

Interactive comment on “On-line determination of ammonia at low pptv mixing ratios in the CLOUD chamber” by F. Bianchi et al.

Anonymous Referee #2

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This paper describes and characterizes a technique used to measure gas phase ammonia (NH₃) by transferring NH₃ to the liquid phase followed with analysis by long path absorption spectrophotometry. The instrument described here was used to measure NH₃ during the CLOUD-3 campaign to study the influence of NH₃ on aerosol nucleation rates. This material is of interest to AMT readers. I suggest minor revisions and clarifications before publication.

Introduction

Page 2113, line 10. Ambient NH₃ levels in the atmosphere range over many orders of magnitude depending on proximity to sources. Therefore, it is important to clearly define here what concentrations constitute ‘low NH₃’ as applied to this study early in the manuscript.

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Page 2113, line 11 – page 2114, line 8. NH₃ measurements at low concentrations are difficult not only because the absolute background level can be high but also due to variability in the background. Since for many of the instruments described here the background can only be determined periodically, variability between background determinations greatly influences the limit of detection. Also, many of the papers discussed here are describing the detection limits of ambient measurements. The background levels and, therefore, the detection limits of these instruments will be influenced by changes in ambient NH₃ levels and ambient conditions, e.g. temperature and relative humidity. The study described in this paper at CERN is essentially a laboratory study under much more controlled conditions than ambient measurements. Whether detection limits of any of these instruments would be improved under the conditions of this study is unknown. Conversely, whether the technique described here would have similar limits of detection under ambient conditions is also unknown. Thus, the comparison implied here is not exactly fair.

Page 2114, lines 16 – 18. The inlets used in the papers cited here vary considerably in length, flow rate, and materials. What is meant by slow response time? I find it curious that Hanson et al., 2011 and Nowak et al. 2007 are not cited here. Hanson et al. 2011 claim time response on the order of 1 minute. Nowak et al., 2007 present data showing a 5 s time response determined from the signal decay after removal of a standard addition calibration value. They also claim in a more recent paper not cited here, Nowak et al. Airborne observations of ammonia and ammonium nitrate formation over Houston, Texas, *J. Geophys. Res.*, 115, D22304, doi:10.1029/2010JD014195, 2010, to have made improvements reducing the time response to 1-2 s. These appear to be fast compared to the time scales discussed in the experimental section here.

Because of the difficulty sampling and quantifying NH₃, it is difficult to make general statements regarding time response and detection limits. These quantities need to be justified at the levels appropriate for the analysis presented for every study performed.

Experimental

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There is no description or definition of what constitutes a background measurement. Section 3.1 refers to a blank signal. Is the blank signal taken as the instrument background? How is the blank signal determined? Where in relation to Fig 1 is the blank added?

Though the manuscript states early (page 2115, line 1) that this is a high time resolution technique, the time resolution is not explicitly stated. What is the time resolution of the measurement? How is it defined or determined? Section 2.2 states that the residence time in the reaction coil is 540 s. Section 2.4 states that data is provided every 2 s but, also, that due to the reaction time and the detection time there is an 18 minute time delay for the concentration of ammonia. Is the reaction time in 2.4 the same as the residence time stated in 2.2? What is meant by the detection time? With a 540 s residence time how meaningful is the data reported at 2 s? Also, as a follow-up on my earlier comment on detection limits, averaging over longer measurement periods can lower the detection limit of many instruments. Therefore, the measurement period should be noted when comparing detection limits.

The liquid and gas flow rates seem to be important, in particular for controlling the residence time between sampling and the de-bubbler. How are these quantities measured? Where are they measured in Fig. 1?

Results

Page 2118 section 3.1 Where is the NH₄Cl solution added when the calibration curve determined? Is it between the I.E. column and sampling line or after the sampling line in Fig 1? What is the uncertainty in the standard NH₄Cl solutions used to calibrate?

Page 2119, lines 4 – 8. The stripping efficiency was checked by adjusting the water flow rate until there was no change in NH₃ signal. Does this measured NH₃ level agree with the estimated concentration added to the chamber? Does the water flow rate needed to strip 100% of the NH₃ from ambient air change as a function of ambient NH₃ concentration, i.e., is more or less water flow needed to strip 10 ppbv than 100

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pptv? How many times was the stripping efficiency checked? What do the error bars in Fig. 4 represent?

P 2120 lines 4 -13. I agree that the behavior observed in the CLOUD chamber is a function of the properties of NH₃. However, the chamber characteristics, such as, total surface area, residence time, and materials used, are quite different than any of the inlets used in papers cited in the introduction. Therefore, a blanket comparison of the CLOUD chamber behavior to all inlets in general is not valid.

Minor Editorial Comments:

Page 2112, line 7. Here the campaign name appears as CLOUD3 not CLOUD-3 as in page 2114, line 23.

Page 2116, line 21 Change shown to discussed because this point is not shown by any data presented here.

Figure 2. Section 2.3 gives dimensions in the description of the sample line. They should be added to Figure 2, even if the figure is not to scale.

Figure 5. Remove the single quote from the legend labels. Change left y-axis and legend label to Observe NH₃ mixing ratio for consistency with the figure caption. Change units of left y-axis to pptv to agree with x-axis of figure 6.

Figure 6. Change the x-axis label to Ammonia Mixing Ratio since that is what is plotted, not concentration.

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