

Methods for Preparing Standard Nitrate Radical (NO₃) Gas to Calibrate the LIF-based Instrument for Measurements in the Atmosphere

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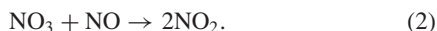
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Preparation of standard NO₃ gas is explored at the level of ppbv for atmospheric measurements utilizing an LIF instrument. The sequence of thermal decomposition of N₂O₅ and gas phase titration of NO₃ by adding NO is useful. To reduce NO₂ contamination in N₂O₅, N₂O₅ trapping after mixing NO_x and O₃ was adopted. As a convenient method in the field studies, dynamic mixing of NO_x and O₃ was explored.

Nitrate radical (NO₃) and dinitrogen pentoxide (N₂O₅) in the nocturnal atmosphere have been focused as critical intermediates to discuss NO_x cycle, acidification, and atmospheric lifetime of various compounds.¹ Measurements of atmospheric NO₃/N₂O₅ have been difficult because of their high reactivity and low abundance at the level of pptv (parts per trillion by volume; 10⁻¹² v/v). In this decade, however, a number of observational studies on NO₃/N₂O₅ were reported.^{2,3} An instrument for measuring atmospheric NO₃/N₂O₅ has been developed by the laser-induced fluorescence technique (LIF).⁴ The LIF instrument should be calibrated accurately. Preparation methods for gaseous NO₃ have been reported.⁵ Halogen atoms can react with nitric acid (HNO₃) to form NO₃. However, such radical reactions are applicable only to the experiments at the low pressure. For application in the atmosphere, standard NO₃ should be supplied conveniently at the level of ppbv (10⁻⁹ v/v) or less for the pressure $P = 1$ atm. For preparing NO₃, decomposition of N₂O₅ is promising.⁴⁻⁶



The equilibrium shifts towards NO₃ + NO₂ side with temperature increase. The LIF instrument is capable of monitoring both NO₃ and NO₂ when the excitation wavelengths are alternated between 623 and 613 nm. It is easy to calibrate the instrument for NO₂. Calibration for NO₃ is possible when NO₃ is converted to NO₂ by NO as:

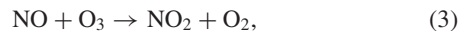


Increment of NO₂ corresponds to twice of decreasing NO₃ as $\Delta[\text{NO}_2] = -2\Delta[\text{NO}_3]$. Thus, the information on NO₃ concentration can be acquired from the increment of NO₂. It is desirable to preserve stable supplement of gaseous N₂O₅ with reduced contamination of NO₂. In this study, validation of the methods for preparing standard NO₃ gas is reported to realize an accurate and/or convenient calibrator for application of the LIF instrument to the field studies.

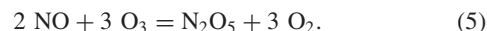
At first, dehydration of HNO₃ by P₂O₅ was examined, which is typical for preparing powdery N₂O₅.⁷ In a glass flask, 97% fuming HNO₃ was dehydrated by P₂O₅ for 5 h. Formed N₂O₅ was gathered at a trap chilled by a methanol bath (183 K). To

reduce the NO₂ impurity, the flow of O₃ was added. Then, acquired white powder was used as the N₂O₅ source. As a result, measured [NO₂] were 8.5 and 11.4 ppmv (10⁻⁶ v/v) before and after adding NO. [NO₃] titrated by NO was determined as 1.5 ppmv. NO₂ impurity in the initial N₂O₅ sample was estimated as 7.0 ppmv, which was 4.7 times higher than the formed NO₃. Such contamination of NO₂ in N₂O₅ is unavoidable because of the impurity of NO₂ in HNO₃, hydrolysis of N₂O₅, and thermal decomposition of N₂O₅ during the exothermic dehydration reaction. To reduce the NO₂ impurity, the trap-to-trap purification of N₂O₅ is essential. However, such a complex procedure is not suitable for field studies. In addition, it is difficult to control the yield of N₂O₅ and the NO₃ output at the level of ppbv.

To synthesize N₂O₅ controllably, mixing of gaseous NO_x and O₃ was adopted. NO_x is oxidized by O₃ to form NO₃ as:



N₂O₅ is generated from NO₂ and NO₃ via the reverse reaction of (1). From reactions (1), (3), and (4), the stoichiometry among NO, O₃, and N₂O₅ can be described as:



Excess O₃ is needed to rapidly convert NO to N₂O₅. Figure 1 shows the schematic diagram of experimental configurations for trapping N₂O₅ from NO_x + O₃ (arrow A) and introduction of vaporized N₂O₅ into the LIF NO₃/NO₂ detector (arrow B). PFA tubes were used to reduce the loss of NO₃/N₂O₅ on the wall

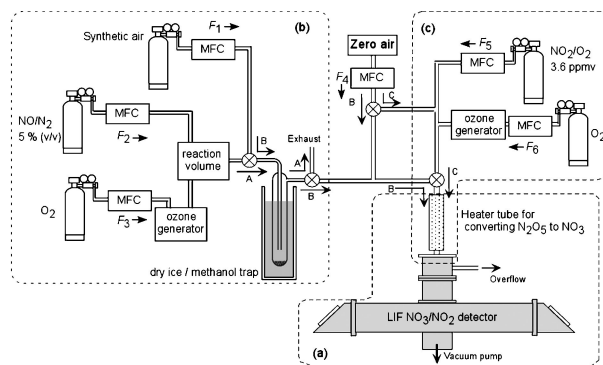


Figure 1. Schematic diagram for preparing NO₃: (a) LIF instrument; (b) Flow for N₂O₅ synthesis and supply; (c) In-line supply for NO₃ by mixing of NO_x and O₃. MFC: mass flow controller; F₁–F₆: mass flow rates. Arrows indicate the flows for three modes: A: N₂O₅ synthesis, B: supply of N₂O₅ vapor from the trap, C: convenient supply of NO₃.

surface. Representative settings for trapping N_2O_5 were as follows: total flow rate $F_2 + F_3 = 230 \text{ sccm}$ ($\text{cm}^3 \cdot \text{min}^{-1}$ at STP); initial diluted concentrations $[\text{NO}] = 0.17\%$, $[\text{O}_3] = 2.9\%$; reaction volume $V_r = 300 \text{ cm}^3$; trap temperature $T_t = 195 \text{ K}$ (dry-ice/methanol bath). Because of excess O_3 , $>99\%$ of NO_x can be rapidly converted to N_2O_5 in the reaction volume. NO_2 impurity can be suppressed. The upper limit of N_2O_5 synthesis rate was estimated as $5.3 \times 10^{-2} \text{ g} \cdot \text{h}^{-1}$ from the flow rates and concentrations when complete trapping of N_2O_5 was assumed. Note that practical collection efficiency of N_2O_5 is not 100% because of heterogeneous loss and incomplete trapping. It is remarkable that the reactions can be controlled easily only by adjusting the flow rates and concentrations of initial NO_x and O_3 . After trapping N_2O_5 , high-grade synthetic air was passed through the trap and N_2O_5 was vaporized. N_2O_5 was diluted to a suitable level by adding zero air, which was purified by a charcoal filter. Then, NO_2 and NO_3 were monitored by the LIF instrument. Observed concentrations of NO_2 were 209 and 398 ppbv before and after NO addition to the LIF cell, respectively. Titrated NO_3 was 94 ppbv and NO_2 impurity in N_2O_5 was 115 ppbv, which was only 1.2 times higher than the formed NO_3 . The LIF instrument can be calibrated for NO_3 successfully with less NO_2 contamination. For calibration on N_2O_5 , excess NO was added just after the N_2O_5 source to convert N_2O_5 to NO_2 completely. From reactions (1) and (2), 1 molecule of N_2O_5 generates 3 NO_2 . Concentration of N_2O_5 can be determined from the NO_2 increment. When the heater tube with 1/2 inch diameter and 50 cm length was heated to $T = 353 \text{ K}$, the conversion yield of NO_3 from N_2O_5 was 80%.⁴ The yield was limited because of the NO_3 loss on the wall. After the instrument is calibrated, N_2O_5 concentration can be quantified from the LIF signal of converted NO_3 . As another experiment, the stability of the N_2O_5 source was explored. After 3 h of reaction and proper dilution of N_2O_5 , the averaged concentration of N_2O_5 was $143 \pm 5 \text{ ppbv}$ as shown in Figure 2. N_2O_5 supply was stable for 3 h with deviation of $\pm 4\%$. The deviation was mainly due to variation of bath temperature and consumption of N_2O_5 powder in the trap. Short-term variation of N_2O_5 was $<1\%$ as the standard deviation of 1-min data for 10-min averaging. Consumption rate of N_2O_5 was estimated from flow rates and observed concentration as $1.2 \times 10^{-4} \text{ g} \cdot \text{h}^{-1}$, which was much smaller than N_2O_5 synthesis rate. Thus, reaction period can be shortened in principle. For example, it was confirmed that N_2O_5 was supplied for 7 h at least after 3 h of reaction. Consequently, the procedure was established to calibrate the LIF instrument accurately.

Finally, the secondary standard supply for NO_3 was established and validated by the LIF instrument. In field studies, it is desirable to generate the standard sample conveniently with-

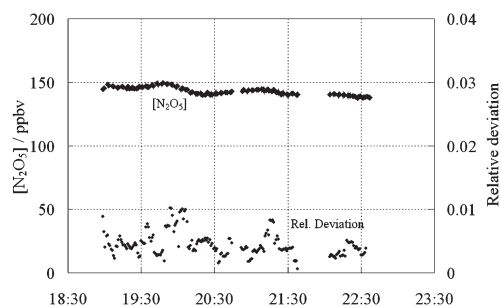


Figure 2. Long-term stability of N_2O_5 source.

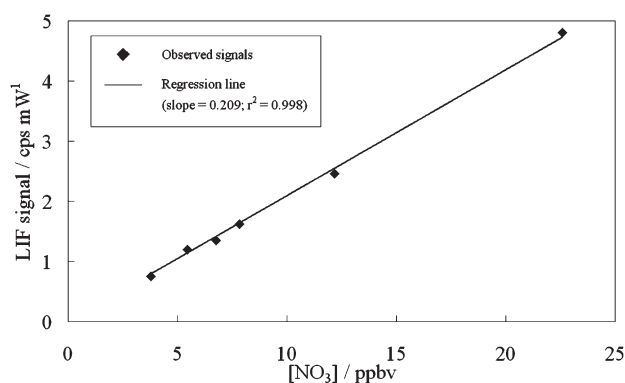


Figure 3. Relationships between calculated $[\text{NO}_3]$ and LIF signals for the convenient source of NO_3 .

out solvent and dry ice. As shown in reactions (3) and (4), NO_3 can be generated when NO_x is mixed with excess O_3 . As indicated by the arrow C in Figure 1, the convenient supply of NO_3 was constructed. It consisted of a standard NO_2 cylinder, an O_3 generator and a mixing system. No wet reagents were used and the setup was easy and reproducible. The LIF instrument detected the generated NO_3 successfully. NO_3 concentration can be calculated theoretically from several parameters (e.g. initial concentrations, temperature, reaction time, and rate constants), with gas phase reactions considered.⁸ For example, $[\text{NO}_3] = 23 \text{ ppbv}$ for $F_4 = 3000 \text{ sccm}$, $F_5 = 300 \text{ sccm}$, $F_6 = 80 \text{ sccm}$, $[\text{NO}_2] = 320 \text{ ppbv}$, $[\text{O}_3] = 71 \text{ ppmv}$, $V_r = 45 \text{ cm}^3$, $T = 353 \text{ K}$, and $P = 1 \text{ atm}$. The calculation has large uncertainties because NO_3 loss on the wall was not considered. However, the production rate of NO_3 is reasonable with the gas phase reactions considered. Thus, the relative response of NO_3 on the material NO_2 and O_3 is proper. Figure 3 shows an example of the relationship between the observed LIF signal and calculated NO_3 concentration for the convenient source of NO_3 . As a result, excellent linearity was observed between the signal and the relative concentration ($r^2 = 0.998$). It was confirmed that the convenient source is promising to prepare the “relative standard sample” of NO_3 . From the slope of the regression line, the “preliminary sensitivity” can be determined in the field as $0.209 \text{ cps mW}^{-1} \text{ ppbv}^{-1}$. In practical uses, after the relative variation of the preliminary sensitivity is monitored frequently in the field campaign, the comparison between the convenient source and the accurate calibration should be explored to determine the correction factor to acquire the absolute sensitivity. Note that the configurations and settings of the convenient source should be preserved.

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