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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

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Abstract. In the last few decades, various techniques, including spectroscopic, wet chemical and mass spectrometric methods, had been developed and applied for the detection of gaseous ammonia (NH_3). We developed an online NH_3 monitoring system (SAC-LOPAP) based on Berthelot reactions and a long path absorption photometer (LOPAP), which could run statically for a long time and be applied to the continuous online measurement of low concentrations of ambient air by optimizing the reaction conditions, adding a constant temperature module and liquid flow controller. The detection limit reached with this instrument was 40.5 ppt under stable conditions. In addition, the range of NH_3 measurement varied from background contamination (<40.5 ppt) to approximately 100 ppb in the current condition (a stripping liquid flow rate of 0.49 ml min^{-1} and a gas sample flow rate of 0.70 L min^{-1}). An inter-comparison of our system with another established system in a field campaign in Beijing was presented, and the results showed that the two instruments had good correlation, indicating that the SAC-LOPAP involved in this study could be used for the accurate measurement of NH_3.

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1. Introduction

Gaseous ammonia (NH_3) widely exists in the atmosphere and plays an important role in many atmospheric chemical reactions (Swati and Hait, 2018; Klimczyk et al., 2021; Wang et al., 2018). As the most abundant alkaline gas in the atmosphere, NH_3 easily forms ammonium ions (NH_4^+) with water and reacts with acid precursors such as SO_2 and NOx ($NO+NO_2$) to generate secondary aerosols, which have a significant impact on the generation of particulate matter (Baek and Aneja, 2004; Behera et al., 2013). Kirkby, j. et al. found that trace amounts of NH_3 (less than 100 ppt) could increase the nucleation rate of sulfate radicals by 2-10 times in a CLOUD experiment on the nucleation of new particles. B. Bessagnet et al. found that the estimation of ammonium particle formation was insufficient, arguing that the role of ammonium in PM was more significant than initially thought (Bessagnet et al., 2014). In recent decades, the emissions of SO_2 and NOx have been controlled to some extent, but the emission reduction of NH_3 is less than that of SO_2 and NOx (Scab et al., 2020). Therefore, accurate measurement of NH_3 is essential for public health and to further reduce secondary aerosol generation.

There are several difficulties in detecting NH_3 in the atmosphere due to its strong adsorption and hygroscopicity. The adsorption and hygroscopic properties of NH_3 are caused by the formation of a strong hydrogen bond between water and NH_3 (Hüglin, 2004). Due to the character of NH_3, it can readily be adsorbed on the surface of the sampling tube, resulting in low measurements and slow response. In particular, NH_3 is likely to be adsorbed on the metal surface of optical systems in the spectrometric monitoring instrument, resulting in increased background (Whitehead et al., 2008; Yokelson and R., 2003). In addition, the temperature difference between the indoor and outdoor environments and the humidity difference between the inside and outside of the instrument will reduce the accuracy of measurement and calibration.

In recent years, researchers have developed techniques and methods for detecting NH_3 in the atmosphere, which include spectroscopic, wet chemical and mass spectrometric methods (Von et al., 2009). Spectroscopy methods, such as Cavity Enhanced Absorption Spectroscopy (CEAS) (Gong et al., 2017; Berden et al., 2000) and Cavity Ring-Down Spectroscopy (CRDS) (Qu et al., 2012; Martin et al., 2016), can greatly improve spectral absorption's effective optical path length by using the optical cavity structure. However, NH_3 has a high viscosity and easily adheres to the metal

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surface of optical systems in spectrometric monitoring instruments, thus affecting the background, detection efficiency and detection response time of the instrument (Whitehead et al., 2008; Yokelson and R., 2003). Utilizing a quantum cascade laser (QCL) or a DFB laser in a near-infrared band as the light source can achieve high detection accuracy and a low detection limit (Gadedjisso-Tossou et al., 2020), realizing the measurement of low concentrations of NH_3 in ambient air. The chemical ionization mass spectrometer (CIMS) technique is based on an ion-molecule reaction to selectively ionize and detect trace NH_3 species in the atmosphere, which features a fast response and in situ measurement (Benson et al., 2010). The sensor measurement method relies on the response of special materials to NH_3. It has the advantages of small volume and wide measurement range, but its detection limit is very high (Ajay and Beniwal., 2019). Wet chemistry methods usually require a combination of a wet chemistry collection system and a wet chemistry analyzer, such as a dull-polished wet tubing denuder (WAD), which can separate gaseous NH_3 and aerosol particles. NH_3 is absorbed and ionized to NH_4^+ to be analyzed by ion chromatography (Dong et al., 2012). A field inter-comparison of NH_3 measurement techniques (Von et al., 2009) found that wet chemistry instruments showed better long-term stability and agreement than other analyzers, which was due to the wet chemical trapping method and standard calibration solutions, humidity did not affect the measurement, and the standard solution was more stable than standard gases. However, they failed to capture the peak because of lower time resolution. Mass-spectrography analyzers provide highly sensitive techniques but may be less specific and can be affected by competing ion chemistries. Furthermore, the Berthelot reaction and absorption spectrophotometry collect NH_3 (and ammonium) by aqueous scrubbing in glass frit impactors (Bianchi et al., 2012; Bae et al., 2007), which is a new wet chemistry method for the determination of NH_3 that has also been reported by scholars (Bae et al., 2007).

In this study, we provide an online NH_3 monitoring system based on wet chemistry stripping of atmospheric NH_3, followed by the formation of a highly light-absorbing indophenol after a salicylic acid chromogenic reaction and quantification of the reaction product by a home-made long-path absorption photometer (LOPAP). We call this monitoring system the salicylic acid chromogenic and long path absorption photometer (SAC-LOPAP). The objective of this study is to optimize the key parameters based on the Berthelot reaction and absorption spectrophotometry,

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establish a method suitable for the instrument can run statically for a long time and can be used for the continuous online measurement of low concentrations ammonia of ambient air.

2. Methods

Our instrument is designed to measure NH_3 in a low-concentration environment with the good stability, low detection limit and small size. There is a brief introduction to the principle of the instrument. The measurement of NH_3 in the SAC-LOPAP instrument is achieved by the Berthelot reaction method. Samples containing dissolved ammonia and ammonium react with a phenolic compound and a chlorine-donating reagent to form indophenol blue during the reaction, with the strongest absorption at a wavelength of 665 nm. This reaction is more sensitive than other chromogenic reactions, such as reactions based on Nesslers's reagent (Krom and Michael, 1980; Searle and Phillip, 1984). Fig. 1 shows the reaction mechanism of the chromogenic reactions. Furthermore, to measure the absorbance of the sample, we used a long path absorption photometer (LOPAP) based on liquid-waveguide capillary cell (LWCC) technology to obtain a better detection limit, continuity and stability (Heland et al., 2001).

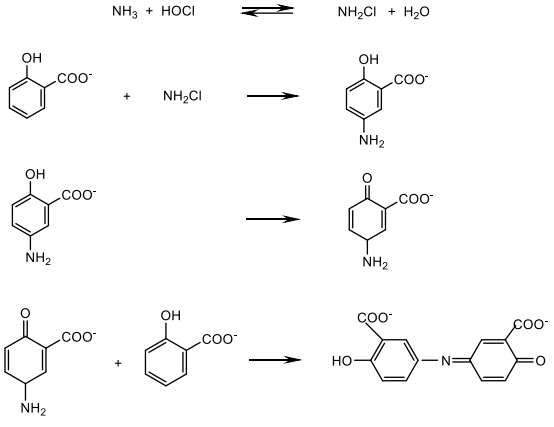

Fig. 1. The reaction mechanism of salicylic acid chromogenic reactions

As shown in Fig. 2, we designed our system to consist of four modules: the sampling module, the reacting module, the detecting module, and the control module. The sampling module contains a stripping coil (a glass coil in which the air contacts the stripping solution), an air pump, a gas flowmeter and circulating cooling water. The air is pumped into the stripping coil under the action of a vacuum diaphragm air pump (Nidec, Japan) and flow meter (Horiba, China) (Chen et al., 2004).

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At the same time, the stripping solution, regulated by the liquid flow control system, is injected into the stripping coil to capture NH_3 components in the air and form a mixture of ammonium-salicylic acid. To achieve higher absorption efficiency, circulating cooling water with a temperature of 10-15 ºC is provided outside the stripping coil. The center part of the reacting module is a reaction kettle and a debubble. The liquid sample is mixed with an alkaline derivatization solution, and chromogenic reaction occurs in the heated reaction kettle, which is made of a 90 cm length of Teflon tubes coiled on a heat-conducting metal cylinder, and the built-in heating rod and temperature sensor control the temperature of the reactor at 40-75 ºC to accelerate the derivatization reaction. After the chromogenic reaction, the sample is sent to the detecting module, which comprises a liquid waveguide capillary cell (LWCC, World Precision Instruments, USA), an LED light source, and a photoelectric detector. The sample solution to be tested is filtered by a 1.0 μm filter before passing through LWCC to avoid contamination by precipitates in the solution. All instrument functions are controlled by the control module, including an integrated circuit and a touch panel. The optical path length of LWCC is 100 cm. The NH_4^+ standard solution was produced by the National Institute of Metrology, China.

Eq. (1) can help invert the concentration of NH_4^+ solution $C_{NH_4^+}$ to the NH_3 concentration in the gas production sample C_{NH_3}.

$$C_{NH_3} = \frac{C_{NH_4^+} F_l R T}{M_{NH_3} F_g P \gamma} \quad (1)$$

Where C_{NH_3} denotes the content of NH_3 in the air sample, P denotes atmospheric pressure (101.3 kPa), M_{NH_3} denotes the molar mass of NH_3 (g/mol), R=8.314 Pa·m^3·mol^{-1}·K^{-1}. T denotes the temperature in the stripping solution (the temperature of the cycling water, the unit is K), F_l denotes the flow rate of stripping solution, F_g denotes the flow rate of sampling gas, γ denotes the capture efficiency of air NH_3 in the stripping solution (a constant determined by laboratory).

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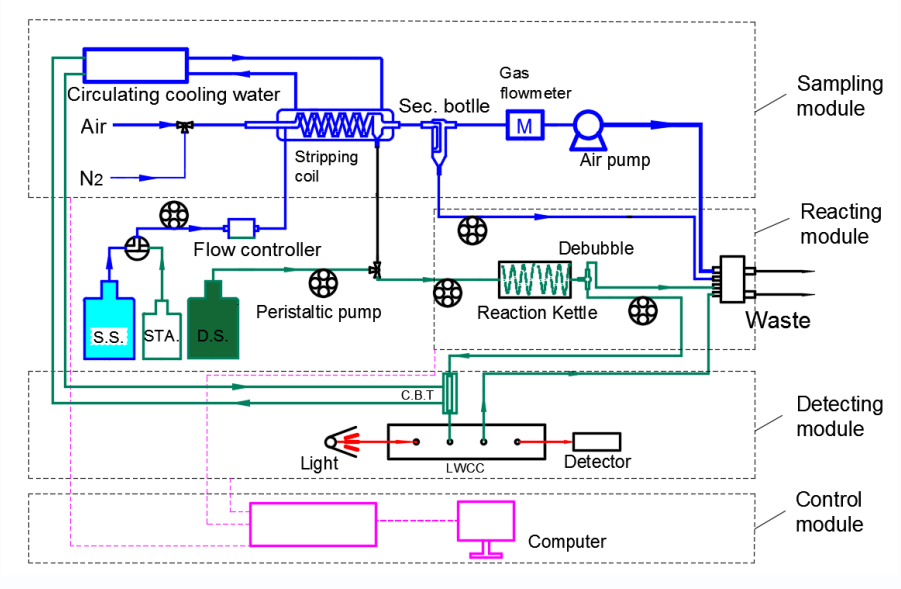

Fig. 2. Schematic diagram of SAC-LOPAP

3 Characterization and optimization

We acknowledge that Berthelot reactions must be carried out under catalytic and alkaline conditions. $[Fe(CN)_5NO]^{2-}$ is recognized as a high-efficiency catalytic to increase the sensitivity of the Berthelot reactions (Krom and Michael, 1980; Searle and Phillip, 1984). However, precipitates containing $Fe(OH)_3$ form during the reaction process, which comes from the reaction of $[Fe(CN)_5NO]^{2-}$ with NaOH. These precipitates have little effect on off-line instruments. But for on-line instruments, precipitates can attach to the wall of the pipeline and LWCC, which leads to pipeline blockage and baseline drift. Therefore, we need to optimize reaction conditions, add the constant temperature module and liquid flow controller temperature, and so on to achieve continuous online measurement of low-concentration ammonia in ambient air.

3.1 Setting reaction conditions

The stripping solution contained 1 g L^{-1} $C_6H_4(OH)(COOH)$, 0.1 g L^{-1} s $Na_2[Fe(CN)_5NO]^{2-}$, and 1 g L^{-1} NaOH. 0.5 ml L^{-1} NaClO and 3 g L^{-1} NaOH were used as derivatization solution based on the former scholar (Krom and Michael, 1980; Searle and Phillip, 1984), and the state of our experiment status (Longer optical path and lower sampling volume) in the initial reaction condition. In addition,

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particulate matter filter was introduced, which could minimize the influence of sediment (Bianchi et al., 2012), but a large deviation of the baseline would still occur during the long run in our experiment. According to reaction kinetics, reducing the solution concentration and [OH^-] of the system can greatly reduce the formation of precipitates in the solution. Therefore, we need to find the optimal reaction conditions to produce the least amount of precipitate. As shown in Figure 3, higher [OH^-] leaded to a lower voltage signal and higher absorbance, but the effect was no longer apparent when [OH^-] increased to 18.75 mmol L^{-1}. We chose an 18.75 mmol L^{-1} OH^- solution system with the aim of obtaining a high absorbance of light and a slow speed of precipitate formation, which meant that 1.5 g L^{-1} NaOH was added to the derivatization solution. And in this study, the stripping solution was prepared by dissolving 0.75 g L^{-1} $C_6H_4(OH)(COOH)$ (TCI, 99.5%, Japan), 0.014 g L^{-1} $Na_2[Fe(CN)_5NO]^{2-}$ (TCI, 99%, Japan), and 0.2 g L^{-1} NaOH. For the derivatization solution, 0.188 ml L^{-1} NaClO (Aladdin, active chlorine10%, China) and 1.5 g L^{-1} NaOH were used, which resulted in the precipitate in the solution being too small to cause pipeline blockage and baseline drift. Importantly, the concentrations of $C_6H_4(OH)(COOH)$, $Na_2[Fe(CN)_5NO]^{2-}$ and NaClO were 96 %, 98 %, and 99 % lower than those in previous research, respectively (Bianchi et al., 2012).

In other words, the amount of iron-containing precipitation is very small by reducing the content of components and alkali of the solution system, and the voltage of the instrument will not drop significantly due to contamination, which is conducive to better maintenance of the baseline (Fig. 4).

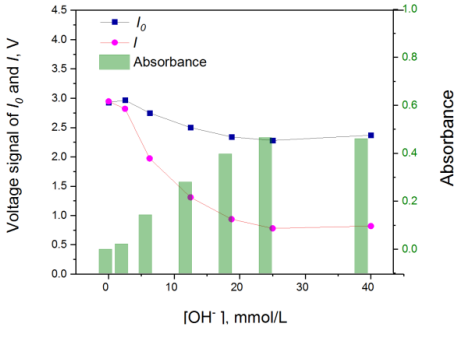

Fig. 3. The influence of [OH^-] on the voltage signal and absorbance

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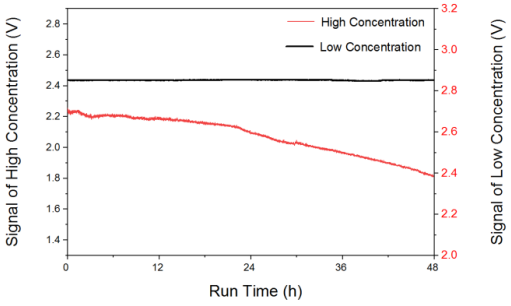

Fig. 4. The blank time series of the NH_3 detector ran continuously for 72 h.

3.2 Setup of the temperature

However, the reduction of the content of components in the solution will lead to a decrease in absorbance, so it is necessary to adjust the temperature to speed up the reaction process and achieve a higher absorbance. As shown in Figure 5a, the voltage signal decreased with increasing temperature; conversely, the absorbance increased with temperature. However, if the temperature is too high, there is a danger that the pipeline interface of the instrument will fall off. Considering the stability and detection range of the instrument, 55 ºC was selected as the best reaction operating temperature of the instrument, at which sufficient absorbance could be achieved to detect low concentrations of ammonia gas.

Furthermore, 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} (Fig. 5), indicating that the measurement range was background contamination up to 100 μg L^{-1} for NH_4^+ solutions. Under the above reaction conditions and temperatures, the detection limit of NH_3 was 40.5 ppt (gas flow rate of 0.70 L min^{-1}, liquid flow rate of 0.49 ml min^{-1}), the measurement range was 40.5 ppt up to 100 ppb for NH_3, which was well suited for the investigation of the NH_3 budget from urban to rural conditions in China. Importantly, the detection limit can be decreased by improving the gas flow. We can increase our detection range by reducing the temperature and shortening the length of LWCC. When the temperature drops to 50 ºC, the range can be up to 200 ppb. In addition, the minimum reading of the detection signal is 0.1 mV. According to the zero point data and the calibration, the corresponding concentration to the voltage signal of 0.1 mV is 3.1 ppt, which far meets our requirements for actual environmental measurement.

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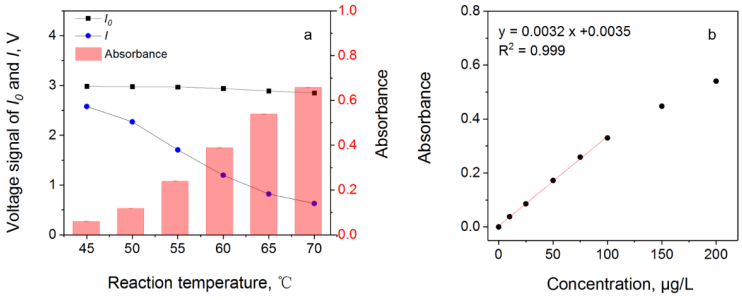

Fig. 5. Influence of reaction temperature on voltage signal and absorbance

3.3 Stability of liquid flow and temperature

The temperature control module and flow control system were designed because of the sensitivity of chrominance to ambient temperature and residence time. A commercial PID temperature controller was used to control the temperature of the reaction kettle with the accuracy of ±0.1 ℃. The temperature control module was used to control the constant temperature from the reaction kettle to LWCC at 55.0±0.1 ℃. At the same time, the flow control system could control the rotational speed of the peristaltic. This system used a new type of photoelectric detection to bubbly flow, which could detect the flow rate and feedback to the peristaltic pump control, which further improved the stability of the reaction process. In other words, the flow control system could avoid the flow rate dropping caused by the abrasion of the pump tube and the bump up of the flow rate caused by the replacement of the pump tube, keeping the stripping solution flow at a constant set point (0.49 ml min^{-1}).

In addition, we designed a buffer tube with a cooling function to further reduce the effects of precipitation. After the chromogenic reaction in the reaction kettle at 55.0 ℃, the mixed solution entered the cooling buffer tube. Most of the precipitation was generated in the buffer tube and attached to the tube wall, while some of the precipitation generated in the downstream pipeline was intercepted by an in-line precipitate filter with a pore size of 1.0 μm before the LWCC.

Overall, the above work can make the instrument maintain a relatively stable reaction time and temperature, which can promote a relatively stable reaction process, resulting in a high reproducibility to the same concentration of NH_4^+. Fig. 6 showed the calibration with the NH_4^+ concentration gradient of 0-100 μg L^{-1}, and the relative standard deviations calculated from four

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consecutive measurements ranged from 0.32 % to 2.65 %. Moreover, the RSD of the blank signal in continuous operation for one month (blank tests were made every one or two days) was 1.8 %, showing good stability. After calculating 10-90 % of the full signal after a change in concentration, the time resolution was approximately 140 s, which was much quicker than the method described by Bianchi (measured to be 10 min) (Bianchi et al., 2012).

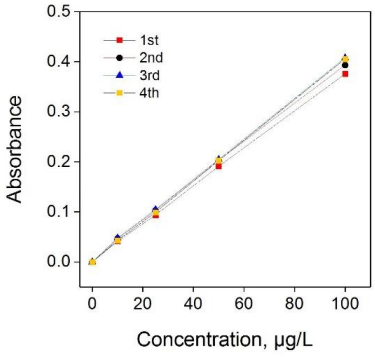

Fig. 6. Calibration curves of standard solution with the same concentration gradient 4 times

Table 1. Reproducibility test by quickly switching between 50 μg L^{-1} NH_4^+ standard and 0 μg L^{-1} solution

Number	0 μg L^{-1} solution (μg L^{-1})	Response of standard solutions (μg L^{-1})
1	-0.014	49.529
2	-0.082	49.615
3	-0.014	50.773
4	0.019	50.599
5	0.053	50.019
6	0.086	50.019
7	-0.048	49.443
AVG	0.000	50.000
STD	0.053	0.484
RSD		0.97%

4. Field comparison in urban Beijing

The field campaign of SAC-LOPAP was conducted at the College of Environment Sciences and Engineering, Peking University, located within the 4th ring road in northern Beijing (40° N, 116° E), China. A commercial instrument Picarro G2103 analyzer (Picarro, US) used for atmospheric NH_3 measurement based on the CRDS method was deployed concurrently with SAC-LOPAP in the field comparison, which could be used to calibrate and validate other instruments (Twigg et al., 2022). The inter-comparison experiment took place from 15 September 2021 to 15 October 2021,

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with the instruments installed in a field container. Two instruments were deployed with a common inlet height of 2.5 m above the ground. The inlet tube was a 3.8 m long 1/4′ Teflon tube covered with thermo-isolation materials. Additionally, we removed the particles with a Teflon filter at the front of the sampling inlet and changed the filter every day with the aim of avoiding uncertainties. Data acquisition times were different for the above instruments during the inter-comparison. The base reporting periods for Picarro and SAC-LOPAP were 1 s and 30 s. For the purposes of comparison, data from the two instruments presented in this section were averaged to 5 min. In addition, zero point was carried out every 7 days, and the standard gas was usually introduced into the instruments 40 min after zero gas so that they could maintain stability in the measurement process and ensured quality control.

The time series of the concentration of NH_3 during the inter-comparison period of Picarro and SAC-LOPAP were presented in Fig. 7a. There were a few data gaps for the above instruments caused by calibration operations and instrument maintenance. Instruments display similar temporal features for NH_3 concentrations over the duration of the study. Fig.7b and Fig.7c showed that the two instruments had a deviation in response to the peak formed by the rapid rise and fall of NH_3 concentration, which might be caused by the blank deviation between both instruments. Still, the response speed was similar, indicated that SAC-LOPAP responded in time to rapid changed in NH_3 concentration at the five-minute resolution. Furthermore, 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. In general, our instrument run relatively stable with the STD of zero gas during the one month of observations being within 26 ppt, and both systems agreed for the RSD of the standard gas within 0.76 % (Table 2), which meant that our instrument could keep steady for a long time and it could be used for the continuous online measurement of low concentration of ambient air.

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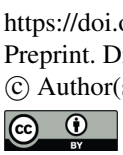

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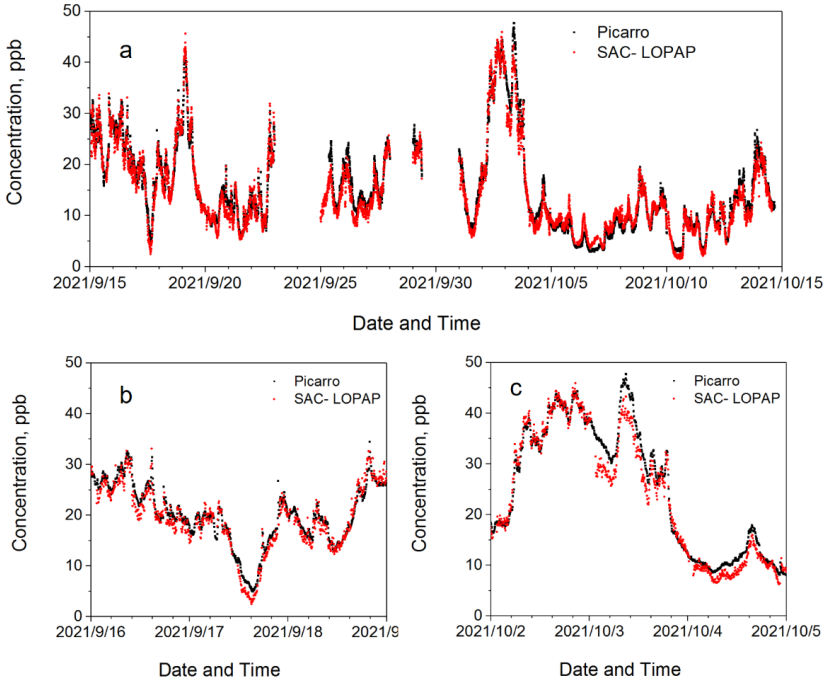

Fig. 7. (a) Time series of NH_3 concentration during the field comparison, and (b), (c) Magnified view of time series.

Table 2. Reproducibility test by zero gas and standard gas

Test number	Zero gas (ppb)		NH_3 standard (ppb)	
	SAC-LOPAP	Picarro	SAC-LOPAP	Picarro
1	0.014	0.856	40.732	40.291
2	0.074	0.898	40.221	40.072
3	0.069	0.859	40.710	39.995
4	0.031	0.908	40.022	40.011
5	0.062	0.876	40.373	40.076

5. Conclusions

We improved on-line monitoring technology to measure NH_3 in the atmosphere, which had been used for continuous on-line measurement of low concentration ambient air for a long time. Our SAC-LOPAP is a combination of the Berthelot reaction and long path absorption photometer for gaseous ammonia measurement. It has several notable improvements compared to previous setups, as reported by other studies, and one is the optimization of reaction conditions. The low concentration but higher flow rate of solutions decreases the precipitate's production, and the

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cooling buffer tube and the filter trap most of the precipitates. The others are the constant temperature module and liquid flow controller. The constant temperature module in the system reduces the influence of ambient temperature on the reaction process and color degree. Similarly, adding a liquid flow controller is helpful to the stability of the flow rate and further increases the stability of the reaction process. These improvements reduce the system error and significantly increase the sustainability of SAC-LOPAP operation. The detection limit reached with this instrument is 40.5 ppt under stable conditions. The range of NH_3 measurement vary from background contamination (<40.5 ppt) to approximately 100 ppb with a stripping liquid flow rate of 0.49 ml min^{-1} and a gas sample flow rate of 0.70 L min^{-1} in the current condition. SAC-LOPAP had a STD of zero point signal within 26 ppt, also agreed for the RSD of the standard gas within 0.76 % within a month, which indicating that the instrument could run statically for a long time and the repeatability was good. Therefore, we conclude that our update of the ammonia measurement experimental framework has been successful. However, more research about field measurement and comparison is needed to verify the equipment's performance in routine observation, and the influence of particulate ammonium on the results of NH_3 detection also requires further study.

Data availability. The datasets used in this study are available from the corresponding author upon request (hbdong@pku.edu.cn).

Author contributions. H.B.D. designed the study. S.S.T., K.X.Z. set up and characterized the instrument, analyzed the data and wrote the paper with the input of H.B.D. As co-authors, S.S.T and K.X.Z. contributed equally to this paper. All authors contributed to the field measurements, discussed and improved the paper.

Competing interests. The authors declare that they have no conflict of interest.

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