Differential optical absorption spectroscopy of atmospheric NO₂
with a pulsed, white flashlight

Yotsumi Yoshii, Hiroaki Kuze, and Nobuo Takeuchi
Center for Environmental Remote Sensing, Chiba University
1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan
+81-43-290-3852, yyoshii@graduate.chiba-u.jp

Abstract -- We propose and demonstrate a novel method of differential optical absorption spectroscopy (DOAS), in which an obstruction flashlight equipped on a tall stack is exploited for monitoring concentration of atmospheric NO₂. This pulsed DOAS measurement also brings about information on the aerosol optical thickness through the horizontal atmospheres.

INTRODUCTION

In the monitoring of atmospheric pollutant species such as NO₂, NO, SO₂, and O₃, conventional point measurements at ground sampling sites lead to concentrations for local environments. Differential optical absorption spectroscopy (DOAS) in the visible and near UV region provides additional information of regional concentrations measured over several hundred meters to several kilometers.¹,²) In the conventional long-path DOAS method, a continuously emitting light source is employed, and the source (or occasionally a retroreflector) is placed at a certain distance from the observation site.

Here we report a novel DOAS spectrometer based on a flashlight source. After transmission in the atmosphere, the spectral analysis is easily attained by use of a commercially available CCD spectrometer, which enables us to measure the spectrum of the pulsed signal. The motivation of this work is to utilize white flashlights (obstruction lights) installed on tall constructions such as towers, bridges, and stacks, for the DOAS measurement. Such white flashlights are widely used for the safety of aviation traffic in many countries. In Japan, it is mandatory for tall constructions to operate highly illuminant white flashlights during the daytime that are detectable in every direction from several kilometers away. Normally, Xenon lamps are used for this purpose, giving a strobe emission in every 1.5 s. Compared with the conventional DOAS measurements, the present scheme has an inherent advantage that if one can find an appropriate obstruction light, as is the case in the city or industrial areas, the DOAS measurement can be carried out without bothering to prepare light sources. Other advantages are as follows. First, the background from the sky radiation is easily subtracted, since the spectra with and without the strobe flash are straightforwardly distinguished from the difference in the observed intensity. Second, simultaneous observation of several trace gas species is feasible, if the relevant spectral features fall within the considered wavelength interval of the lamp and the CCD. Third, when the spectral intensity of the flashlight is known at the strobe site, the transmitted spectra provide information on the aerosol extinction along the optical path.

EXPERIMENT

An astronomical telescope (Meade DS-115, with an aperture diameter of 115 mm and a focal length of 910 mm) is used to focus the image of a point light source located at a far distance. The image is formed near the eyepiece location, at which the entrance slit of a compact CCD spectrometer (Ocean Optics, USB2000) is placed. The CCD consists of 2048 elements and it is sensitive in a wavelength range of 200-800 nm, resulting in an average resolution of 0.3 nm/pixel. The CCD gate duration is set at 300 ms in the experiment. Between successive gating each spectral data is sent to a PC through the universal serial bus.

The detector setup is situated in our laboratory at an elevation level of 31 m. The telescope is placed on top of a standard tripod and no particular consideration is given to the pointing stability of the system. Once the system is aligned properly, it can be operated for a few days without any readjustment. For the measurement, we make use of a Xenon strobe (Sanken, FX-7) as a light source installed at the top of a 130 m tall stack at a municipal incinerator, 5.5 km from our laboratory. All the lamps flash for about 0.5 ms in every 1.5 s (40 flashes a min, in accordance with the regulation) in a synchronous manner. The data from nearby ground stations (operated by the municipal environmental department and available through the Web) are compared with the
present result.

Since the gate of the CCD detector is opened for 300 ms, the flash event is observed once in every five data acquisitions. The discrimination of data with and without the flash event is automatically achieved by comparing the light intensity integrated over a wavelength region of 400-450 nm, which is used for the present NO2 detection. The spectral difference between the flash and no-flash events exhibits the net strobe intensity after the 5.5 km transmission in the urban atmosphere. A total of 500 events, including both the flash and no-flash cases, are averaged for about 2.5 min before calculating the net intensity (another 2.5 min is reserved for the PC data processing). The observed intensity is relatively stable for the no-flash events, since the average time span of 2.5 min is much shorter than the time scale of diurnal variation of the skylight. On the contrary, the intensity of the flash events scatters to some extent after the transmission distance of 5.5 km.

RETRIEVAL ALGORITHM

In DOAS analysis, usually a narrow spectral range is chosen and the technique of spectral matching is employed to derive the concentration of the molecular species under investigation. The rapidly varying part of the DOAS spectrum is extracted, and compared with the absorption cross-section data. For that purpose, the observed spectrum is first divided by the intermediary "reference" spectrum, observed under relatively clean air conditions. Then, an appropriately chosen, linear function of the wavelength is subtracted from the logarithm of the divided spectrum. Finally, the relevant concentration is determined by matching the peak-to-peak intensity variations between the resulting spectrum and the cross-section data.

Results of the present pulsed DOAS measurement can also be analyzed using a similar procedure. For the wavelength region, we choose a region of 400-450 nm, which is wider than the region of 430-450 nm usually employed for NO2 measurements.1) The reason for this choice is that by exploiting the wide spectral response of the spectrometer system, simultaneous measurement of the aerosol effect on the light transmission becomes feasible. The NO2 transmittance is expressed by means of the Lambert-Beer's law as

\[ T_{\text{NO2}}(\lambda) = \exp[-\sigma(\lambda)Nl] \]  

(1)

where \( \sigma(\lambda) \), \( N \), and \( l \) stand for the absorption cross-section of NO2, number density, and optical path length, respectively. The procedure mentioned above ensures the retrieval without the knowledge about the source spectrum.

Here we describe another algorithm developed for the retrieval of both the NO2 concentration and aerosol optical thickness. After the background subtraction, the observed light intensity, \( I_{\text{obs}}(\lambda) \), can be expressed as

\[ I_{\text{obs}}(\lambda) = k I_0(\lambda) T_m(\lambda) T_a(\lambda) T_{\text{NO2}}(\lambda) \]  

(2)

Here, \( k \) is an empirically determined coefficient, \( I_0(\lambda) \) the spectrum of the light source observed at a location very close to the light source, \( T_m(\lambda) \) the transmittance of air molecules (Rayleigh scattering), \( T_a(\lambda) \) the transmittance of aerosol particles (Mie scattering), and \( T_{\text{NO2}}(\lambda) \) the transmittance representing the NO2 absorption.

In the present algorithm involving both the NO2 and aerosol retrieval, first we correct the observed spectrum \( I_{\text{obs}}(\lambda) \) for the first three factors on the right-hand side of Eq. (2):

\[ I'_{\text{obs}}(\lambda) = \frac{I_{\text{obs}}(\lambda)}{k I_0(\lambda) T_m(\lambda)} = T_a(\lambda) T_{\text{NO2}}(\lambda) \]  

(3)

Moreover, if it is assumed that the aerosol optical thickness exhibits wavelength dependence as given by the Angstrom exponent, we obtain

\[ -\ln I'_{\text{obs}}(\lambda) = B\lambda^{-d} + \sigma(\lambda)C \]  

(4)

Removing the slowly varying contribution from Eq. (4), and applying the spectral matching to the rapidly varying part with the laboratory cross-section data, we obtain the value of \( C \). Then, substituting \( C \) into Eq. (4) leads to the value of \( B\lambda^{-d} \). In the actual data analysis, this process has to be operated in an iterative way.
RESULTS

Simultaneous measurement of NO$_2$ and aerosol

An example of the simultaneous retrieval of NO$_2$ and aerosol amount is shown in Fig. 1, where values of the optical thickness for the three quantities in Eq. (4), $-\ln I_{\text{obs}}^*(\lambda)$, $B\lambda^{-4}$, and $\sigma(\lambda)C$ are plotted (June 19, 2002 16:55-16:58 JST). The relevant parameters, i.e. $A$, $B$, $C$ in Eq. (4) with $k$ in Eq. (3), are optimized in an iteration procedure, assuming $A=1$ in the initial condition. Note that in the present analysis, we included $k$ in the iteration process, though this parameter could also be estimated empirically from the intensity fluctuation measurement.

Diurnal variation of NO$_2$ concentration

An example of the diurnal change of NO$_2$ concentration is shown in Fig. 2, from the data observed on July 27, 2002. A reasonable correlation is found between the result of the long-path measurement (solid line) and the data from a ground station below the optical path (squares).

Sensitivity of the present method

As explained above, a wavelength range of 400-450 nm has been chosen in the present analysis. Relatively large values of the absorption cross-section and the Xenon lamp intensity in this spectral range contribute to attaining good accuracy. The advantage of a wider range is that it enables one to measure not only the NO$_2$ concentration but also the wavelength dependence of aerosol optical thickness. In the simultaneous retrieval of NO$_2$ and aerosol, however, correlation among parameters ($A$, $B$, $C$, and $k$) often hinders reliable evaluation of the "Angstrom parameter" $A$, especially when this parameter is smaller than unity (weak wavelength dependence). In contrast, it is usually easy to determine the parameter $C$, since this is related to the rapidly varying component of the DOAS spectrum. Judging from the spectral matching features for spectra taken on relatively clean days, a detection limit of 1 ppb is estimated for the present scheme of the DOAS measurement.

CONCLUSIONS

We described a new DOAS detection method for measuring NO$_2$ using ubiquitous flashlight sources. Any types of blinking or rotating white lights (e.g. on tall buildings, bridges, lighthouses, etc.) can be used for this purpose. Owing to the wide spectrum of the emitted light, this method can easily be extended to measure several molecular species simultaneously. It has also been pointed out that the DOAS method provides the possibility of measuring the aerosol optical thickness along the optical path.

REFERENCES