



Technical note

Development of atmospheric NO analyzer by using a laser-induced fluorescence NO₂ detectorKoji Miyazaki^{a,*}, Jun Matsumoto^b, Shungo Kato^a, Yoshizumi Kajii^a^a Graduate school of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1, Minamiohsawa, Hachioji, Tokyo 192-0397, Japan^b Integrated Research Institute, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan

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ABSTRACT

In this study, we propose a new principle for measuring atmospheric NO using a laser-induced fluorescence (LIF) NO₂ detector. NO is chemically converted into NO₂; then, NO₂ is detected by the LIF technique. To convert NO into NO₂, ozone is added to sample air. Since there exists un-reacted NO and loss of NO₂ due to further reaction of NO₂ with ozone depending on both the concentration of ozone and reaction time, the enhanced NO₂ concentration is less than the initial NO concentration. Using chemical kinetic analysis, we successfully derive the relationship between NO concentration and LIF signals. We also propose a unique calibration method for an LIF NO₂ detector without using a chemiluminescent NO_x analyzer; this method is based on the gas phase titration technique. The limits of the detection of the developed instrument for NO₂ and NO measurements are 14 ppt and 22 ppt, respectively. We perform ambient air measurements in a suburb of Tokyo using the developed LIF NO analyzer and a commercial chemiluminescent NO analyzer. A comparison of the measurement results reveals that they are in excellent agreement, with a slope of 0.99 and a correlation coefficient of 0.99.

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1. Introduction

Nitrogen oxides (NO_x = NO + NO₂) are some of the most important species in tropospheric photochemistry. They are initially emitted in the atmosphere as NO and rapidly converted into NO₂ through the following reactions with O₃, HO₂, or RO₂:



In the daytime, NO₂ dissociates into NO and O(³P) by the photolysis of ultraviolet solar radiation, and O(³P) rapidly combines with an oxygen molecule to re-form ozone as follows:



Thus, NO and NO₂ are interconverted within a few minutes, thereby resulting in a photostationary state (PSS) relationship among NO, NO₂, peroxy radicals, and O₃ (e.g., Parrish et al., 1986; Cantrell et al., 1993, 1997; Hauglustaine et al., 1996, 1999; Thornton et al., 2003; Matsumoto et al., 2006). Tropospheric ozone is one of the main constituents of photochemical oxidants, and it causes global warming and various human diseases. In recent

* Corresponding author. Tel.: +81 426 77 2833; fax: +81 426 77 2837.

E-mail address: miyazaki@atmchem.apchem.metro-u.ac.jp (K. Miyazaki).

years, there has been a significant increase in the amount of tropospheric ozone (Akimoto, 2003). Accurate measurements of ambient NO_x are essential in order to determine the mechanism of increase in the amount of tropospheric ozone.

NO_x has been measured by the ozone chemiluminescence (CL) technique. A chemiluminescent NO analyzer is widely used for the measurement of NO_x . Because of its simplicity, ease of handling, and sufficient sensitivity, this analyzer has significant advantages over techniques such as laser-induced multiphoton ionization mass spectrometry with supersonic expansion fluorescence (Lee et al., 2000) and laser-induced fluorescence (LIF; Bloss et al., 2003). However, some problems have been reported in the NO_2 measurement using the chemiluminescent NO analyzer (Winer et al., 1974; Steinbacher et al., 2007). In NO_2 measurement, NO_2 should be converted into NO and then measured. This method measures NO_2 indirectly, and it causes technical problems such as chemical interference and instability of conversion efficiency. For example, a photolytic converter decomposes HONO and its conversion efficiency changes due to a change in light intensity; further, a metallic catalyst causes the decomposition of other nitrogen oxides such as PAN, HNO_3 , and HONO.

Therefore, methods such as the LIF technique have been employed for the direct measurement of atmospheric NO_2 . Recently, LIF NO_2 instruments that comprise various excitation light sources and employ various excitation methods have been reported. For example, Fong and Brune (1997) and Thornton et al. (2000) have adopted a tunable dye laser with multipass excitation. Cleary et al. (2002) have employed a continuous wave (CW) external-cavity tunable diode laser (640 nm) and continuous supersonic expansion. Matsumi et al. (2001) have adopted an Nd:YAG pumped optical parametric oscillator (OPO) laser. Matsumoto et al. (2001) and Matsumoto and Kajii (2003) have employed a compact and powerful single-wavelength Nd:YVO₄ pulsed laser. In the studies conducted by these researchers, atmospheric NO_2 has been measured with high selectivity.

However, only NO_2 can be measured by these LIF instruments. To extend the utility of the LIF NO_2 instrument, this method is used to measure atmospheric NO. In this study, we propose the principle of a system for the measurement of atmospheric NO using an LIF NO_2 instrument based on Matsumoto and Kajii (2003); further, the practical utility of the developed instrument is evaluated through measurements of atmospheric NO and NO_2 .

2. Experimental

2.1. Principle of NO measurement

We demonstrate the principle of NO measurement using a NO_2 sensor. NO is converted into NO_2 when it reacts with O_3 . When O_3 is added to the gas mixture of NO and NO_2 diluted by zero air, the following reactions proceed in a reaction tube:



where k_i denotes the reaction rate constant of reaction R_i . The generated NO_2 reacts with ozone to produce NO_3 , which may react with NO_2 to produce N_2O_5 . This process results in the loss of NO_2 due to the addition of ozone. Un-reacted NO may be present inside the tube, depending on the concentration of ozone and the reaction time. Therefore, the amount by which NO_2 increases (D_{NO_2}) due to the addition of ozone is not always equal to the amount of initial NO that is present in the gas mixture. An effective and selective conversion of NO into NO_2 is highly desirable. The general relationship among the NO_x before and after the ozone addition is shown in Fig. 1. The initial NO concentration $[\text{NO}]_0$ can be determined from the value of Δ_{NO_2} by chemical kinetic analysis. The time evolution of NO_2 , $[\text{NO}_2]_t$, after the addition of ozone can be obtained by the following reaction rate equations:

$$\frac{d[\text{NO}]}{dt} = -k_1[\text{NO}][\text{O}_3] - k_7[\text{NO}_3][\text{NO}], \quad (1)$$

$$\begin{aligned} \frac{d[\text{NO}_2]}{dt} = & k_1[\text{NO}][\text{O}_3] - k_6[\text{NO}_2][\text{O}_3] + 2k_7[\text{NO}_3][\text{NO}] \\ & - k_8[\text{NO}_3][\text{NO}_2][\text{M}] + k_9[\text{N}_2\text{O}_5], \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{d[\text{NO}_3]}{dt} = & k_6[\text{NO}_2][\text{O}_3] - k_7[\text{NO}_3][\text{NO}] - k_8[\text{NO}_2][\text{NO}_3][\text{M}] \\ & + k_9[\text{N}_2\text{O}_5], \end{aligned} \quad (3)$$

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = k_8[\text{NO}_2][\text{NO}_3][\text{M}] - k_9[\text{N}_2\text{O}_5]. \quad (4)$$

The differential Eq. (2) described above is solved under following two assumptions: (1) NO_3 radical concentration is in the steady-state condition due to a rapid reaction with NO_x ; (2) the concentration of ozone added to the reaction tube is maintained constant due to much higher than ambient O_3 and NO_x concentration level; as follows:

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