Response to Referees

Manuscript Number: amt-2023-33

Manuscript Title: Improvement of online monitoring technology based on the Berthelot reaction and long path absorption photometer for the measurement of ambient NH$_3$: Field applications in low-concentration environments

The discussion below includes the complete text from the referees, along with our responses to the specific comments and the corresponding changes made to the revised manuscript.

The detailed answers to the individual referee's comments in blue.

All of the line numbers refer to the original manuscript.

Response to Referee #2 Comments:

We would like to thank the referee for his/her detailed comments and suggestions which helped us a lot to improve the quality of the paper. Our revised manuscript has been further edited by professional language services.

Review of "Improvement of online monitoring technology based on the Berthelot reaction and long path absorption photometer for the measurement of ambient NH$_3$: Field applications in low-concentration environments", by Tian (2023)

The authors report the development of a new technique to measure atmospheric ammonia (NH$_3$) 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$_3$, the authors should be commended for developing a new NH$_3$ 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_3 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_3 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_3 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.

We thank the reviewer for taking the time to review this study and providing the constructive feedback of the manuscript.

Specific Comments:

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

The "established system" has been revised as "a commercial instrument Picarro G2103 analyzer (Picarro, US)".

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

The "good correlation" has been revised as "good correlation with a slope of 1.00 and an R^2 of 0.96"

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

We think this sentence is inappropriate. we deleted it.

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

We think this sentence is inappropriate. we deleted it.

Line 62 – define DFB.

We think this statement is inappropriate. We deleted it.

Line 66 – what is meant by "NH$_3$ species"? This should be "NH$_3$", "NH$_x$ species", or "NR$_x$ species".

We agree with the referee and the "NH$_3$ species" has been revised as "NH$_3$".

Lines 67-68 – what does "special materials" mean?

We think this statement is inappropriate. We deleted it.

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

We agree with the referee. we deleted this sentence.

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

We agree with the referee that the inlet is important for ambient measurements of NH$_3$ and detection limits. However, this article is mainly aimed at the discussion of new instruments. More detailed inter-comparison about inlet for these NH$_3$ instruments will be analyzed in a future publication.

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

We agree with the referee and we added this sentence: that it can be set up and left to run for long periods of time stably for one months used for the continuous online measurement of low concentrations ammonia of ambient air.

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

We agree with the referee and the "Our instrument is designed to measure NH$_3$ in a low-concentration environment with the good stability, low detection limit and small size." has been revised as "Our instrument is designed to measure NH$_3$ in a low-concentration environment (under 20 ppb) with the good stability, low detection limit (less than 60 ppt) and small size".

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).

This equation does not list all the reaction products, only the major reactants and products.

Line 111 – clarify what "NH$_3$ components" means.

The "NH$_3$ components" has been revised as "NH$_3$".

Line 125 – correct "invert" to "convert" and provide the units for C NH$_4^+$.

The "invert" has been revised as "convert" and "Where C_{NH_3} denotes the content of NH$_3$ in the air sample" has been revised as "Where C_{NH_3} denotes the content of NH$_3$ in the air sample (ppb)".

Line 126 – what is meant by gas "production sample"?

The "NH$_3$ concentration in the gas production sample C_{NH_3}" has been revised as "NH$_3$ concentration in the gas C_{NH_3}".

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

In fact, the "temperature" refers to room temperature, because our gas flow is measured at room temperature.

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)?

We agree with the referee and we added the text:

3.1 Sampling efficiency

NH$_3$ Standard gas of 54.96 ppb was used as the sample to be collected through two identical serial stripping coils, and the concentration of liquid samples collected by the two stripping coils was measured to calculate the capture efficiency. The calculation formula is as below.

$$\gamma_1 = \frac{c_1}{c_1 + c_2} \times 100\% \tag{6}$$

Where, γ_1 denotes the collection efficiency of the first stripping coil, c_1 and c_2 denote the concentration of NH$_4^+$ trapped in the first stripping coil and the second stripping coil, respectively.

The collection efficiency of NH$_3$ from the R1 reached more than 99% under different c_{NaOH}, F_l, and F_g. Figure 2a and Figure 2b show that the F_l and the F_g had almost no influence on collection efficiency. Figure 2c shows that c_{NaOH} of 1.25 mmol L^{-1} achieved the greatest collection efficiency in the R1 (99.9%). Therefore, the c_{NaOH} of 1.25 mmol L^{-1} was selected as the R1 of the NH$_3$. And we selected F_l as 0.49 ml /min and F_g as 0.7 L min^{-1} in order to achieve the required detection range in this study.
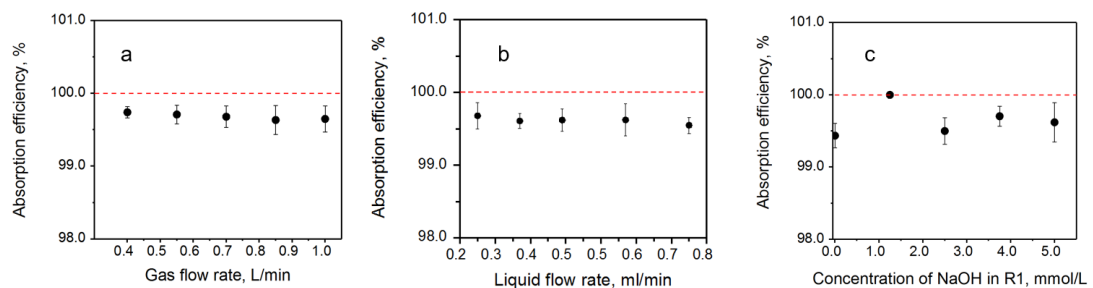

Fig. 2. The absorption efficiency of stripping coil versus (a) gas flow rate (c_{NaOH} = 4.0 mmol L^{-1}, F_l

= 0.49 ml min^{-1}), (b) liquid flow rate (c_{NaOH} = 4.0 mmol L^{-1}, F_g = 0.7 L min^{-1}), (c) concentration of

NaOH in R1 (F_l = 0.49 ml min^{-1}, F_g = 0.7L min^{-1}).

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

We agree with the referee and list of all the measures needed to achieve continuous online measurement. We deleted the "and so on".

Line 150 – should this be precipitate instead of sediment?

The "sediment" has been revised as "precipitate".

Line 156 – at a pH of ~12 and temperature of 55°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?

Ammonia gas is captured by the stripping solution, which is the mixed solution of salicylic acid and sodium hydroxide with a pH of 5.0, which is weakly acidic. Under the flow condition in this paper, the stripping solution can capture more than 99% of ammonia gas. And cycling water kept the trap at room temperature, and did not reach 55□ in the reaction zone. The pH of ~12 and temperature of 55°C mentioned in this paper are in the reaction zone and will not affect the ammonia trapping

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

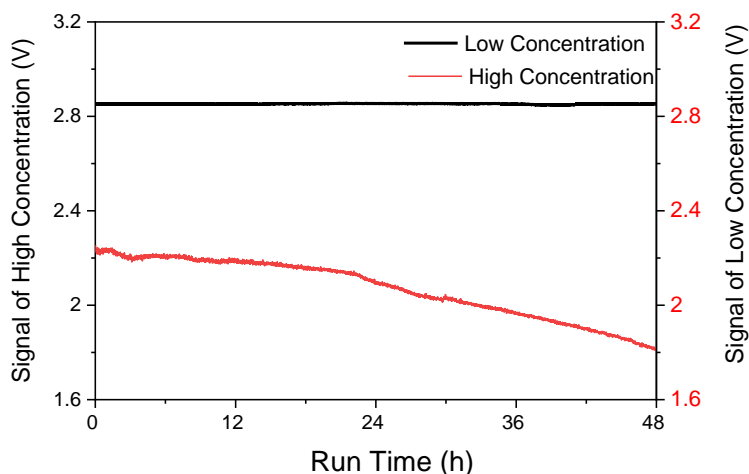We defined "high" and "low" concentration in Figure 4 as suggested.

Fig. 4. The blank time series of the NH$_3$ detector ran continuously for 48 h.(low concentration: 0.75g L^{-1} salicylic acid, 0.014 g L^{-1} sodium nitroferricyanide, and 0.2 g L^{-1} NaOH as R1, then the 0.188ml L^{-1} Sodium hypochlorite and 1.5 g L^{-1} NaOH as R2; High concentration: 1g L^{-1} salicylic acid, 0.1 g

L^{-1} sodium nitroferricyanide, and 1 g L^{-1} NaOH as R1, then the 0.5ml L^{-1} Sodium hypochlorite and 3 g L^{-1} NaOH as R2).

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

We describe in detail how detection limits are determined as suggested: "however, due to the incomplete reaction of NH_4^+ with dye products, there are two points outside of the linear fit (standard solution concentrations are 150 and 200 µg L^{-1}). Therefore, the approximate mixing ratio of NH_3 corresponding to the standard liquid concentration is 0-99.1 ppb. The detection limit for NH_4^+ liquid solution is about 40.9 ng L^{-1}, which is calculated as 3 times the average standard deviation of blank signal noise in one hour. With an air sample flow rate of 0.7 L min^{-1} and a liquid flow rate of 0.49 ml min^{-1}, this translates to a gas phase mixing ratio of about 40.5 ppt".

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

We added the text as suggested:

The standard solution entered the solution system instead of the absorption solution, then the measured absorbance values were used as absorbance-standard solution concentration plot and regression calculation (The experimental process is described in Section 3.3). The result is shown in Fig. 5, a high degree of correlation was found between the standard solution and absorbance with a correlation coefficient of $R^2 = 0.99$ for the standard solution of 0-100 µg L^{-1}, however, due to the incomplete reaction of NH_4^+ with dye products and the limitation of the detector, there are two points outside of the linear fit in panel b. Therefore, the approximate mixing ratio of NH_3 corresponding to the standard liquid concentration is 0-99.1 ppb.

Line 215 – at a pH ~12 most of the NHx would NH_3, and not NH_4^+.

The "NH_4^+" has been revised as "NH_3".

Line 222 (Figure 6) – describe what approximate mixing ratio of NH_3 the calibration concentrations correspond to.

We agree with the referee and we added the describe in Section 3.3.

"R1 was used as diluent and the concentrations were 10, 25, 50, 75, 100, 150, and 200µg L^{-1} of NH_4^+ standard solution. In the calibration process, high purity N_2 was used as blank gas into the sampling tube, and the standard solution entered the solution system instead of the absorption solution. Fig. 5 showed the calibration with the NH_4^+ concentration gradient of 0, 10, 25, 50 and 100 µg L^{-1} (150, and 200µg L^{-1} of ammonium ion standard solution were out of the detection range,

which was discussed in section 3.4)".

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

The CRDS and SAC-LOPAP share an inlet.

Lines 249-251 – recommend including other statistical metrics in addition to R2, such as mean bias or slope of linear regression.

We agree with the referee. The "The NH_3 concentrations measured by those instruments were strongly correlated (R^2 = 0.967), which significantly indicated that the SAC-LOPAP developed in this study could measure the NH_3 concentration accurately." has been revised as "relatively good correlations for the NH_3 data observed by these t instruments were achieved over a large dynamic range of concentration with a slope of 1.00 and an R^2 of 0.96".

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 NH_3 relative to other NH_3 measurement technologies. This sentence should be rephrased to clarify this nuance.

We agree with the referee and we also think this sentence is inappropriate. We deleted the sentence.

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

We describe in detail how detection limits are determined as suggested: "however, due to the incomplete reaction of NH_4^+ with dye products, there are two points outside of the linear fit (standard solution concentrations are 150 and 200 μg L^{-1}). Therefore, the approximate mixing ratio of NH_3 corresponding to the standard liquid concentration is 0-99.1 ppb. The detection limit for NH_4^+ liquid solution is about 40.9 ng L^{-1}, which is calculated as 3 times the average standard deviation of blank signal noise in one hour. With an air sample flow rate of 0.7 L min^{-1} and a liquid flow rate of 0.49 ml min^{-1}, this translates to a gas phase mixing ratio of about 40.5 ppt".