Measurement of NO$_2$, SO$_2$, O$_3$, H$_2$O and aerosol in the troposphere using differential optical absorption spectroscopy (DOAS)

Toru Kimura, Toyofumi Umekawa
Kyoto Electronics Manufacturing Co.,Ltd.
68 Ninodan-cho, Kisshoin Minami-ku, Kyoto 601-8317, Japan
Si Fuqi, Hiroaki Kuze, Nobuo Takeuchi
Center for Environmental Remote Sensing, Chiba University
1-33 Yoyoi-cho, Inage-ku, Chiba 263-8522, Japan

Abstract

We report on air-pollution monitoring campaign in the Kyoto and Chiba area during 2004. With differential optical absorption spectroscopy (DOAS) method, average concentrations of NO$_2$, SO$_2$, O$_3$, H$_2$O and aerosol particles can be measured. For NO$_2$, SO$_2$, O$_3$ and H$_2$O, the DOAS results are found to be consistent with the results of the ground sampling measurements. For aerosol, the optical thickness at 550 nm is correlated with the concentration of ground-measured suspended particulate matter (SPM), leading to a good correlation between the DOAS and SPM data. Also, the mass extinction efficiency (MEE) is analyzed for aerosol particles in the lower troposphere. From Chiba measurements, it is found that the average MEE is about 7.6 m^{2}g^{-1}, and the value exhibits a good inverse correlation with the particle size.

1. Introduction

The technique of differential optical absorption spectroscopy (DOAS) is widely used to monitor atmospheric pollutant species such as NO$_2$, NO, SO$_2$, and O$_3$.[1-3] These molecular species exhibit characteristic absorption patterns in the visible and UV parts of the spectrum. By using the path length of a few kilometers, and by extracting the absorption features that vary rapidly with the wavelength, the DOAS method enables the retrieval of molecular concentrations of the order of ppb.

In the present paper, we describe our recent DOAS results measured in Chiba and Kyoto urban regions. The Chiba data are based on the novel method of pulsed DOAS, in which an aviation obstruction light is utilized as the light source.[3] Figure 1 shows a schematic of the experimental setup. The path length is about 5.5 km, and the wavelength range covered in this experiment is about 300-800 nm. From Chiba data, the absorption of NO$_2$, H$_2$O, and the extinction due to aerosol particles are investigated. The measurement of aerosols is feasible by monitoring the change in the received intensity, since if the alignment of the system is sufficiently stable, the intensity change is brought about solely from the variation of aerosol quantity along the light path. The monitoring of H$_2$O along the path is important from the viewpoint of the increase in the aerosol extinction efficiency due to high relative humidity.[4] The

Kyoto system, on the other hand, is operated with a cw light source dedicated to the DOAS measurement, with a distance of 2.4 km. The operational wavelength range is extended to 280 nm, thus making it possible to observe the absorption of SO_2, O_3, and NO_2 simultaneously.
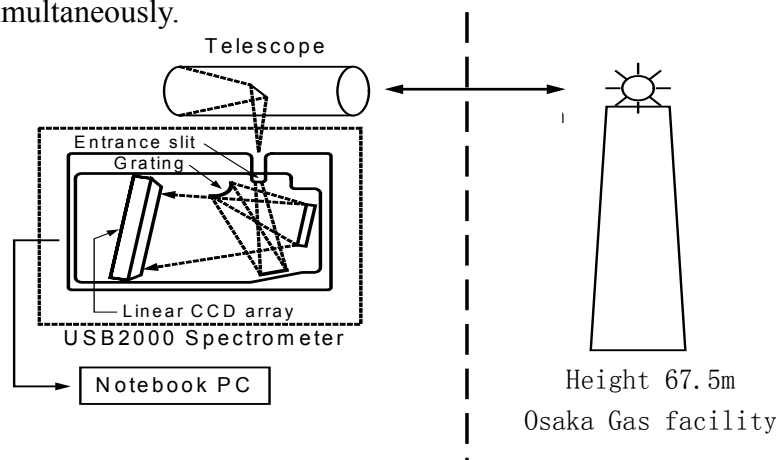

Fig. 1 Experimental setup for measuring NO_2, H_2O, and aerosol extinction.

2. DOAS spectrum

2.1 Retrieval of NO_2, SO_2, O_3 and H_2O retrieval

In the Chiba measurement (resolution = 0.3 nm/channel), the wavelength range of 400-450 nm is used for NO_2, 500-550 nm for aerosol, and 710-740 nm for H_2O. In the Kyoto measurement (resolution = 0.11 nm/channel), NO_2 is measured in a wavelength range of 350-360 nm, O_3 in 280-290 nm, and SO_2 in 295-305 nm.

The analysis of the DOAS spectra is based on the Beer-Lambert's law expressed as

$$I(\lambda) = kI_0(\lambda)e^{-L\sigma(\lambda)n} , \tag{1}$$

where k is the system constant, $I(\lambda)$ is the measured intensity, $I_0(\lambda)$ the unattenuated reference intensity, L the path length, $\sigma(\lambda)$ the wavelength-dependent absorption cross section, and n the number density of the species. The dimensionless quantity $\tau = L\,\sigma\,n$ is referred to as the optical thickness.

In the real atmosphere both molecules (Rayleigh scattering) and aerosols (Mie scattering) contribute to the radiation extinction. Adding these contributions to eq. (1) gives

$$\tau(\lambda) = \ln\frac{I_0(\lambda)}{I(\lambda)} = L\big(\sigma(\lambda)n + \varepsilon^{M}(\lambda) + \varepsilon^{A}(\lambda)\big) - \ln k . \tag{2}$$

Here $\varepsilon^{M}(\lambda)$ is the molecular extinction coefficient which is the product of the molecular cross section, $\sigma^{M}(\lambda)$, and the number density of air molecules, n_m. Similarly, the aerosol extinction coefficient, $\varepsilon^{A}(\lambda)$, is defined as $\sigma^{A}(\lambda)n_a$, where $\sigma^{A}(\lambda)$ is the aerosol cross section, and n_a the number density of the aerosol particles.

Cross sections in eq.(2) can be separated into two components, slowly varying one, $\sigma_i^{s}(\lambda)$, and rapidly varying one, $\sigma_i(\lambda)$, with wavelength. Both the molecular and

aerosol cross sections are slowly varying components of the optical thickness. Hence we obtain

$$\tau(\lambda) = L\sum_i \sigma_i(\lambda)n_i + L\left(\sum_i \sigma_i^{\,s}(\lambda)a_i + \sigma^{M}(\lambda)n^{M} + \sigma^{A}(\lambda)n^{A}\right) - \ln k, \qquad (3)$$

where subscript i denotes trace gas species such as NO_2, O_3 or SO_2. On the right-hand side of eq. (3), the first term describes the rapidly varying part, and the second the slowly varying part.

2.2 Aerosol retrieval and MEE

The aerosol optical thickness α_a can be defined as

$$\tau_a = \alpha_a L = \ln k I_0(\lambda) - \ln I(\lambda) - \tau_{Rayleigh}(\lambda) - \tau_{gas}(\lambda), \qquad (4)$$

where I, $\tau_{Rayleigh}$ and τ_{gas} can be obtained from the analysis of DOAS signals. After removing contributions of the gas absorption and Rayleigh scattering, we can determine the aerosol optical thickness if the correlation factor k is known. The visibility at 550 nm, V, can be calculated from Mie extinction coefficient using the well known Koschmieder relationship:

$$V = 3.912 / \alpha_a. \qquad (5)$$

Here we assume that the visibility of $V = 50$ km represents a typical condition for a relatively clear atmosphere. Since in the Chiba case, the distance of the DOAS measurement is 5.5 km, V=50 km leads to the aerosol optical thickness of $\tau_a = 0.43$. This value is used to empirically determine the system constant k. It is noted that when the value of V is changed by $\pm 10\%$, for instance, the resulting value of k changes only slightly (k=9.0$\pm$0.2).

The basic principle of the aerosol retrieval was described in our previous paper (Yoshii et al., 2003). The following dependence on the wavelength λ is assumed for the aerosol optical thickness $\tau_a(\lambda)$:

$$\tau_a(\lambda) = B(\frac{\lambda}{550})^{-A} \qquad (6)$$

Here, constants A (Angstrom exponent) and B (turbidity constant, i.e. the aerosol extinction coefficient corresponding to the wavelength of 550 nm) are to be determined by fitting this expression to the optical thickness derived from the DOAS spectra. The aerosol extinction coefficient at 550 nm is calculated by the relationship of α_a (550) =B/L, and the mass extinction efficiency (MEE) is obtained by

$$MEE = \alpha_a(550)/\rho, \qquad (7)$$

where ρ is the SPM concentration measured by the ground sampling (with a β-ray detector).

3. Results and discussion

3.1 Concentration of NO_2 from DOAS and ground point measurements

In the Kyoto measurement, we measured O_3, SO_2, NO_2, and aerosols. The Chiba measurement, on the other hand, is used for the retrieval of NO_2, H_2O, and aerosols. Figure 2(a) shows the NO_2, SO_2, O_3 data observed for one day in Kyoto, and Fig. 2 (b) shows H_2O and absolute humidity observed for one month in Chiba. From these figures, reasonable correlations are found between the result of the long-path DOAS measurement and the data from ground stations below the optical paths.
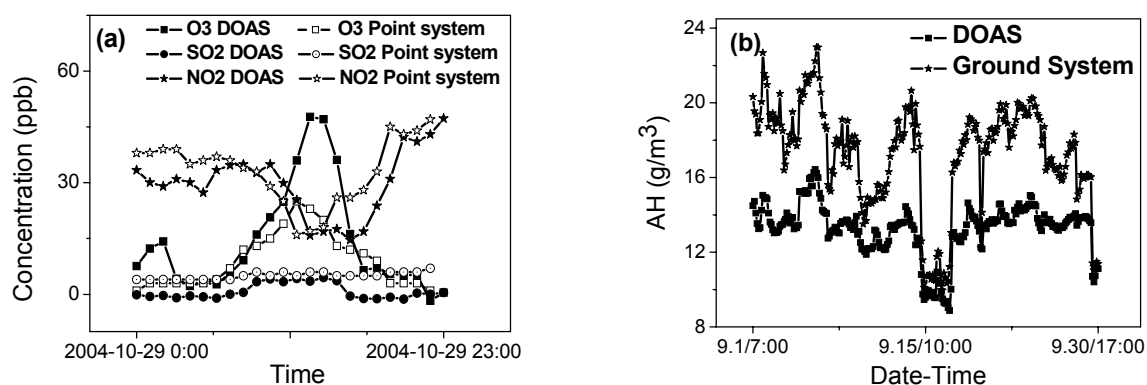
Fig. 2. (a) One day change of NO_2, SO_2 and O_3 concentration observed in the Kyoto measurement on 29 October 2004. (b) One month change of absolute humidity measured by the DOAS and ground systems in Chiba.
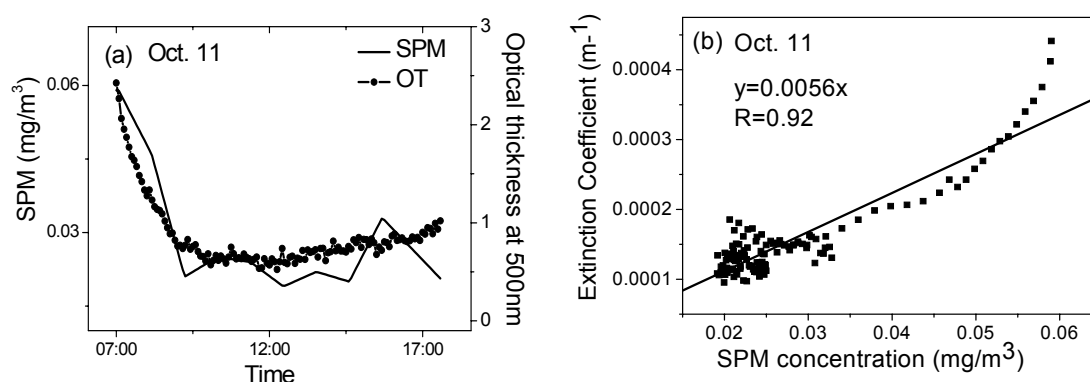
3.2 Aerosol retrieval

Fig. 3. (a) Optical thickness at 550 nm data and SPM data on 15 December 2004, and (b) the correlation plot to derive the MEE value (5.6 m^2g^{-1}).

Here we describe the aerosol retrieval from the Chiba data. Figure 3(a) shows the correlation between the SPM concentration and aerosol optical thickness at 550 nm and Fig. 3(b) the correlation between the SPM concentration and aerosol extinction coefficient in a day (daytime). For both cases, good correlations are evident, and the MEE value is calculated to be about 5.6 m^2g^{-1}. The variations of MEE and the

Angstrom exponent during one month are shown in Fig. 4, in which a data point represents an average of the diurnal data. Also a good correlation can be found between these two parameters. The Angstrom exponent is a good measure of the particle size, high and low values suggesting the dominance of fine and coarse particles, respectively. This result indicates well that the particle size is influential to the value of MEE, as recently proposed as the size effect on the MEE value.[4]
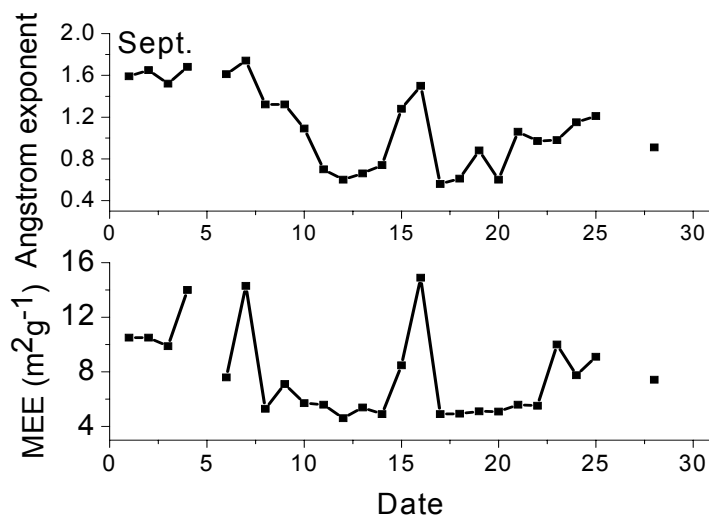

Fig. 4 One month variation of the MEE and Angstrom exponent, leading to a correlation coefficient of about 0.83. The average value for the MEE data is about 7.6 m^2g^{-1} and that for the Angstrom exponent is 1.1.

4. Conclusion

We have applied the pulsed DOAS technique to the measurement of NO_2, SO_2, O_3, H_2O and aerosol particles. Through the Kyoto and Chiba campaigns, reasonable correlations have been found between the long-path and ground-based observations of the NO_2, SO_2, O_3 and H_2O concentrations. For aerosol retrieval, the optical thickness at 550 nm is correlated with the concentration of ground-measured suspended particulate matter (SPM), also leading to a good correlation between the DOAS and SPM data. This correlation makes it possible to analyze the mass extinction efficiency (MEE) of aerosol particles in the lower troposphere. It is found that the monthly average value of MEE in Chiba (September 2004) is about 7.6 m^2g^{-1}. This relatively high value of MEE suggests the dominance of fine aerosols, though additional effect of the humidity should also be considered.

Organization for Small & Medium Enterprises and Regional Innovation, Japan.

References

1) J. Stutz, U. Platt, Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares method. Appl. Opt. 35, 6041–6053 (1996).
2) H. Edner, P. Ragnarson, S. Spannare, S. Svanberg, Differential optical absorption spectroscopy (DOAS) system for urban atmospheric pollution monitoring. Appl. Opt. 32, 327–333 (1993).
3) Y. Yoshii, H. Kuze, N. Takeuchi, Long-path measurement of atmospheric NO_2 with an obstruction flashlight and a charge-coupled-device spectrometer, Appl.Opt.42, 4362-4368 (2003).
4) N. Lagrosas, H. Kuze, N. Takeuchi, S. Fukagawa, G. Bagtasa, Y. Yoshii, S. Naito, M. Yabuki, Correlation study between suspended particulate matter and portable automated lidar data, Aerosol Science, in press (2005).