Methods for Preparing Standard Nitrate Radical (NO_3) Gas to Calibrate the LIF-based Instrument for Measurements in the Atmosphere

Jun Matsumoto,*[†] Hidekazu Imai, Naohiro Kosugi, and Yoshizumi Kajii
Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397
[†]*Division of Atmospheric Environment, Solar-Terrestrial Environment Laboratory, Nagoya University,*
3-13 Honohara, Toyokawa, Aichi 442-8507

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Preparation of standard NO_3 gas is explored at the level of ppbv for atmospheric measurements utilizing an LIF instrument. The sequence of thermal decomposition of N_2O_5 and gas phase titration of NO_3 by adding NO is useful. To reduce NO_2 contamination in N_2O_5, N_2O_5 trapping after mixing NO*x* and O_3 was adopted. As a convenient method in the field studies, dynamic mixing of NO*x* and O_3 was explored.

Nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) 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 NO_3/N_2O_5 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 NO_3/N_2O_5 were reported.[2,3] An instrument for measuring atmospheric NO_3/N_2O_5 has been developed by the laser-induced fluorescence technique (LIF).[4] The LIF instrument should be calibrated accurately. Preparation methods for gaseous NO_3 have been reported.[5] Halogen atoms can react with nitric acid (HNO_3) to form NO_3. However, such radical reactions are applicable only to the experiments at the low pressure. For application in the atmosphere, standard NO_3 should be supplied conveniently at the level of ppbv (10^{-9} v/v) or less for the pressure $P = 1$ atm. For preparing NO_3, decomposition of N_2O_5 is promising.[4–6]

$$N_2O_5 + M \rightleftharpoons NO_3 + NO_2 + M. \tag{1}$$

The equilibrium shifts towards $NO_3 + NO_2$ side with temperature increase. The LIF instrument is capable of monitoring both NO_3 and NO_2 when the excitation wavelengths are alternated between 623 and 613 nm. It is easy to calibrate the instrument for NO_2. Calibration for NO_3 is possible when NO_3 is converted to NO_2 by NO as:

$$NO_3 + NO \rightarrow 2NO_2. \tag{2}$$

Increment of NO_2 corresponds to twice of decreasing NO_3 as $\Delta[NO_2] = -2\Delta[NO_3]$. Thus, the information on NO_3 concentration can be acquired from the increment of NO_2. It is desirable to preserve stable supplement of gaseous N_2O_5 with reduced contamination of NO_2. In this study, validation of the methods for preparing standard NO_3 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 HNO_3 by P_2O_5 was examined, which is typical for preparing powdery N_2O_5.[7] In a glass flask, 97% fuming HNO_3 was dehydrated by P_2O_5 for 5 h. Formed N_2O_5 was gathered at a trap chilled by a methanol bath (183 K). To reduce the NO_2 impurity, the flow of O_3 was added. Then, acquired white powder was used as the N_2O_5 source. As a result, measured $[NO_2]$ were 8.5 and 11.4 ppmv (10^{-6} v/v) before and after adding NO. $[NO_3]$ titrated by NO was determined as 1.5 ppmv. NO_2 impurity in the initial N_2O_5 sample was estimated as 7.0 ppmv, which was 4.7 times higher than the formed NO_3. Such contamination of NO_2 in N_2O_5 is unavoidable because of the impurity of NO_2 in HNO_3, hydrolysis of N_2O_5, and thermal decomposition of N_2O_5 during the exothermic dehydration reaction. To reduce the NO_2 impurity, the trap-to-trap purification of N_2O_5 is essential. However, such a complex procedure is not suitable for field studies. In addition, it is difficult to control the yield of N_2O_5 and the NO_3 output at the level of ppbv.

To synthesize N_2O_5 controllably, mixing of gaseous NO*x* and O_3 was adopted. NO*x* is oxidized by O_3 to form NO_3 as:

$$NO + O_3 \rightarrow NO_2 + O_2, \tag{3}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2. \tag{4}$$

N_2O_5 is generated from NO_2 and NO_3 via the reverse reaction of (1). From reactions (1), (3), and (4), the stoichiometry among NO, O_3, and N_2O_5 can be described as:

$$2\ NO + 3\ O_3 = N_2O_5 + 3\ O_2. \tag{5}$$

Excess O_3 is needed to rapidly convert NO to N_2O_5. Figure 1 shows the schematic diagram of experimental configurations for trapping N_2O_5 from NO*x* + O_3 (arrow A) and introduction of vaporized N_2O_5 into the LIF NO_3/NO_2 detector (arrow B). PFA tubes were used to reduce the loss of NO_3/N_2O_5 on the wall

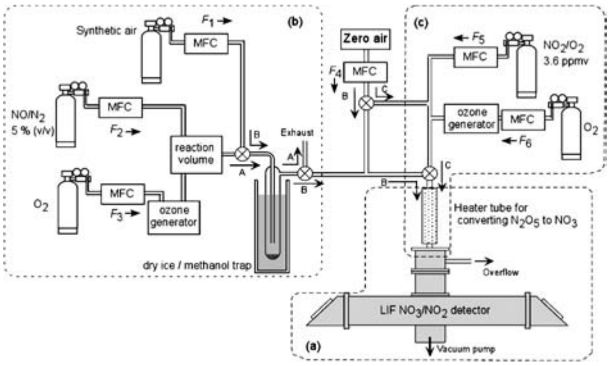

Figure 1. Schematic diagram for preparing NO_3: (a) LIF instrument; (b) Flow for N_2O_5 synthesis and supply; (c) In-line supply for NO_3 by mixing of NO*x* and O_3. MFC: mass flow controller; F_1–F_6: mass flow rates. Arrows indicate the flows for three modes: A. N_2O_5 synthesis, B: supply of N_2O_5 vapor from the trap, C: convenient supply of NO_3.

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surface. Representative settings for trapping N_2O_5 were as follows: total flow rate $F_2 + F_3 = 230$ sccm ($cm^3 \cdot min^{-1}$ at STP); initial diluted concentrations [NO] = 0.17%, $[O_3] = 2.9\%$; reaction volume $V_r = 300\,cm^3$; trap temperature $T_t = 195$ K (dry-ice/methanol bath). Because of excess O_3, >99% of NOx 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 $5.3 \times 10^{-2}\,g \cdot h^{-1}$ 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 NOx 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 $T = 353$ 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 ± 5 ppbv as shown in Figure 2. N_2O_5 supply was stable for 3 h with deviation of ±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 $1.2 \times 10^{-4}\,g \cdot h^{-1}$, 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 without solvent and dry ice. As shown in reactions (3) and (4), NO_3 can be generated when NOx 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, $[NO_3] =$ 23 ppbv for $F_4 = 3000$ sccm, $F_5 = 300$ sccm, $F_6 = 80$ sccm, $[NO_2] = 320$ ppbv, $[O_3] = 71$ ppmv, $V_r = 45\,cm^3$, $T = 353$ K, and $P = 1$ 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 $0.209\,cps\,mW^{-1}\,ppbv^{-1}$. 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.

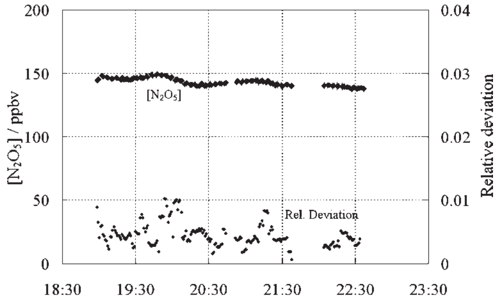

Figure 2. Long-term stability of N_2O_5 source.

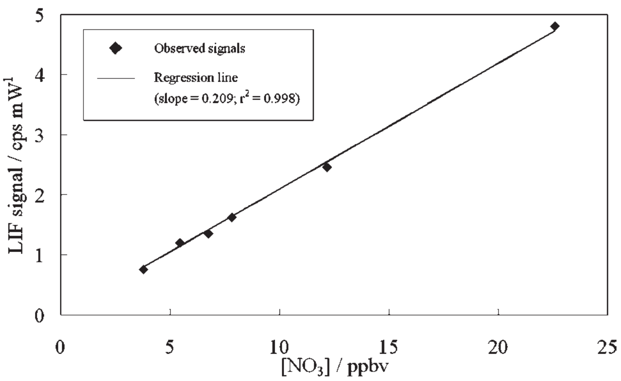

Figure 3. Relationships between calculated $[NO_3]$ and LIF signals for the convenient source of NO_3.

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