Response to Referees

Manuscript Number: amt-2023-33

Manuscript Title: Colorimetric derivatization of ambient ammonia (NH_3) for detection by long path absorption photometry

The discussion below includes the complete text from the referee, 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 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.

The authors introduce an innovative and online technique for the precise wet chemical measurement of atmospheric ammonia (NH_3). This technique is based on the salicylic acid derivatization reaction in conjunction with a long path absorption photometer (SAC-LOPAP). Through refinement of reaction parameters, incorporation of a consistent temperature control module, and integration of a liquid flow controller, the online NH_3 monitoring system demonstrates prolonged operational stability. The study also provides the outcomes from a comprehensive 1-month field assessment, conducted alongside a commercially available Cavity Ring Down Spectroscopy instrument (CRDS), ensuring the reliability and accuracy of the developed approach. Given the persisting complexities in the measurement of environmental NH_3, the authors warrant commendation for their pioneering efforts in advancing online NH_3 measurement techniques.

Comments:

1. Line 27: The manuscript refers to "recent research", but the references provided are not from the last three years.

Many thanks to the reviewer for the comment. References from the last three years have been added to the article

2. Line 33: Pay attention to the subscript notation of NH_3.

The "NH3" has been revised as "NH_3" according to the journal guidelines.

3. Line 55: Is "traceNH3" intended to be denoted as "trace NH3"?

The "traceNH$_3$" has been revised "trace NH$_3$" as suggested.

4. Line 59: Could "The NH3 mining ratio" potentially be intended as "The NH3 mixing ratio"?

The "The NH$_3$ mining ratio" has been revised "The NH$_3$ mixing ratio" as suggested.

5. Line 75: What is "long-1 path"?

This sentence was miswritten. The "long-1 path" has been revised "long path".

6. Line 111: How to determine the temperature of circulating cooling water outside the stripping coil? Why set 10-15 ° C? What happens if the temperature is too high or too low? There is no clear explanation in the manuscript.

The sampling temperature could be kept low (10~15 °C) by using the cooling device, which favors the capture of gaseous pollutant. In addition, this temperature could satisfy 99% of the sampling efficiency according to Section 3.1.

7. Figure 1 shows the debubbler after the reaction coil, is there always a bubble in the pipeline before that? Does it affect the efficiency of the derivatization reaction? Why not add a debubbler after the stripping coil?

Yes, there was always a bubble in the pipeline before reaction coil and it did not affect the efficiency of the derivatization reaction. In this study, the Segmented Continuous Flow Analysis (SCFA) created by American professor Skeggs was used as reference, which could speed up the sample update speed and shorten the response time compared with the condition without bubbles in the pipeline. Furthermore, the purpose of added a debubbler was to prevent bubbles from entering the LWCC. If added a debubbler after the stripping coil, it was possible for bubbles to re-enter LWCC.

8. Line 162-164: "the sample gas……" Is there any adsorption loss of NH3 in Teflon tube? Have any experiments been carried out to substantiate this?

There was a small adsorption loss of NH_3 in Teflon tubes. The influence of temperature, humidity, correction methods on the adsorption loss of NH_3 in Teflon tube were carried out, in which humidity was the key factor, so it was very important to keep the sample tube insulated.

9. Figure 2a and 2b show that Fl and Fg have no effect on collection efficiency. Then why do the optimal Fl and Fg appear? What is the definition of optimal flow rate?

Yes, F_l and F_g had no effect on collection efficiency. Because NH_3 was "sticky" and highly soluble in water, it had little effect on collection efficiency. However, the F_l and F_g were parameters that affect the measurement range of NH_3 according to Formula 5. The peristaltic pump and air pump were relatively stable in the range of 0.3-0.7 ml min^{-1} and 0.4-1.0 L min^{-1} in this instrument, respectively, so the middle values were taken as the parameter.

10. Line 198: What does "temperatureto" refer to?

This sentence was miswritten. The "temperatureto" has been revised "temperature".

11. There is a problem with the color of the curve corresponding to the left and right ordinates in Figure 3.
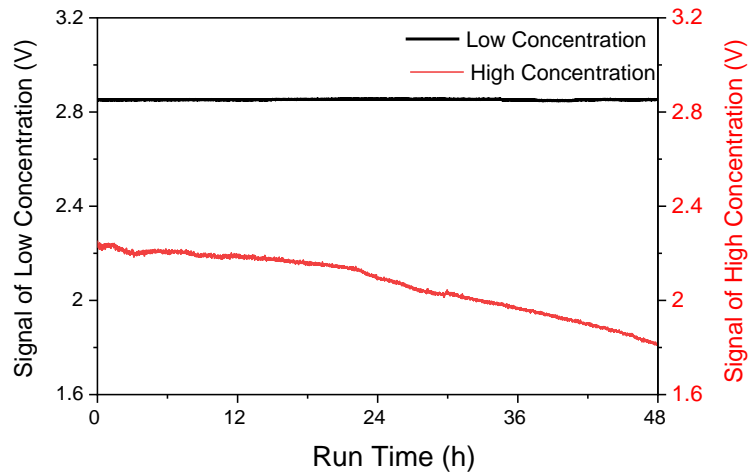
We corrected the Figure 3 as suggested.

Fig. 3. 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).

12. Line 254: "RSD" is introduced here for the first instance; it is advisable to provide its complete expansion or offer an explanation.

We agree with the referee. We revised "RSD" as "relative standard deviation (RSD)".

13. In lines 287-289, it is highlighted that within the prevailing instrument settings, the discernible range for NH3 concentrations spans from 40.5 ppt to 99.1 ppb. However, the "Conclusion" section denotes the instrument's detection range as 0-99.1 ppb. Do these two references indeed pertain to the identical detection span, and if so, what accounts for the numerical disparity?

Yes, the discernible range for NH$_3$ concentrations spans from 40.5 ppt to 99.1 ppb under existing conditions. We made a mistake in the "Conclusion" section and revised "0-99.1 ppb" as "40.5 ppt to 99.1 ppb".

14. The manuscript indicates that two identical serial stripping coils are used in series, but it is not clear what the role of the second stripping coils is. Just to calculate the NH3 collection efficiency?

Or is it the same as the HONO-LOPAP to eliminate the effects of distractions? There is no detail in the manuscript.

Yes, two identical serial stripping coils were used in series to calculate the NH_3 collection efficiency. In fact, the role of the second stripping coil of HONO-LOPAP was to evaluate the interference of NO_2 in the air, while gaseous ammonia was very stable and there is no interference from other components in the atmosphere. Importantly, the first stripping coils of SAC-LOPAP has a very high sampling efficiency with 99%, so a second channel was not needed.

15. The manuscript lacks detailed information regarding the frequency of filter replacements preceding LWCC and the expected lifespan of R1 and R2 solutions. Could you provide further clarification on these aspects?

We agree with the referee and we added this sentence in section 2.3 "The ideal use cycle of R1 and R2 was half a month" and in section 3.3 "and the filter was changed weekly."

16. It is mentioned in the introduction that ambient NH3 is 5 ppt-500 ppb, but the instrument in the manuscript can measure 99.1ppb according to the existing conditions. Elaborating in detail on the specific conditions that necessitate modification, along with quantifying the potential expansion of the detection range, and supplementing these insights with an accompanying data chart, would substantially enhance the richness of the article's content.

 We agree with the referee and we added this sentence in section 3.4 "For example, the following table could be obtained according to Formula 5 and the stability ranges of F_l and the F_g. The detection limit could be reduced to 14.47 ppt and the detection upper limit can be increased to 519.02 ppb by adjusting the F_l and the F_g (Table.2)".

Table 2. Relationship between F_l , F_g and detection range of SAC-LOPAP

F_l, ml min^{-1}	F_g, L min^{-1}	C(NH$_3$)$_{min}$, ppt, [NH$_4^+$] = 40.9 ng L^{-1}	C(NH$_3$)$_{max}$, ppb, [NH$_4^+$] =100 µg L^{-1}
0.25	1	14.47	35.38
0.35	0.85	23.84	58.29
0.5	0.7	41.35	101.11
0.75	0.4	108.55	265.41
1.1	0.3	212.28	519.02