Measurements of NO_2 mixing ratios with topographic target light scattering-differential optical absorption spectroscopy system and comparisons to point monitoring technique*

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A topographic target light scattering-differential optical absorption spectroscopy (ToTaL-DOAS) system is developed for measuring average concentrations along a known optical path and studying surface-near distributions of atmospheric trace gases. The telescope of the ToTaL-DOAS system points to targets which are located at known distances from the measurement device and illuminated by sunlight. Average concentrations with high spatial resolution can be retrieved by receiving sunlight reflected from the targets. A filed measurement of NO_2 concentration is performed with the ToTaL-DOAS system in Shijiazhuang in the autumn of 2011. The measurement data are compared with concentrations measured by the point monitoring technique at the same site. The results show that the ToTaL-DOAS system is sensitive to the variation of NO_2 concentrations along the optical path.

Keywords: atmospheric optics, target light scattering-differential optical absorption spectroscopy (ToTaL-DOAS), atmospheric trace gas, averaging mixing ratio

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1. Introduction

Optical remote sensing technology, with ultraviolet sunlight as the light source, used in an inversion of trace gas concentrations based on the principle of differential absorption spectroscopy, is called passive differential optical absorption spectroscopy.[1] In recent years, developments of passive DOAS include passive multi-axis DOAS,[2,3] direct sunlight DOAS,[4] hyperspectral imaging DOAS,[5] mobile DOAS,[6] and airborne DOAS. They are extensively used to monitor the air pollution of the troposphere, stratosphere, and source emissions. High temporal and spatial resolution is desirable to describe trace gas dispersion.[7] The first requirement is achieved by several passive and active optical detection methods. The second requirement is also fulfilled by some optical techniques, such as LIDAR[8] and tomographic DOAS.[9] Unfortunately, the application is associated with high expenses and staff requirements. The target light scattering-differential optical absorption spectroscopy (ToTaL-DOAS) is a novel experimental procedure which can fulfil the requirements. It can be used to measure the surface-near horizontal and vertical distributions of atmospheric trace gases.[10] In addition, this method has advantages of simple structure, low cost, no artificial light source, and coverage of multiple species.[10]

The idea consists of pointing the receiving telescope to a target which is illuminated by sunlight and placed at a known distance from the measurement device. Scattered sunlight (diffuse or specular) reflected from a natural or artificial target is detected and then analyzed based on the DOAS. Therefore, the average

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mixing ratios of different trace gases like NO_2 and SO_2 along a line of sight (LOS) between the target and the instrument could be retrieved.

Frins' group first discussed the principles of the ToTaL-DOAS system and analytical methods in 2006.[10] The application of the ToTaL-DOAS system to large areas in order to obtain average mixing ratios of NO_2 in the path of 1.9 km and 2.3 km was reported by them. The group explored the spatial resolution of the ToTaL-DOAS system using three targets, which were 146, 196, and 280 m away from the instrument in 2008.[7] Muhammad *et al.* reported the results from a field measurement, and the comparison of daily averaging data between the ToTaL-DOAS system and Max-DOAS in Bremen University.[11]

In this paper, we not only discuss the measurement methods and the principles of inversion, but also introduce the home-made ToTaL-DOAS system. As a part of the instrument, the telescope has a small field of view (FOV) and a large aperture. A two-dimensional rotating platform is built for receiving the sunlight reflected from targets. Observations pointing at four targets are performed in the center of Shijiazhuang city, Hebei province. An NO_2analyzer (ECOTECH NO_2 analyzer) operated at the same site can obtain real-time mixing ratios of NO_2. The average mixing ratios of NO_2 derived from the ToTaL-DOAS are compared with the results from the NO_2analyzer. The comparisons show that the ToTaL-DOAS system can describe the variation of NO_2 average mixing ratios along an optical path.

2. Algorithm and method of ToTal-DOAS measurements

The ToTaL-DOAS method is based on passive DOAS technology.[1] The telescope of a ToTaL-DOAS system pointing to measurement targets illuminated by sunlight detects photons which have traversed two basic sections in the atmosphere: the distance between the top of atmosphere and the target (the first path), and the distance between the target and the instrument (the second path) (see Fig. 1). The $S_{\mathrm{CD},1}$ is the trace gas concentration integrated along the first path, and $S_{\mathrm{CD},2}$is the trace gas concentration integrated along the second path. Since we are only interested in $S_{\mathrm{CD},2}$, we have to remove $S_{\mathrm{CD},1}$ from the total signal S_{CD}. The key problem is how to select a reference spectrum which only contains $S_{\mathrm{CD},1}$. To measure the reference spectrum the telescope should be directed at a target (reference target) close to the telescope, which has similar properties as the measurement targets. We select white diffuse reflecting panel as the reference target. We introduce S_{ref} to denote the trace gas concentration integrated between the reference target and the top of the atmosphere. If the reference target and the measurement target are illuminated by sunlight in the same direction, S_{ref} is equal to $S_{\mathrm{CD},1}$in the ideal condition (see Fig. 2). The concentration $S_{\mathrm{CD},2}$ is retrieved as follows:

$$S_{\mathrm{CD}} - S_{\mathrm{ref}} = (S_{\mathrm{CD},1} + S_{\mathrm{CD},2}) - S_{\mathrm{ref}} = S_{\mathrm{CD},2} \quad (1)$$

In addition, the reflectance ratio of the target surface may be dependent on the wavelength. This phenomenon would cause some structures in target spectra, and these kinds of structures would vary slowly with the wavelength. This would increase the error from the DOAS fit. In order to minimize the error, firstly, the white measurement targets, which have similar properties as the reference target, should be selected. Secondly, processing the ratios of target spectra for white targets to reference spectra for white diffuse reflecting panel with high pass filtering, can effectively wipe off this effect. Finally, the DOAS fit window, in which there is the lowest fit residual structure, should be selected.

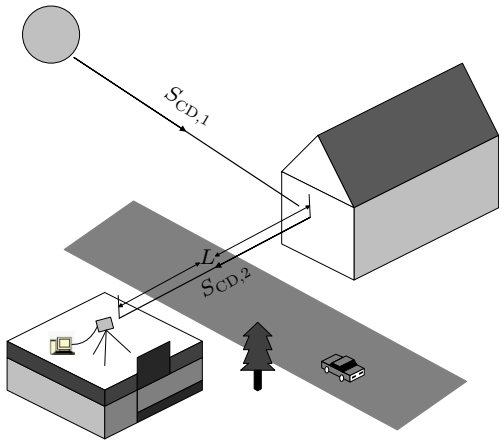


Fig. 1. Optical path of sunlight received by the Total-DOAS system.

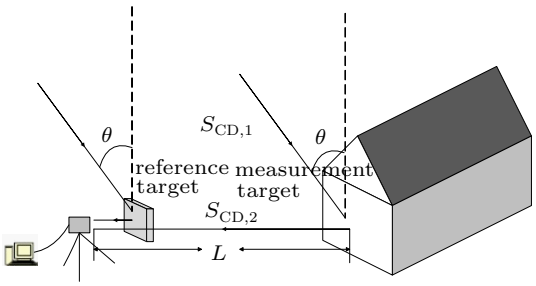


Fig. 2. Measurement of the reference spectrum in order to get $S_{\mathrm{CD},2}$.

The sunlight reflected by the target and scattered by molecules and aerosols between the target and the telescope goes into the LOS of the telescope. However, in clear sky without haze or fog, in the short distance condition, the sunlight scattered by molecules and aerosols is still a small part of the total signal.[10] Thus, the average concentration C_{av} can be given by

$$C_{\rm av} = \frac{S_{\rm CD,2}}{L}, \tag{2}$$

where L is the distance between the telescope and the measurement target, and can be measured by a laser rangefinder

If the time interval between the "reference spectrum" measurement and the "target spectrum" measurement is large, two problems would be caused. First, the optical path between the top of atmosphere and the target may change with the variation of the sun zenith angle. Second, the concentration of trace gases in the optical path may change. Consequently, the $S_{\rm ref}$ may be not equal to $S_{\rm CD,1}$. Therefore, it is necessary to minimize the time interval. The measurement results would be more precise at noon because the rate of the optical path changing with the variation of the solar zenith angle is lower. In addition, for measurements under cloud cover, multiple scattering may enlarge the optical path.[12] The increment would change with time. Based on the above analysis, measurements should be performed at noon in a clear sky. In this way, the difference between $S_{\rm ref}$ and $S_{\rm CD,1}$ can be minimized.

3. ToTaL-DOAS measurements

3.1. Instrument and site description

Figure 3 shows the schematic diagram of the setup of the ToTaL-DOAS system. It consists of a small commercial temperature controlled fibre-optic spectrometer with a spectral resolution of 0.5 nm and a spectral range from 294–415 nm. To reduce dark current the detector is cooled to a stabilized temperature of −20 °C. Light is coupled into the spectrometer through a reflecting telescope and a quartz fibre bundle. The FOV is about 0.2. The instrument is mounted on a tripod and can be pointed to different targets. It can also be oriented to different elevation angles (0°–90°) and different azimuth angles (0°–360°) to make sure that our instrument is pointed to a specific target. Its pointing precision is 0.015°. The entire system (spectrometer and stepper motor) is controlled by a laptop. Data acquisition is automatically performed by the computer and a column density of NO_2 is retrieved based on the DOAS algorithm

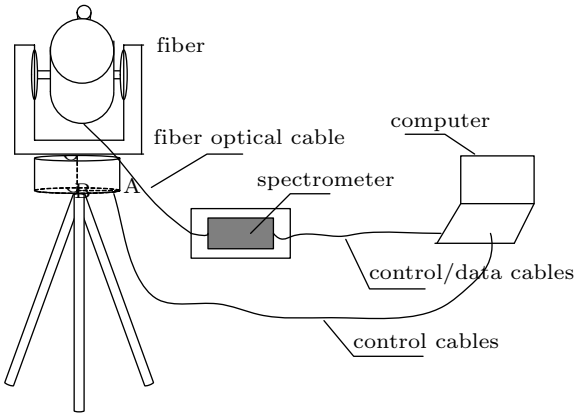


Fig. 3. Schematic diagram of the setup of the ToTaL-DOAS system.

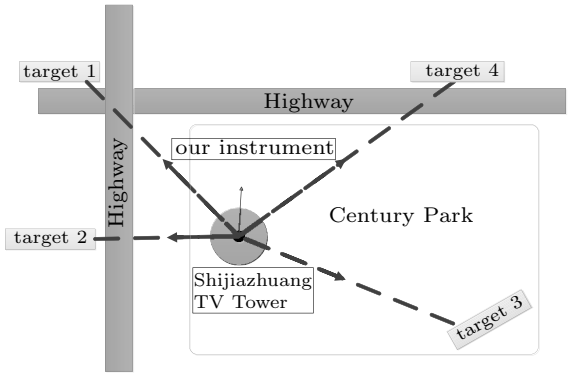


Fig. 4. Location of the Total-DOAS system. The black dashed arrow indicates the viewing direction of the telescope.

We located our instrument on a platform on Shijiazhuang TV tower, approximately 20 m above the ground (see Fig. 4). Almost four white buildings were selected as measurement targets. These buildings were located at distances of 418, 300, 510, and 550 m from our instrument. We call these buildings Target 1, Target 2, Target 3, and Target 4 respectively. Then the lines of sight about Targets 1, 2, and 3 cross over the highway, but most of the LOS about Target 3 is in Century park. All of the LOS about Target 4 is in the park. A white diffuse reflecting panel placed at a distance of about 0.5 m from the instrument was selected as the reference target. In order to minimize the time interval between the "reference spectrum" and the "target spectrum", the reference spectrum and target spectrum were measured alternately. In this way the time interval was limited to one minute. Directing the instrument at the 4 targets, we performed measurements in six days.

3.2. Spectral analysis

The inversion is based on the passive DOAS.[2] The spectral range for the evaluation of NO_2 is chosen between 345 nm and 383 nm. In the fit window, the residual from the DOAS fit would be minimal. It shows that the best signal-to-noise ratio of DOAS fit can be achieved. The NO_2 S_{CD} (the integrated concentration along the light path between Targets (1, 2, 3, and 4) and instrument) are derived from the spectral analysis using the software WINDOAS package.[13] The absorption cross sections of O_4,[14] NO_2[15] at 294 K, O_3[16] at 273 K, and the Ring spectrum,[17] which is obtained using the method proposed by Solomon *et al.*,[18] are fitted to the logarithm of the ratios between the target spectrum and reference spectrum.

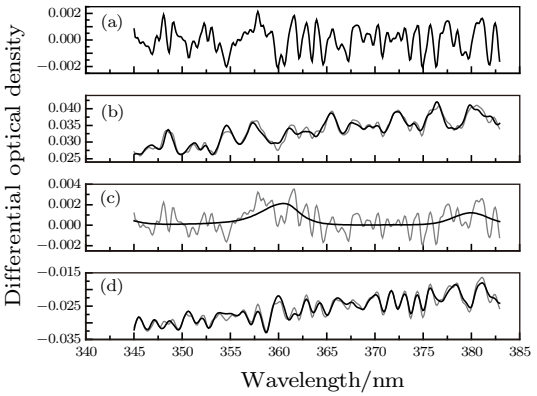


Fig. 5. Spectra of the DOAS fit measured at 12:45:19 on 14 November 2011, and the instrument is directed to Target 4. (a) A typical fitting residual structure. (b) NO_2 fit, (c) O_4 fit, and (d) ring fit. The black line is the fitted slant column optical depths for the measurement (the gray line) in (b), (c) and (d).

An example DOAS fit of a measured spectrum taken at 12:45 on 14 November 2011 is showed in Fig. 5 when the telescope was directed to Target 4. The column density of NO_2 is 6.17×10^{16} cm^{-2}, i.e., 24.56 ppm·m. The RMS of residual is 1.42×10^{-3}. The error of the spectral analysis from the DOAS fit is 2.5×10^{15} cm^{-2}. The distance between our instrument and Target 4 is 550 m. The average mixing ratio along the optical path, calculated based on Eq. 2, is 0.0447 ppm. Ignoring the measurement error of the distance, the retrieval error of NO_2 average mixing ratio is 0.0018 ppm.

4. Results and comparison with the point monitoring technique

In the following, figure 6 presents the 5-minute mean values of results from the ToTaL-DOAS system and from the point monitoring technique, respectively, during the whole field measurement. Although the variation trends of NO_2 mixing ratios measured by the two methods are similar, there is still some bias between their values. The bias results from the differences in the methods. First, average mixing ratios from the ToTaL-DOAS system are more susceptible to rapid transmission of pollution in the optical path. However, the point monitoring technique only reflects the mixing ratios at one point. Second, the S_{ref} may be somewhat different from $S_{CD,1}$, which would cause some error into $S_{CD,2}$.

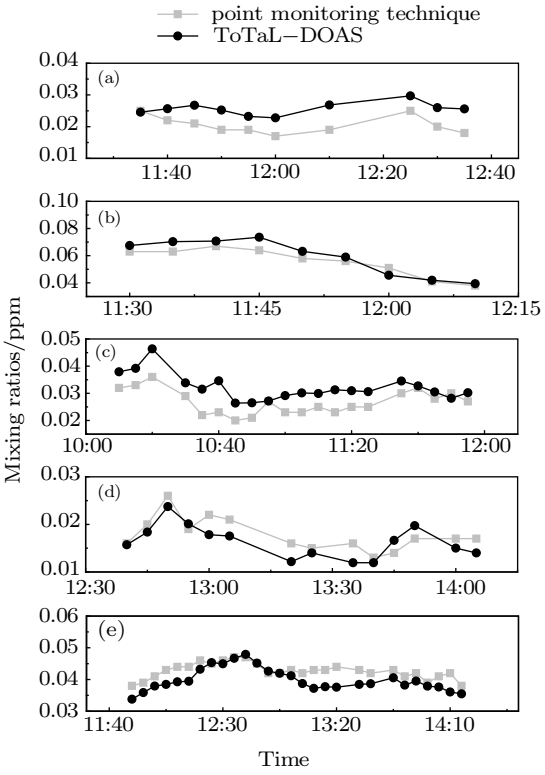


Fig. 6. Comparison between 5-min mean values of NO_2 average mixing ratios from the ToTaL-DOAS system and that from the point NO_2 analyzer during the whole filed measurement in 2011. (a) October 27 for target 1, (b) October 29 for target 2, (c) November 10 for target 2, (d) November 9 for target 3, and (e) November 14 for target 4.

The average mixing ratios measured by the ToTaL-DOAS system are affected by the source of NO_2. When our instrument is directed to Targets 1 and 2, the optical path crosses over the highway, which is the source of NO_2. It causes larger relative deviations (see Table 1). However, when our instrument is directed to Targets 3 and 4, the optical path crosses over Century Park, far away from the source of NO_2. Thus, the relative deviations are negative, indicating that the average mixing ratios measured by the ToTaL-DOAS system are smaller than results from the point NO_2 analyzer as estimated.

Table 1. Average values during daily operating time of the ToTaL-DOAS and the point monitoring instrument. Relative deviations indicate that the data of the ToTaL-DOAS are different from the data of the point NO_2 analyzer.

Target	Date	Average data of the ToTaL-DOAS system/ppm	Average data of the point monitoring technique/ppm	Relative deviation
Target 1	2011-10-27	0.0256	0.0205	+24.9%
Target 2	2011-10-29	0.0590	0.0557	+5.9%
Target 2	2011-11-10	0.0321	0.0267	+20.2%
Target 3	2011-11-9	0.0163	0.0178	−8.4%
Target 4	2011-11-14	0.0399	0.0427	−6.6%

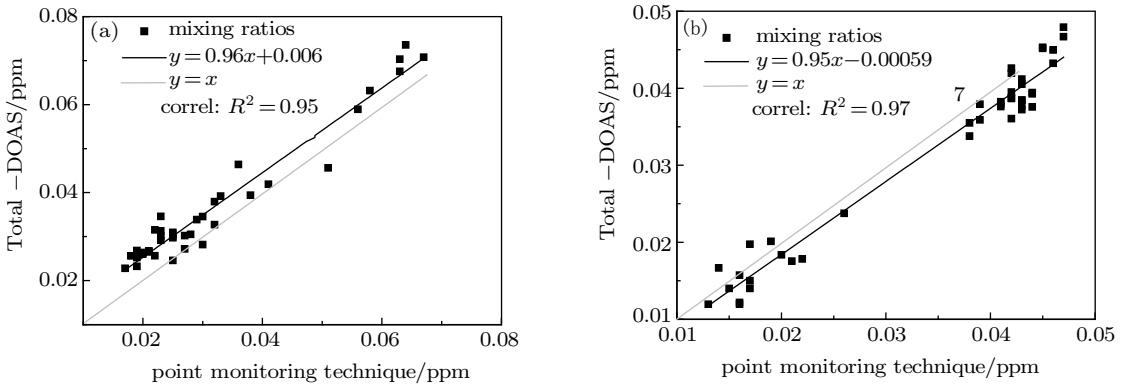


Fig. 7. Comparison of 5-minute mean values measured by the ToTaL-DOAS system and the point NO_2 analyzer. 39 data points about Targets 1 and 2 are analyzed in Fig. 7(a). 42 data points about Targets 3 and 4 are analyzed in Fig. 7(b). The black lines indicate the linear relation between the point monitoring technique and the ToTaL-DOAS system. The gray lines indicate the function $y = x$.

The level of agreement achieved between the ToTaL-DOAS system and the point monitoring technique is quantitatively summarized in correlation plots (see Fig. 7). Good agreement is found between them. When our instrument is directed to Targets 1 and 2, we obtain a correlation coefficient of 0.95, a slope of 0.96, and an intercept of 0.006 (see Fig. 7(a)). When our instrument is directed at Targets 3 and 4, an even better agreement is found, reaching a correlation coefficient of 0.97, a slope of 0.95, and an intercept of −0.00059 (see Fig. 7(b)). The intercept and correlation coefficient of the left fitting line are larger and smaller than that of the right fitting line, respectively. The phenomenon is due to the impact of the source of NO_2 from the highway.

In addition, these comparisons show that the ToTaL-DOAS method effectively reflects the variation of NO_2 mixing ratios along the optical path between the target and the instrument. Directing the instrument to different targets located in different directions can be used to study trace gas distributions in cities and places near a pollution source.

5. Conclusion

In summary, target spectra are measured by receiving the sunlight reflected from natural or artificial targets, and reference spectra are measured by receiving the sunlight reflected from a white diffuse reflecting panel placed close to the telescope. Based on the principle of DOAS, NO_2 average mixing ratios with high space resolution can be retrieved. Minimizing the time difference between the reference spectrum and the target spectra can improve the precision of results. The comparison between the Total-DOAS system and the point monitoring technique indicates that average mixing ratios obtained from the Total-DOAS system are sensitive to variation of NO_2 concentration along the optical path. In addition, since the radiance received by the instrument is sufficiently high, the acquisition time is less than 1 min, depending on the target. Thus, if automatic measurement by the ToTaL-DOAS system is accomplished, a considerable temporal resolution can be achieved. The method could be used to study the surface-near distribution of atmospheric trace gases. Furthermore, by choosing suitable targets well, it is feasible to apply tomographic techniques to retrieve trace gas distributions in two dimensions.

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