S5-3 Dual-DIAL Measurements of Vertical Concentration Profiles of ppb-order Atmospheric SO_2

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1. Introduction

Long-range transport models to estimate sulfur deposition in Japan and East Asia have recently been developed [1,2]. In order to validate these transport models, vertical concentration profiles of approximately 300-m range resolution and 0.5-ppb concentration resolution for sulfur compounds such as SO_2 are considered necessary. These profiles can be measured by *in situ* sampling using aircraft, or more conveniently and economically by a ground-based differential absorption lidar (DIAL).

Localized, relatively high concentrations of SO_2, such as smokestack exhaust or volcanic emission have been measured by DIAL in the past [3-5]. In these cases, the SO_2 concentrations were in the order of 100 ppb with range resolution in the order of 10 m. Range-resolved DIAL measurements of ambient SO_2, whose concentration is in the order of several ppb, have been very few in number. The sensitivity limit results in part from the presence of interference species such as O_3 and aerosol, whose influence cannot be removed in ordinary DIAL.

In order to improve the resolution of SO_2 measurement, we proposed a multiwavelength method consisting of two DIAL pairs (dual-DIAL) [6] and developed a multiwavelength DIAL (MDIAL) system for precise measurement by dual-DIAL or multispecies measurements of atmospheric trace substances[7]. In this paper, we report the results of simultaneous measurements of atmospheric SO_2 and O_3, and dual-DIAL measurement of SO_2 using the MDIAL system.

2. Theory of dual-DIAL SO_2 measurement

In DIAL measurement including multiwavelength cases, the range-resolved concentration profile $n(R)$ of the measurement target species can be obtained from the following equation:

$$n = \frac{1}{2\Delta R \sigma'_0} \sum_{i=1}^{m} e_i \ln\left[\frac{N(R,\lambda_i)}{N(R+\Delta R,\lambda_i)}\right] - \frac{\alpha'_x}{\sigma'_0}. \qquad (1)$$

Here $N(R,\lambda_i)$ is the number of backscattered photons received from ranges between R and $R+\Delta R$, λ_i is the illumination and detection wavelength, $e_i = +1$ for large values of $\sigma_0(\lambda_i)$, corresponding to the *on* wavelengths at which the absorption by the measurement target species is large, $e_i = -1$ for small values thereof, corresponding to the *off* wavelengths at which the absorption is small, and

$$\sigma'_0 = \sum_{i=1}^{m} e_i \sigma_0(\lambda_i), \quad \alpha'_x = \sum_{i=1}^{m} e_i \alpha_x(\lambda_i), \qquad (2)$$

where $\sigma_0(\lambda_i)$ is the absorption cross section of the measurement target species, and $\alpha_x(\lambda_i)$ is the extinction coefficient due to other molecules and particles. Considering the multiwavelength case to be a combination of DIAL pairs, each consisting of an *on* and an *off* wavelength, m is an even integer and $\sum_{i=1}^{m} e_i = 0$. In order to obtain precise concentration of the target species, the assumption $n\sigma'_0 >> \alpha'_x$ must hold. However, in conventional 2-wavelength DIAL measurement of atmospheric SO_2 whose concentration is a few ppb, the assumption does not hold due to the interference of O_3 and aerosols. The condition $n\sigma'_0 >> \alpha'_\lambda$ can be easily met in a multiwavelength case, as one has the freedom to select the wavelength of the DIAL pairs in such a way that α'_λ is minimized.

3. Simultaneous measurements of atmospheric SO_2 and O_3 concentrations

We measured the concentration of atmospheric SO_2 by simultaneous 2-wavelength DIAL measurements of SO_2 and O_3 using the MDIAL system. The details of the MDIAL system is described in another paper in this conference [7]. The MDIAL transmitter consists of two dye lasers, each is capable of emitting two wavelengths (λ_a, λ_b) on alternate pulses. One dye laser (dye laser 1) was used for SO_2 measurements and the other (dye laser 2) was used for O_3 measurements. In the case of SO_2 measurements, λ_a was fixed at 299.35 nm, and λ_b was set at various wavelengths such as 299.35 nm, 299.75 nm, 299.90 nm, 300.05 nm, 300.55 nm and 301.10 nm. The null profile was obtained for $\lambda_a = \lambda_b =$ 299.35 nm and DIAL profiles were obtained for each pair (λ_a, λ_b) for which $\lambda_a \neq \lambda_b$. λ_b was first scanned from 299.35 nm to 301.10 nm and then scanned in reverse so that two measurements were made at each value of λ_b, except for λ_b = 301.10 nm for which one measurement was made. As a result, a total of eleven measurements were made. Each measurement consisted of a sequence of five profiles, each with 1 minute integration time. Absorption cross sections of SO_2 and O_3 are shown in Fig. 1, and the wavelengths used in these measurements are indicated by broken lines. Vertical profiles of O_3 concentration were measured within 30 minutes before and after the series of SO_2 measurements. Laser energies used in the SO_2 and O_3 measurements were 17 ~ 19 mJ and 12 ~ 17 mJ, respectively. These measurements were performed at 6: 00 ~ 9: 22 on February 14, 1999 in Komae city.

The two O_3 measurements performed before and after the SO_2 measurements showed the same profiles, and an O_3 concentration of 1.27×10^{18} molecule/m^3 at 3300 m altitude was obtained. Figure 2 shows the results of SO_2 concentration measurements at 3300 m altitude with range resolution of 300 m. Figure 2 (a) shows the S-values, which are defined as

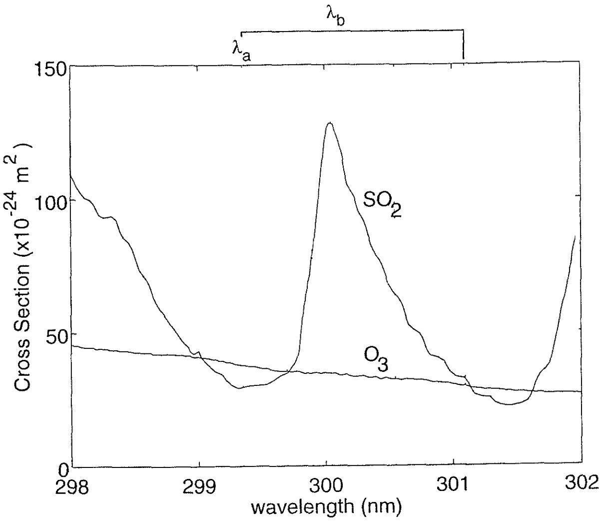

Fig. 1. Absorption cross section of SO_2 and O_3, and wavelengths used in the SO_2 measurement.

$$S \equiv \sum_{i=1}^{m} e_i \ln\left[\frac{N(R,\lambda_i)}{N(R+\Delta R,\lambda_i)}\right] = 2\Delta R(\sigma'_0 n + \alpha'_\lambda) \quad . (3)$$

Here λ_a and λ_b correspond to the *off* and *on* wavelengths, respectively. In each graph, the circles correspond to average S-values for five profiles, each with 1 minute integration time, as λ_b was scanned from 299.35 nm to 301.10 nm. The ×'s correspond to those when λ_b was scanned in reverse, and are plotted with 0.01 nm shift for clarity. The error bars correspond to the standard deviation of the five profiles. Figure 2 (b) shows the S-value versus λ_b after subtracting the O_3 contribution calculated from the measured O_3 concentration. Figure 2 (a) shows that the S-value becomes negative with increasing λ_b due to the O_3 contribution, and (b) shows that the S-value at each λ_b becomes zero after subtracting the O_3 contribution. Although SO_2 concentration is too low to be measured, it was shown experimentally that O_3 caused measurement error in SO_2 measurements.

4. Dual-DIAL measurements of vertical SO_2 concentration profiles

Three-wavelength dual-DIAL measurements of vertical SO_2 concentration profiles were performed. Wavelengths used in the measurements are shown in Fig. 3 along with the absorption cross sections of SO_2 and O_3. The measurements used two different DIAL pairs, DIAL 1 and DIAL 2. DIAL 1 used 300.05 nm and

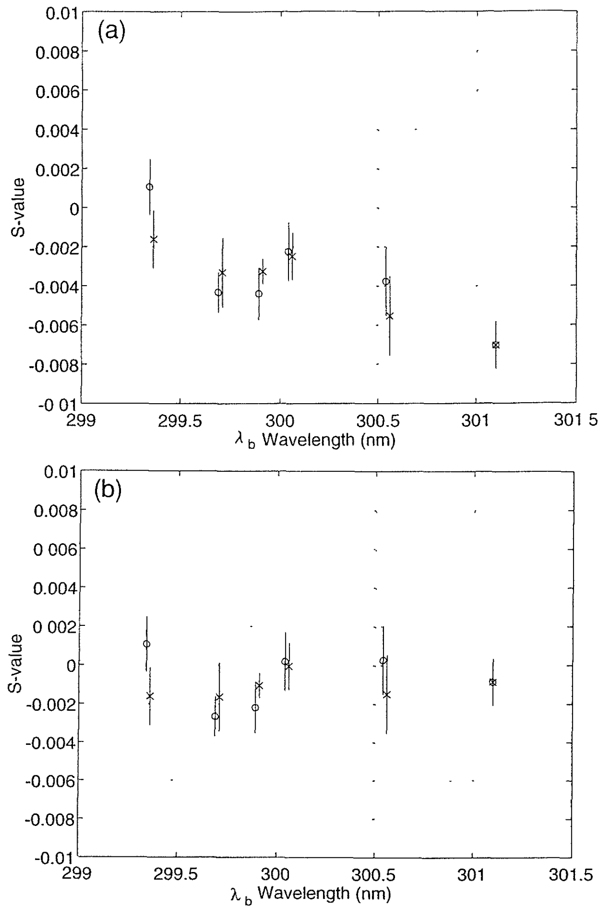

Fig. 2. Measurement results of SO_2 concentration at 3300 m altitude. λ_a and λ_b are treated as *off* and *on* wavelengths, respectively. (a) S-value versus λ_b. (b) S-value versus λ_b after subtracting O_3 contribution calculated from the O_3 measurement data.

○: Measurements when λ_b was scanned from 299.35 nm to 301.10 nm.

×: Measurements when λ_b was scanned from 301.10 nm to 299.35 nm.

299.35 nm as the *on* and *off* wavelengths, respectively, while DIAL 2 used 298.65 nm and 299.35 nm as the *on* and *off* wavelengths, respectively. Two measurements, A and B, were performed. In measurement A, dye laser 1 and 2 were used for DIAL 2 and DIAL 1, respectively, while in measurement B the dye lasers used for each DIAL pair were reversed, for checking instrumental systematic errors. Measurements A and B consisted of a sequence of 6 and 3 profiles, respectively, each with 5 minutes integration time. These measurements were performed at 12: 19 ~ 13: 45 on June 8, 1999 in Komae city.

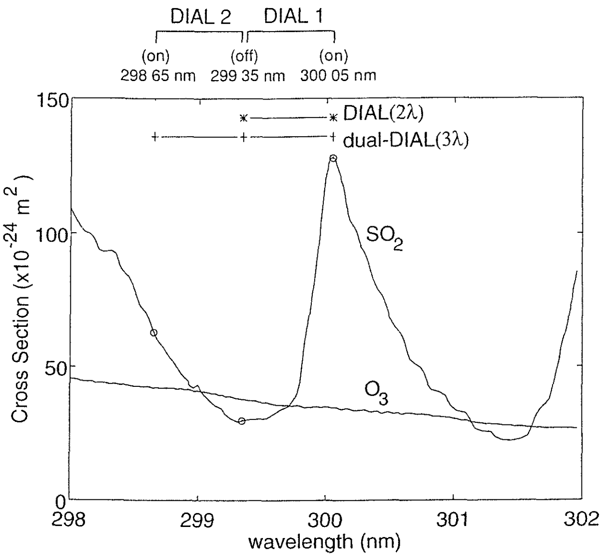

Fig. 3. Wavelengths used in 3-wavelength dual DIAL, and absorption cross section of SO_2 and O_3.

Figure 4 shows vertical SO_2 concentration profiles measured by 3-wavelength dual-DIAL. Each plot and error bar shows the averaged value and standard deviation, respectively, for the 6 or 3 profiles. Since measurement A and B showed the same results, the experimental systematic error is quite low. SO_2 concentrations obtained only with DIAL 1 or DIAL 2 show that the error was caused mainly by O_3. The differential absorption cross section in DIAL 1 for SO_2 is 3 times larger than that of DIAL 2. Therefore, the influence of O_3 is larger in DIAL 2 than in DIAL 1. The errors due to O_3 and aerosols were successfully reduced in 3-wavelength dual-DIAL, and an average SO_2 concentration for 2400 ~ 3000 m altitude of 1.2 ppb, with respect to atmospheric density on the ground (1976 U.S. standard atmosphere), was obtained.

Measurement errors for SO_2 concentration measurement for altitude 2400 ~ 3000 m were calculated and are shown in Table 1. Errors due to inaccuracy of differential absorption cross section were estimated from published values [8,9] and the wavelength resettability of the dye lasers. Statistical errors were estimated from standard deviations of the sequence of 6 or 3 measurements. Errors due to absorption by other molecules and particles were estimated from the results of DIAL 1 on the assumption that the measured concentration was interfered only by O_3 of which concentration was estimated to be about 70 ppb. Null errors which show the instrumental error were estimated

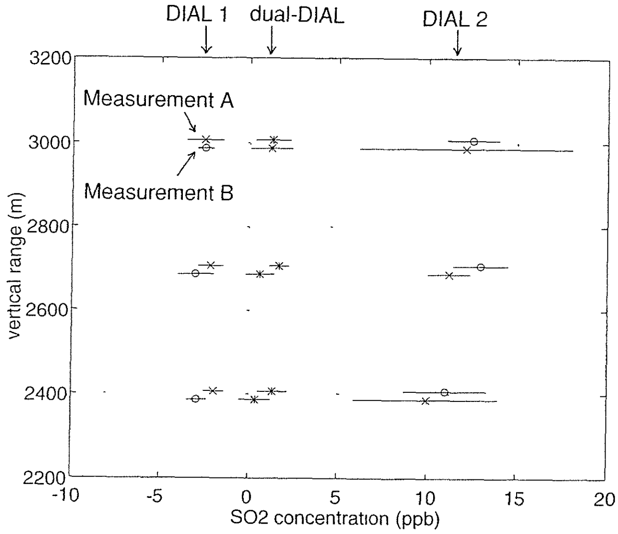

Fig. 4. Vertical SO_2 concentration profiles measured by 3-wavelength dual-DIAL. Profiles measured by only DIAL 1 or DIAL 2 are also indicated.
○: DIAL measurements using dye laser 1.
×: DIAL measurements using dye laser 2.
*: dual-DIAL measurements using dye laser 1 and 2.

Table 1. Averaged errors of SO_2 concentration measurement for altitude 2400 m ~ 3000 m. (1999/6/8)

Factors	Errors (ppb)	
	DIAL 1 (2-wavelength)	Dual-DIAL (3-wavelength)
Inaccuracy of differential absorption cross section	<0.2	<0.2
Statistical errors	0.71	0.84
Absorption by other molecules and particles	<2.5	<0.56
Null errors	0.52	0.47
Total	<2.7	<1.1

from the average deviation from zero of null profiles at 299.35 nm measured just before the DIAL measurements for altitude 2400 ~ 3000 m. As a result, the total SO_2 measurement error of 3-wavelength dual-DIAL was obtained by adding the squares of these four errors and taking the square root, and estimated to be below 1.1 ppb. Although the error in DIAL 1 is below 3 ppb, the O_3 concentration is variable so this value does not always hold.

5. Conclusions

Simultaneous measurements of atmospheric SO_2 and O_3 and dual-DIAL measurement of SO_2 were performed using a multiwavelength DIAL (MDIAL) system. Simultaneous measurements of atmospheric SO_2 and O_3 showed that O_3 caused error in SO_2 measurements. 3-wavelength dual-DIAL measurement of atmospheric SO_2 was performed and showed that the error due to O_3 and aerosols can be reduced. A SO_2 concentration of 1.2 ppb averaged for altitude 2400 ~ 3000 m with error <1.1 ppb was obtained from dual-DIAL measurements. This system can be used for measurement of SO_2 transport whose concentration is of ppb order.

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