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A novel calibration method for atmospheric NO₃ radical via high reflectivity cavity

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Abstract

The NO₃ radical is one of the important indicators of atmospheric oxidation capability at night, and its accurate detection has been extensively investigated. High reflectivity cavity instruments, such as cavity ring-down spectroscopy (CRDS) and cavity-enhanced absorption spectroscopy (CEAS), are generally employed for NO₃ radical detection. However, sampling detection easily adsorbs radicals on surfaces, which causes complications and even additional loss. According to the chemical conversion relationship between NO₃ radical and NO₂, a method of absolute calibration different from the previous relative calibration method is applied by combining the CRDS and CEAS instruments for the NO₃ radical and NO₂, respectively. Experimental results show that the overall transmission efficiency of the NO₃ radical for the CRDS instrument is approximately 75% ± 9% at a flow rate of 6.5 SLPM. Comparative experiments between the two methods are conducted to estimate the accuracy of this method. The achieved results indicate that absolute calibration is a reliable and feasible method for radical calibration in the laboratory. Furthermore, the absolute calibration method has the potential to realize accurate real-time calibration in field measurements.

Keywords: NO₃ radical, calibration, detection, atmospheric, optical cavity

(Some figures may appear in colour only in the online journal)

1. Introduction

The NO₃ radical is a key nocturnal form of nitrogen oxide, which is a major oxidant for pollutants during the night and plays an important role in the nocturnal chemical process

[1, 2]. NO₃ also contributes to the oxidative capacity of the atmosphere [3–5]. Accurately measuring NO₃ radical concentrations in the atmosphere is challenging due to their high reactivity and low concentration (dozens of pptv) [6–9].

In recent years, several spectrometers for *in situ*, or point measurements of NO₃ and N₂O₅ concentrations in ambient air, such as cavity-enhanced absorption spectroscopy (CEAS) and cavity ring-down spectroscopy (CRDS), have been constructed [10–12]. CEAS and CRDS have the advantages of high sensitivity, mobility, and flexibility. However, point sampling measurement instruments, such as CEAS and CRDS, will



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cause additional losses because the NO_3 radical is a reactive species. The concentration of NO_3 radical in the atmosphere is only a few decades of pptv, but the loss in the cavity is relatively high. Therefore, the loss of NO_3 radical in point sampling instruments has received increasing attention from researchers [13–16]. Brown *et al* found the loss of NO_3 radical in the system to be as much as 20%, as determined by a relative calibration method based on the variation of detected NO_3 with residence time, due to surface loss of NO_3 radical through the PFA tubing and membrane filter loss [17]. The loss of NO_3 radical in membranes changes over time, and variation reaches 10% per hour [14]. Furthermore, the loss of NO_3 radical in the system is a variable, and it will change as the sampling time, particle concentration, and environmental condition [18–21]. Therefore, accurate real-time calibration is crucial for point measurements of NO_3 radical in ambient air. At present, the relative calibration method is mainly applied. However, this method is relatively complex due to the respective calibrations of surface and membrane filter loss. And it will cause substantial errors due to not real-time correction.

An absolute calibration method, which is different from the previous relative calibration method, is described in the present work. According to the chemical conversion relationship between NO_3 and NO_2 , this accurate real-time calibration method is applied by combining the CRDS and CEAS instruments for the NO_3 radical and NO_2 , respectively. A low stable concentration of NO_3 radical is produced by the synthetic N_2O_5 solid source in the laboratory. Consecutive calibrations are performed by the constructed absolute calibration system of NO_3 radical, and the accuracy of calibration results is further verified by compared with the relative calibration method.

2. Experimental setup

The CRDS and CEAS instruments for the NO_3 radical and NO_2 are respectively combined. The outlet of the CRDS instrument connects with the inlet of the CEAS instrument, and the schematic of the instruments is shown in figure 1. The CRDS instrument mainly comprises a diode laser, a high-finesse optical cavity with HR mirrors, and a PMT. Light is provided by an external modulation diode laser (line width of 0.3 nm and center wavelength of 661.85 nm) with an optical output of approximately 120 mW. The 76 cm long cavity is formed by two high-reflectivity mirrors ($R \geq 99.9985\%$) with 2.54 cm diameter and 1 m curvature radius. The output light of the cavity is detected by PMT. The signals from the PMT are then digitized using an oscilloscope card controlled by the LabVIEW program [16]. The ring-down time of the CRDS system filled with N_2 is approximately 67.0 μs (τ_0), and an effective absorption path length of approximately 20 km is achieved, as shown in figure 2(a). Individual decay profiles are co-added and then averaged to achieve a high signal-to-noise ratio [22]. An example of cavity decay trace is fitted by the Levenberg–Marquardt algorithm in figure 2(a). The best integration time is determined by the Allan variance shown in figure 2(b). Considering high reactivity of NO_3 radical, the

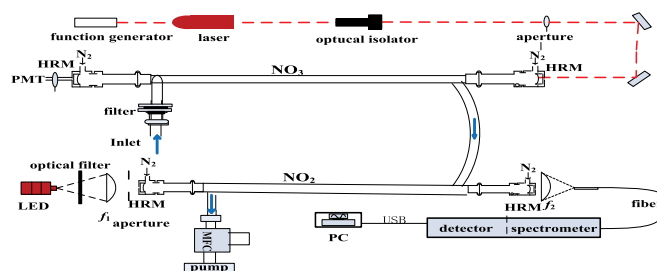


Figure 1. Experimental layout of CRDS and CEAS instruments for NO_3 and NO_2 , respectively.

integration time is 5 s in the process of calibration. In the laboratory, the detection limit of the CRDS system is 2.6 pptv (1σ) for a 5 s integration time using equation (1) [16]. The CEAS set-up comprises a blue light-emitting diode light source (LZ1-00B205, LedEngin) with a peak wavelength of approximately 458 nm and FWHM of 25 nm, a pair of high-reflectivity cavity mirrors (maximum reflectivity of 0.9995 in the range of 440–480 nm) with 25 mm diameter and 1.5 m curvature radius, an optical cavity of 73.5 cm, an optical band-pass filter, and an optical fiber-coupled grating spectrometer. The cavity of CEAS is filled with sample gases in the laboratory, and the detection sensitivity of the CEAS system is evaluated to be approximately 0.25 ppbv (1σ) for NO_2 with a 20 s acquisition time [23, 24]:

$$[A]_{\min} = \frac{R_L \sqrt{2}\sigma(\tau_0)}{c\sigma \tau_0^2}, \quad (1)$$

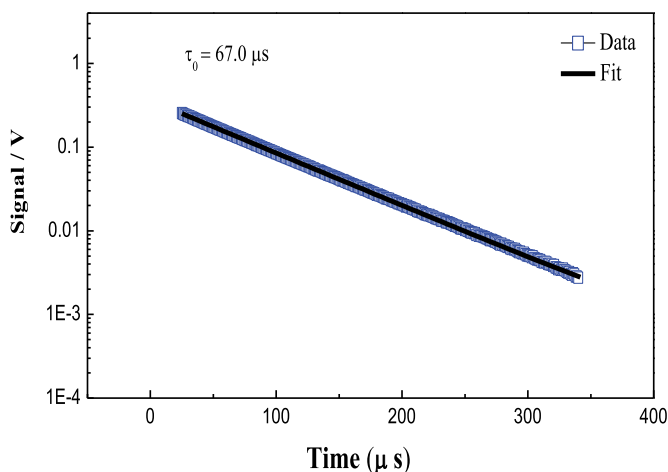
where R_L is the ratio of the total cavity length to the length over which the absorber is present in the cavity. For the CRDS system, τ_0 is roughly 67.0 μs and $\sigma(\tau_0)$ is approximately 0.10 μs for a 5 s integration time under laboratory conditions. Taking the absorption cross section ($\sigma = 2.02 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$) for the NO_3 radical at 661.85 nm [16], the detection limit of NO_3 the radical is 2.6 pptv (1σ) for a 5 s integration time.

3. Experiment results and discussion

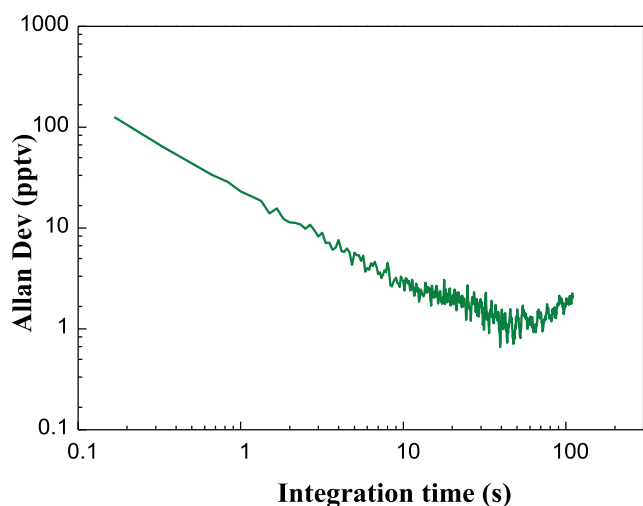
3.1. Formation of standard source of NO_3

NO_3 radical is characterized by its high reactivity and easy collision loss. Thus, NO_3 radical has no standard gas. In order to meet the requirements of loss calibration of NO_3 radical, the method of synthetic N_2O_5 solid source is used to produce standard gas in the laboratory. With the reaction of excessive NO and O_3 , N_2O_5 solid source is synthesized in low temperatures (approximately -80°C). In the process, the synthetic solid is repeatedly purified by the high concentration of O_3 to improve the purity of synthetic gas source. Simultaneously, water vapor interference cannot be ignored, otherwise which will cause synthesis failure by forming HNO_3 .

The schematic of loss calibration of the NO_3 radical is shown in figure 3. The CRDS and CEAS instruments for NO_3 radical and NO_2 , respectively, are applied together to obtain



(a)



(b)

Figure 2. (a) Example ring-down trace at 661.85 nm and the fitted single exponential decay with a ring-down time constant of 67.0 μs . (b) Allan variance plot for the NO_3 radical measurements.

accurate measurements. The stable and low concentration of standard gas, which is the key step of accurate calibration, is generated. The sample gas of N_2O_5 is generated by passing a small flow of N_2 (approximately $10\text{--}20\text{ ml min}^{-1}$) over the synthetic N_2O_5 solid stored at $-78\text{ }^\circ\text{C}$ through the dry ice method. The gas is diluted by N_2 several times to obtain low concentrations of N_2O_5 . The sample gas of N_2O_5 is heated at high temperature (the tube surface is heated to approximately $80\text{ }^\circ\text{C}$ and controlled by temperature controller) to generate NO_3 radical due to the chemical thermal equilibrium relation of N_2O_5 and NO_3 . The high concentration sample gas is then diluted by N_2 again. There are two main reasons for repeated dilution, one is to obtain the low concentration of NO_3 radical (hundreds of pptv), the other is to make the high temperature of sample gas to close to room temperature. The low stable concentration of NO_3 radical is obtained by controlling the gas flow of exhaust and dilution with mass flow meter and

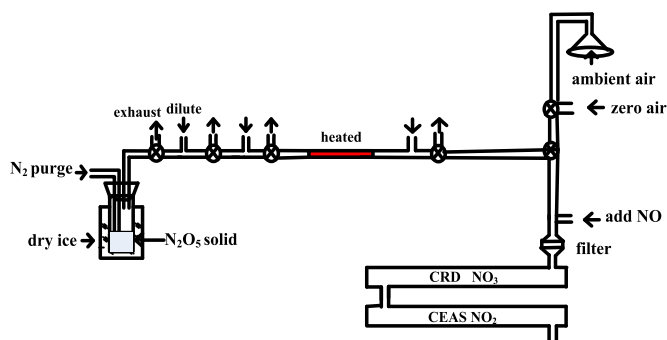


Figure 3. The schematic of loss calibration of the NO_3 radical.

regulating the heated temperature controlled by the temperature controller (precision of approximately $\pm 1\text{ }^\circ\text{C}$). Finally, the low stable concentration gas passes into the CRDS and CEAS instruments for NO_3 radical and NO_2 detection.

3.2. Calibration method

According to the chemical conversion relationship of NO_3 radical and NO_2 (as shown in equation (2)), the overall loss of NO_3 radical in the CRDS system is calibrated by measuring the variation of NO_2 after adding NO . The overall loss calibration of NO_3 radical can be divided into several parts as shown below. First, the two sets of instrument systems are passed into N_2 to detect the background signal without gas absorption. Second, the instruments of CRDS and CEAS are separately applied to detect NO_3 radical and NO_2 of the sample gas through the high-temperature heating and dilution. Third, NO_3 radical sufficiently reacts with NO with the addition of excess NO . Every molecule of NO_3 radical will generate two molecules of NO_2 . Simultaneously, the concentrations of NO_3 radical and NO_2 are respectively measured by CRDS and CEAS. Three main sources of NO_2 concentration detection through the CEAS instrument are available: production through the decomposition of N_2O_5 solid sources, production through the reaction of NO_3 radical and NO , and production through the addition of impure NO . Finally, avoiding passing of the sample gas and only adding NO , the concentration of NO_2 from the impure NO is measured by the CEAS instrument. The transmission efficiency of NO_3 radical can be calculated by equation (3):



$$\text{Te} = \frac{2 \times [\text{NO}_3]}{[\text{NO}_2]_{\text{source}+\text{NO}} - [\text{NO}_2]_{\text{source}} - [\text{NO}_2]_{\text{NO}}}, \quad (3)$$

where $\text{Te}(\text{NO}_3)$ is the transmission efficiency of NO_3 radical in the CRDS system, and $[\text{NO}_3]$ is the concentrations of NO_3 radical from thermal decomposition of N_2O_5 . $[\text{NO}_2]_{\text{source}}$ and $[\text{NO}_2]_{\text{source}+\text{NO}}$ are the concentration of NO_2 from the thermal decomposition of N_2O_5 and after adding NO , respectively. $[\text{NO}_2]_{\text{NO}}$ represents the background of impure NO .

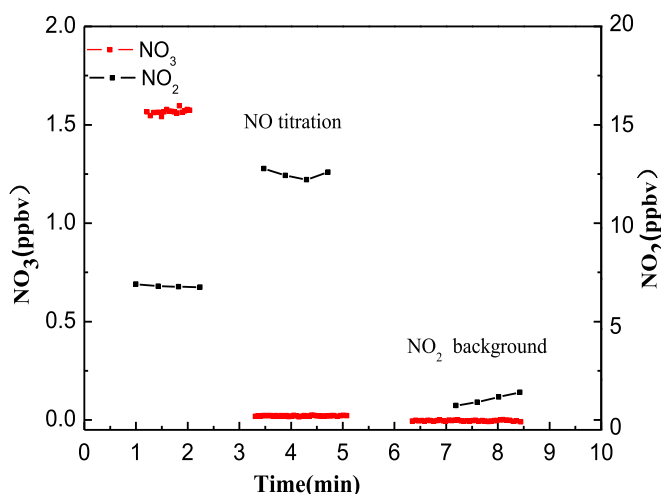


Figure 4. The single calibration process of NO_3 radical in the CRDS system.

3.3. Calibration results

The single calibration process of NO_3 radical in the CRDS system is shown in figure 4. The concentrations of NO_3 radical and NO_2 are respectively presented in red and black lines. The abscissa is the time of calibration, and the ordinate is the concentrations of NO_3 radical and NO_2 . The sample gas obtained from high-temperature decomposition and dilution passes into the two sets of instruments for detection. The concentrations of NO_3 radical and NO_2 respectively attain 1.57 ppbv and 7.13 ppbv. Excess NO is then added to titrate the NO_3 generated from the thermal dissociation of N_2O_5 . NO rapidly reacts with NO_3 radical, and the concentration of NO_3 instantly reduces to the background value. Meanwhile, NO_2 is formed by the reaction as shown in equation, and every molecule of NO_3 radical generates two molecules of NO_2 . Consequently, the concentration of NO_2 rises to approximately 12.61 ppbv. The background concentration of NO_2 is detected considering the problem of impure NO. The sample gas is shut down, and the concentration of NO_2 from the NO source is measured to approximately 1.52 ppbv. In the experiment, the measuring time of each step is approximately 1–2 min.

Figure 5(a) summarizes the results from four consecutive calibrations, and the time of each calibration is approximately 7–8 min. This figure shows the original concentration of NO_3 radical and the corresponding concentration variation of NO_2 . This variation is represented as ΔNO_2 , which is the NO_2 concentration from the formation through the reaction of NO_3 radical and NO. During the measurement, NO_3 radical concentration is approximately 1.33 ppbv and ΔNO_2 is close to 3.54 ppbv. Their concentrations slightly increase during the four consecutive calibration periods but are relatively stable in the process of each calibration. The main reason is that synthetic N_2O_5 solid source is not completely pure. The transmission efficiency of NO_3 radical is obtained in accordance with equation (3) and ΔNO_2 . The transmission efficiency of NO_3 radical in the CRDS system for four consecutive calibrations and the measurement error for each calibration are presented

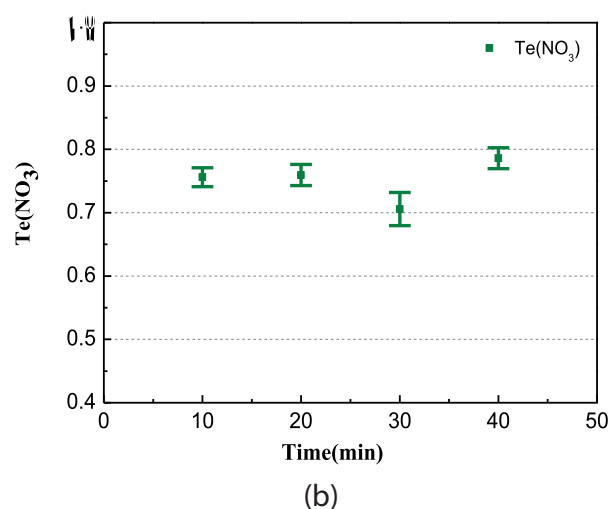
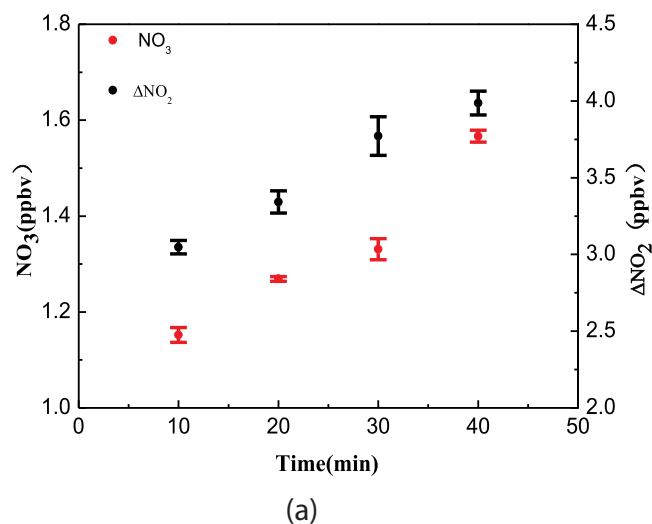


Figure 5. (a) The concentration variation of NO_2 in the calibration. The error bars is provided by the standard deviation of measurement. (b) The transmission efficiency of NO_3 radical in the CRDS system.

in figure 5(b). The accuracies of the CRDS and CEAS instruments are approximately $\pm 8\%$ [16] and $\pm 6\%$ [24], respectively. Considering the standard deviation measurement and the instrument accuracy of CRDS and CEAS, the relative uncertainty of the absolute calibration method is estimated to be 11%. The average transmission efficiency of the NO_3 radical for the CRDS instrument is calculated to be $75\% \pm 9\%$ at a 6.5 SLPM flow rate.

Calibrations for the same CRDS instrument are also performed by the relative calibration method. The relative method requires the calibration of the filter loss of the Teflon membrane and the surface loss of the NO_3 radical through the PFA tubing. The loss rate coefficient of the NO_3 radical through the PFA tubing is $0.19 \pm 0.02 \text{ s}^{-1}$, and the filter loss of the new Teflon membrane filter is approximately $8\% \pm 3\%$ [16]. The surface loss of the NO_3 radical through the PFA tubing is calculated to be approximately $6\% \pm 1\%$ by the loss rate coefficient at a flow rate of 6.5 SLPM. In addition, the surface loss of the filter holder is approximately $9\% \pm 4\%$, and the CRD instrument accuracy is approximately $\pm 8\%$; the details

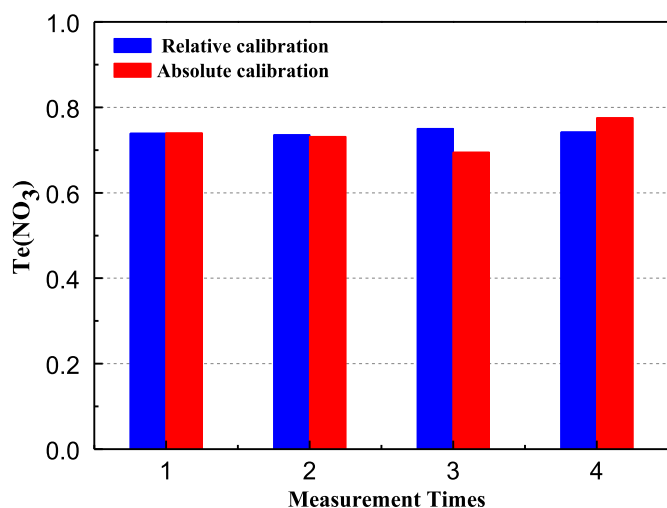


Figure 6. Contrasted results of the relative and absolute calibration methods. The transmission efficiency data of the NO_3 radical for the relative calibration are from [16].

are described by Wang *et al* [16]. The comparative results for the two methods are shown in figure 6. According to the above measurements, the overall inlet transmission efficiencies of the NO_3 radical for the instrument are determined to be $75\% \pm 9\%$ and $77\% \pm 11\%$ through the absolute and the relative calibration methods, respectively, for the same CRDS instrument. The contrasted results are basically consistent. This finding further verifies the accuracy of transmission efficiency of the NO_3 radical for the absolute calibration method.

4. Conclusions

A novel calibration method is described in this study. The calibration system of the NO_3 radical is designed and constructed using the CRDS and CEAS instruments. Meanwhile, the standard gas of the NO_3 radical is produced by the synthetic N_2O_5 solid source in the laboratory. Four consecutive calibrations are conducted by the absolute method, and the average transmission efficiency of the NO_3 radical is approximately $75\% \pm 9\%$ at a flow rate of 6.5 SLPM. Contrast measurements between the two methods are performed, and the results are basically consistent. The method is precise, rapid, and concise. Furthermore, the method can be independently applied to a common point sampling measurement instrument. Future research will focus on automated integrative calibration and application of automated absolute calibration systems for ambient NO_3 radical in field measurements.

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