

## Review of “Improvement of online monitoring technology based on the Berthelot reaction and long path absorption photometer for the measurement of ambient NH<sub>3</sub>: Field applications in low-concentration environments”, by Tian (2023)

The authors report the development of a new technique to measure atmospheric ammonia (NH<sub>3</sub>) using wet chemistry based on the Berthelot reaction and a long path absorption photometer (SAC-LOPAP). The manuscript provides detail on the optimization of reaction conditions within the sampling and reacting modules, as well as a 1-month field evaluation with a co-located commercial Cavity Ring Down Spectroscopy instrument (CRDS). Given challenges inherent to measuring NH<sub>3</sub>, the authors should be commended for developing a new NH<sub>3</sub> measurement technique. However, the manuscript needs major revisions to refocus the paper so that the introduction and conclusions are aligned with the results. Furthermore, additional information is needed in some places of the manuscript. General and specific comments are below.

### General Comments:

The title and parts of the Introduction mention the low detection limit of the SAC-LOPAP and its ability to measure NH<sub>3</sub> in low-concentration environments. However, no detail is given on how the limit of detection (40.5 ppt) was quantified. Since the manuscript discusses how the low detection limit is one of the advantages of the SAC-LOPAP, there needs to be a detailed description of how the detection limit was calculated.

The field application of the SAC-LOPAP was not performed in a low NH<sub>3</sub> environment, with mixing ratios ranging from ~2 ppb to ~45 ppb. The title should be revised to clarify the field application was in an urban environment (i.e., Beijing) and not in a low NH<sub>3</sub> environment. Furthermore, the discussion throughout the manuscript should be reframed so that it focuses on the good agreement with the CRDS. Currently, portions of the manuscript focus on the SAC-LOPAP's ability to measure low concentrations and its low detection limit, neither of which have been shown or adequately explained.

### Specific Comments:

Line 20 – state what the “established system” is in the abstract.

Line 21 – state what the “good correlation” is, as well as other relevant statistical metrics.

Line 38 – this should read “sulphuric acid” instead of “sulfate”; also, please define CLOUD.

Lines 42-43 – clarify that this study is specific to China, and please verify that the citation is correct.

Line 62 – define DFB.

Line 66 – what is meant by “NH<sub>3</sub> species”? This should be “NH<sub>3</sub>”, “NH<sub>x</sub> species”, or “NR<sub>x</sub> species”.

Lines 67-68 – what does “special materials” mean?

Lines 69 and 73 – there appear to be in-text citations errors, please correct/verify.

Lines 75-76 – discuss the importance of inlet design on ambient measurements of  $\text{NH}_3$  and detection limits.

Line 89 – clarify what “statically” means and quantify what a “long time” is (e.g., months, years?).

Lines 92-93 – be quantitative with what is meant by “low-concentration” and “low detection limit”.

Line 104 (Figure 1) – verify that reactants and products balance in the reaction scheme (e.g., the HCl appears to be missing from Step 2).

Line 111 – clarify what “ $\text{NH}_3$  components” means.

Line 125 – correct “invert” to “convert” and provide the units for  $C_{\text{NH}_4^+}$ .

Line 126 – what is meant by gas “production sample”?

Lines 129-130 – should the temperature be for ambient air since the equation was derived by the Ideal Gas Law?

Lines 131-132 – please provide detail on the capture efficiency parameter. How was it determined, what does it depend on, and how sensitive is it to the set-up (e.g., temperature of the solution, pH of the solution, inlet design)?

Line 143 – rather than say “and so on”, list of all the measures needed to achieve continuous online measurement.

Line 150 – should this be precipitate instead of sediment?

Line 156 – at a pH of  $\sim 12$  and temperature of  $55^\circ\text{C}$ , gaseous ammonia won't be as soluble as under typical wet chemistry methods. What effect do the high pH and high temperature on the capture efficiency of ammonia?

Line 172 (Figure 4) – Define “high” and “low” concentration.

Lines 185-186 – Describe in detail how the detection limit was determined.

Lines 190-191 – Describe in detail how the upper range was determined.

Line 215 – at a pH  $\sim 12$  most of the  $\text{NH}_x$  would be  $\text{NH}_3$ , and not  $\text{NH}_4^+$ .

Line 222 (Figure 6) – describe what approximate mixing ratio of  $\text{NH}_3$  the calibration concentrations correspond to.

Line 233 – did the CRDS and SAC-LOPAP share an inlet, or did each have its own inlet at the same height?

Lines 249-251 – recommend including other statistical metrics in addition to  $R^2$ , such as mean bias or slope of linear regression.

Line 261 – most of the Conclusions section describes improvements made to the Berthelot reaction conditions, and do not necessarily represent an improved methodology for quantifying ambient  $\text{NH}_3$  relative to other  $\text{NH}_3$  measurement technologies. This sentence should be rephrased to clarify this nuance.

Lines 272-273 – as noted above, there was insufficient explanation for how the detection limit was determined.