions. The variability under measurement in wet field conditions illustrates the difficulties of field calibration. Further the gas standard was added in to the sampling line, hence the instruments were sampling ambient at the same time, hence a potential effect of RH could not avoid. In addition, some uncertainty is added as this was a standard addition to ambient air because a NH<sub>3</sub> free air at ambient RH (see this Reviewer's comment above) could not be produced at a flow rate sufficient for all instruments considered here.

Anonymus Referee #2: 3.1 Time Series and Figure 3: Figure 3 is difficult to read and discern the different traces. One suggestion is to make two separate larger figures, Fig 3 before and Fig 4 after fertilisation. The shading is very light on both my computer screen and printout.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper





Reply: We have divided Fig. 3 in Fig. 3a before and Fig. 3b after fertilisation with an explanation in the revised caption.

Anonymus Referee #2: The term NH<sub>3</sub>-ref is somewhat misleading. I initially thought this referred to the calibration standard briefly mentioned in section 2.4. The use of the term 'ref' also implies that this is independent and it is not. NH<sub>3</sub>-ref is actually an ensemble average of NH<sub>3</sub> observations made.

Reply: NH<sub>3</sub>-ref was clearly defined in the manuscript, but we are happy to rename it NH<sub>3</sub>-ens throughout the manuscript (ens for 'ensemble').

Anonymus Referee #2: This type of analysis is similar to that used to evaluate regional air quality models, i.e. McKeen, S., et al. J. Geophys. Res., 110, D21307, doi:10.1029/2005JD005858 [2005]. How was this average calculated? Was there any weighting?

Reply: Correct, we are comparing each instrument against the ensemble average, as often done in analysing model variability. We took into account all instruments operational at the time, without weighting a special one. This is explained in more detail in the revised manuscript.

Anonymus Referee #2: Was there a minimum number of data points required from the faster time resolution measurements to be included in the average?

Reply: No there was no minimum data coverage turning high resolution data into 1-hour values.

Anonymus Referee #2: Based on the individual instrument uncertainties, what is the estimated precision and total uncertainty for this NH<sub>3</sub> average value?

Reply: Rather than relying on propagating (manufacturer supplied and apparently under-estimated) instrument specific uncertainties into NH<sub>3</sub>-ens, in the revised manuscript we indicate the error in NH<sub>3</sub>-ens as the statistical standard error between measurements to indicate the range of results and, implicitly, the number of instruments

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



that entered this average.

Anonymus Referee #2: As discussed earlier, comparison to this ensemble can mask important systematic differences.

Reply: Addressed above.

Anonymus Referee #2: The fitting is presented as simple linear regression not taking into account the uncertainty in the measurements. This does not seem realistic. Each instrument does have associated errors. These should be taken into account when performing the fits. If this was taken into account it should be stated more clearly in the text.

Reply: The regressions show relative performance of the instruments against NH<sub>3</sub>-ens or against each other. They do not demonstrate a functional relationship of a dependent to an independent variable. Thus, we do not think that consideration of an a priori uncertainty would be appropriate to this analysis. In addition, this approach would introduce circularity. Although we have an estimate of uncertainty from some manufacturers (Table 1), the paper as a whole demonstrates that the true uncertainties in real life situations are larger than that stated. This uncertainty is a production of the analysis and should not enter the analysis as an a priori assumption.

Anonymus Referee #2: On this same note all scatter plots in figure 4 and in figure 5 should show at least one low and high point with the associated error bars to give the reader a feeling of the uncertainty range.

Reply: We have added error bars for c-QCLAS and CIMS to the graphs to provide a feel for the expected uncertainty of the measurement. This does not include uncertainties due to inlet interferences, as stated in the text. We also have added the statistical standard error on NH<sub>3</sub>-ens.

Anonymus Referee #2: The rest of the section and tables 4 through 8 are very dense with many numbers. It is very hard to put into context what these numbers means.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



This goes back to my earlier comment concerning the take home message of this comparison. For example, what significance is there for relations with noticeable high intercepts? What is the definition of a high intercept?

Reply: It is possible for the reader to use Tables 4 through 8 for individual investigation and compare different combinations of instruments mentioned there. The high intercepts of CIMS, Nitrolux-100 and CRDS point at a contamination of the filters and/or sample lines. So a common high intercept of these three instruments is high in comparison to the other instruments.

Anonymus Referee #2: In Table 4 CIMS vs CRDS yields an intercept 1.6 and is considered high; while RBD vs AMANDA yields an intercept of 1.41 and is not considered high. Whether or no an intercept is high depends on how well an instrument can determine zero and this is not clearly discussed in the text. In short, I'm not sure what to do with all these regression statistics.

Reply: We can explain the intercept of 1.6 between CIMS vs CRDS with a likely explanation of the contamination of the filters and inlet line, because this feature is shared between all instruments sharing this inlet setup and because the intercept of Nitrolux-100 and CRDS are high ( $>1.5$  ppbv) compared with all other instruments. The intercepts between the different instruments and RBD is more variable, with smaller intercepts for AiRRmonia, WaSul-Flux and IMS. Thus, the explanation is not as straightforward. A contributing factor for the lower reading of the RBD around zero is maybe the uncertainty in the blank subtraction. For consistency, we have now put in bold all intercepts that exceed 1.5 ppbv (positive or negative) and explain this in the revised caption.

Anonymus Referee #2: I found the 'dual' nature of these tables difficult to discern. The explanation is that the regression provided is the row against the column. For example, in table 4 RBD against AMANDA yields an intercept of 1.41 ppb but according to the text AMANDA against RBD does not yield a slope of 0.86. I think for the top half of the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



table the regression provided is the row against the column but for the bottom half it switches to the column against row.

Reply: That is understandable, and the reviewer interprets the tables correctly. We felt this nature was the best and most space saving way of presenting the regression results of the 90 regressions. We have expanded the explanation of how to read the tables.

Anonymus Referee #2: Table 8 is completely useless due to the size of the plots, even when blown up on the computer screen. No scale is given on either axis. I agree that there is quite a bit of important information in these plots but in the current format is not being presented to the reader in a clear fashion. Therefore, each should be prepared as in figure 4 but with at least one low and high point showing the associated error bars. This complete set of plots should be submitted as supplemental material to the text. Table 8 then should be stricken from the manuscript.

Reply: We have attempted to reformat Table 8 for maximum visibility and hope that it will be more readable in the final portrait AMT print format. In addition, larger versions are now included as supplemental material.

Anonymus Referee #2: 3.3 Characterisation of instrument time response: This section should be renamed 'Characterisation of instrument time response relative to the c-QCLAS'. Why was the c-QCLAS chosen?

Reply: We chose the c-QCLAS as a fast-response instrument (fast compared with several minutes and more) with high data capture for the campaign, which did not show a major problem in the inter-comparison.

Anonymus Referee #2: I find it more curious why the same time response analysis using exponential decays performed in the references, Whitehead et al., ES&T [2008] and Nowak et al. JGR [2007] was not performed for those instruments with the data available here. This analysis constrains the known slower instruments but does nothing

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



to evaluate the time response of the perceived fast time response instruments.

Reply: Correct, this approach only allows us to characterise the response times of instruments which are much slower than the reference. We had the information and thought it would be useful to use it (just like both referees now want us to extend this analysis to include RH effects). The response tests using exponential decays are typical laboratory experiments, which were not appropriate for the field trial. By contrast, the slow instruments are difficult to characterise in this way as (e.g. for RBD) an NH<sub>3</sub> source would need to be constant for several hours. The analysis provided interesting and useful results in showing that the wet chemistry instruments are slower than stated by the manufacturers.

Anonymus Referee #2: 4.1 Overall measurement accuracy: This section should be renamed 'overall measurement agreement'. This paper focuses on the agreement between instruments relative to each and not the absolute accuracy of the measurements, though I think an attempt to address the accuracy uncertainty of each instrument should be made.

Reply: Yes, this is a more appropriate heading.

Anonymus Referee #2: 4.2 Instrument specific issues: I like the discussion of the issues with inlet filters. However, I think much of the rest of this section is unclear and not well supported. There is not enough evidence presented here to justify the statement on page 1809 line 17 'Three instruments deployed here (DUAL-QCLAS, c-QCLAS and CIMS) have the potential to provide a fast NH<sub>3</sub> spot measurement, of particular interest for aircraft applications and eddy-covariance flux measurements.' As mentioned earlier this paper presents no independent analysis of the time response for these instruments.

Reply: The potential is clearly there. We have expanded and clarified this statement.

Anonymus Referee #2: Another example page 1808 line 26 'CIMS preferentially ex-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



tracts charged ions into the drift tube and thus favours gas molecules over the aerosol'. There is no data presented here or reference(s) given to support this. In fact, none of the references given to describe the CIMS set-up describe instruments that use a drift tube. All references that can be associated with the Georgia Tech CIMS team (table 1) describe systems that use low-pressure flow tubes for the ion-molecule reaction region. According to section 2.3.5 the CIMS in this study samples air through a pinhole, size not given, into the ionization region. How much aerosol does get through the pinhole? What effect does the pressure change have on gas-phase/aerosol partitioning of ammonium nitrate aerosol? This further emphasizes my earlier comment of the uneven and inconsistent instrument descriptions.

Reply: As noted by Fehsenfeld et al. (2002) the residence time within the CIMS system is short and interference from the volatilisation of ammonium nitrate is expected to be negligible, even when reducing the pressure. There is no change on the signal from aerosol being sampled into CIMS. We have performed experiments in the laboratory and the heated inlet does not produce any signal unless temperatures exceed 325 K. This is consistent with previous CIMS papers that stated that heating of the inlet does not impact on the measured gas phase concentration of either  $\text{NH}_3$  or  $\text{HNO}_3$ . Figure 1 shows air sampled from equilibrated ammonium nitrate aerosols and as can be seen the equilibrium  $\text{NH}_3$  concentration is only altered at  $T > 325\text{K}$ . Furthermore, the ambient equilibrium  $\text{NH}_3$  vapour pressure measured by the CIMS was 56  $\mu\text{ppbv}$  and this was in agreement with the predicted  $\text{NH}_3$  vapour pressure of  $\mu\text{ppbv}$  which was measured within our laboratory using Knudsen Effusion Mass Spectrometry. The manuscript has now been altered to read: "The CIMS does not use a filter and the residence within the heated inlet is 0.1 s and thus the interference from  $\text{NH}_4\text{NO}_3$  volatilisation is expected to be negligible, as noted by Fehsenfeld et al., (2002). Indeed, laboratory tests have shown that  $\text{NH}_4\text{NO}_3$  volatilisation only becomes an issue for  $T > 325\text{K}$ ."

Anonymus Referee #2: Page 1810 line 6-7: It is stated here that the c-QCLAS was one

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

of the better performing instruments. What criteria are used to support this statement and is it relative to the ensemble NH3 average?

Reply: In comparison to DUAL-QCLAS with a slope of 1.2 was the c-QCLAS the better performing instrument. We used the NH3-ens. It was also the fast-response instrument that provided highest data coverage.

Anonymus Referee #2: Page 1810 line 9: I disagree with the statement that c-QCLAS and the CIMS require continuous gas-phase calibration in the field. I am not sure how a continuous calibration would work with a spectroscopic measurement. Again there is no evidence presented that the calibration frequency stated in the instrument descriptions is inadequate.

Reply: By 'continuous' we mean 'frequent'. As a matter of good practice the CIMS was calibrated hourly. The sensitivity was  $2.5 \pm 0.5$  Hz ppt-1. This was the first field deployment of the Manchester CIMS system and thus we could only define the narrow range in instrument calibration by carry out calibrations. The section has now been altered to read: "The CIMS provides a fast, highly sensitive technique and this was the first field deployment of this particular instrument, which showed more scatter than most instruments, although it should be noted that it is uncertain how much of this scatter is natural variability and how much is represented by instrumental noise. The instrument was calibrated hourly and the sensitivity of the instrument was  $(2.5 \pm 0.5)$  Hz ppt-1  $1 \sigma$  and the  $1 \sigma$  background noise corresponded to 45 pptv. In a subsequent deployment of this instrument (manuscript in preparation), which employed a similar inlet design and throughput, large variability in NH3 signal was observed on a second by second basis, such variability was not present in the background and calibration cycles, indicating that the inlet is able to respond to rapid changes in [NH3] associated with different plumes and is therefore capturing real rather than artifactual variability."

Anonymus Referee #2: Page 1810 line 20: According to the references Nowak et al.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



2007 is the paper describing the airborne instrument not 2006. This paper seems to emphasize taking frequent instrument backgrounds not doing frequent calibrations, from paragraph 28 in Nowak et al 2007 “The area in need of most improvement is understanding and controlling the background signal from the instrument. Both the absolute level and the variability in the background need to be reduced in order to measure ambient levels from 10 to 100 pptv”.

Reply: Nowak et al. (2007) is the correct reference, but the Referee is correct, we did not sufficiently precisely distinguished between background determinations and calibrations. This has been corrected in the revised manuscript.

Anonymus Referee #2: This leads to another question for this CIMS instrument not addressed in the instrument description how is the instrument background determined and how often is a background performed?

Reply: Backgrounds were taken hourly. The background signal varied from 0.9 to 2.5 ppbv. The 1 $\sigma$  noise on the background signal was 45 pptv. The manuscript has been altered to include the following: “The instrument sampled air through a 0.1 m long 0.95 cm O.D. PFA inlet, temperature controlled to 40  $\pm$  1°C. Inlet flow was 19.5 l min<sup>-1</sup>, with 0.88 l min<sup>-1</sup> being subsampled through a 0.65 mm pinhole into the ionization region, where reaction of NH<sub>3</sub> with H<sup>+</sup>(C<sub>3</sub>H<sub>6</sub>O)<sub>2</sub> proceeds. The instrumental signal was calibrated every hour using a standard addition from a calibrated permeation tube oven and an instrument background was taken hourly.”

Anonymus Referee #2: 4.3 Time responses: This section should be renamed ‘time response relative to the c-QCLAS instrument’. Again, this paper does not present any time response analysis for the ‘faster’ instruments.

Reply: See above.

Anonymus Referee #2: 5 Conclusions: This section presents more vague generalities than conclusions. There seems to be conclusions, in particular about the CIMS and c-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)



QCLAS instruments, made in section 4.2. And, as discussed earlier, those statements are not well supported in the text.

Reply: The statements about the CIMS and c-QCLAS are addressed above. We feel the conclusions are not ‘generalities’ but concrete and appropriate.

Anonymus Referee #2: Table 1: Time resolution in the heading is two words. I think a column stating the estimated accuracy or total uncertainty of each instrument should be added, whether that comes from a manufacturer or is determined by in-situ calibration.

Reply: The spelling of ‘time resolution’ has been corrected. And an estimate of a priori measurement accuracy has been added, where available.

---

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 1783, 2009.

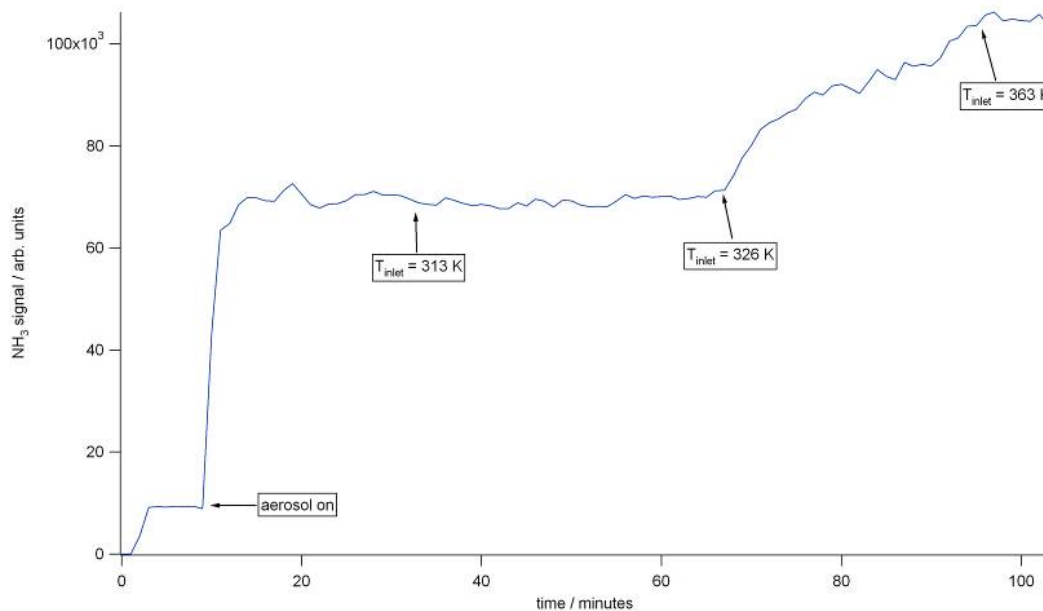
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper





**Fig. 1.** Sampled air from equilibrated ammonium nitrate aerosols.