

Measurement of air pollutants by differential optical absorption spectroscopy using a Cassegrain telescope with fibers*

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A differential optical absorption spectroscopy (DOAS) method is presented and used for the air pollutant detection. The novel measurement frame employs a Cassegrain telescope and a combined fiber bundle. The emitting and receiving fibers are bundled together at one port. The common port is placed at the focus of the Cassegrain telescope. The total length of the prototype is reduced to about 1/2 of the traditional one. Air pollutants of SO₂, NO₂ and O₃ are monitored by the prototype, and the concentrations are inverted. Results show that the correlation coefficients are 0.9490, 0.9614 and 0.9301, respectively. And there is a good consistency between the measured results and the reference data.

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Spectroscopic techniques^[1-4] have been employed for environmental monitoring. Differential optical absorption spectroscopy (DOAS) is a continuous and multi-component spectroscopic measurement technique pioneered by Noxon and Platt in the 1970s^[5,6]. DOAS technique uses the narrow molecular absorption bands to identify the different gases and their absorption intensities to retrieve their concentrations according to the Beer-Lambert law^[7]. The major advantage of DOAS technique is the ability to measure the absolute trace-gas concentrations without disturbing their chemical behavior.

There are two common kinds of frames in DOAS. One is the divided structure^[8,9] in which an artificial light source is placed at one end of the optical path, and a DOAS spectrometer is placed at the other end. The other is the integral frame in which the light source and the receiver are placed at the same site by using retro-reflectors. This is realized by two coaxial Newton-type telescopes^[10] or a Newton-Cassegrain telescope^[11] sharing the same main mirror. Compared with the divided structure, it has the following advantages: a power supply is only necessary at one site, the optical path is pro-

longed, and multi-directional profiles can be obtained by different reflectors^[12]. However, it is difficult to adjust the light source position as well as the two mirrors. Recently, a simpler setup is presented^[13] in which the telescope setups are simplified to a main mirror and a combined fiber bundle. The length of the combined fiber bundle is approximately equal to the focal length of the main mirror.

In this paper, the aim is to set up a smaller instrument, which is simpler to adjust, easier to handle, and more portable. Air monitoring is implemented by the novel measurement frame based on a Newton-Cassegrain telescope system. It consists of a Cassegrain telescope and emitting and receiving fibers which are bundled at one port for light transmitting and receiving.

The schematic diagram of DOAS with Cassegrain telescope and combined fiber bundles is shown in Fig.1. Cassegrain telescope consists of a spherical mirror as the main mirror and an ellipsoidal mirror. The focal length of our telescope is 1500 mm. The added ellipsoidal mirror in our setup can reduce the length of the telescope to 300 mm, which is 4 times shorter than that of the telescope with the same focal length mentioned above in Ref.[13].

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As shown in the inset of Fig.1, the transmitting and receiving fibers are randomly arranged at the common terminal C. It is placed at the focus of Cassegrain telescope to obtain a well-collimated light beam. The diameters of the optical fiber bundle in transmitting terminal A and the receiving terminal B are both 3.5 mm, and that in the common terminal C is 5 mm.

The common port of the fiber bundle is arranged at the focus of the main mirror. The light from the xenon arc lamp is coupled into the emitting fiber, and then it is transmitted parallelly by the Cassegrain telescope. The light is reflected by the retro-reflector, and then reaches the receiving fiber and the detector.

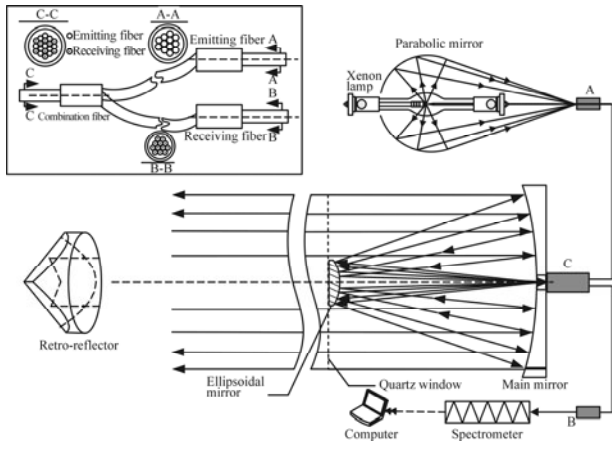


Fig.1 Schematic diagram of DOAS with Cassegrain telescope and combined fiber bundle (The inset shows the emitting and receiving fiber combined into a single bundle and the probe structure.)

DOAS technique is based on the Beer-Lambert's law expressed as

$$I(\lambda) = I_0(\lambda) \exp[-L\sigma(\lambda)c], \quad (1)$$

where $I_0(\lambda)$ denotes the incident intensity emitted by a suitable light source, $I(\lambda)$ is the radiation intensity after the light passes through a layer with thickness of L , c is the concentration of the species to be measured, and $\sigma(\lambda)$ is the absorption cross section at the wavelength λ .

In the atmosphere, the air molecules (Rayleigh scattering) and the atmosphere aerosols (Mie scattering) both contribute to the radiation extinction. Adding these contributions to Eq.(1) and solving it with respect to τ (optical density), we obtain

$$\tau(\lambda) = \ln \frac{I_0(\lambda)}{I(\lambda)} = L \left[\sum \sigma_i(\lambda)c_i + \varepsilon_R(\lambda) + \varepsilon_M(\lambda) \right], \quad (2)$$

where $\sigma_i(\lambda)$ and c_i denote the absorption cross section and the concentration of the i th species, and $\varepsilon_R(\lambda)$ and $\varepsilon_M(\lambda)$ are the Rayleigh and Mie extinction coefficients, respectively.

The absorption cross section of a given molecular species can be written as the sum of two terms

$$\sigma_i(\lambda) = \sigma_{i0}(\lambda) + \sigma'_i(\lambda), \quad (3)$$

where $\sigma_{i0}(\lambda)$ and $\sigma'_i(\lambda)$ denote the slow and rapid varia-

tions of the absorption cross section at the wavelength λ .

The extinction due to Rayleigh and Mie scattering can be assumed to be slowly varying with λ . The effect of the trace species is rapidly varied, and optical density $\tau(\lambda)$ can be divided into two components as

$$\tau(\lambda) = \ln \frac{I_0(\lambda)}{I(\lambda)} = \left[\sum \sigma'_i(\lambda)c_i \right] L + \left[\sum \sigma_{i0}(\lambda)c_i + \varepsilon_R(\lambda) + \varepsilon_M(\lambda) \right] L. \quad (4)$$

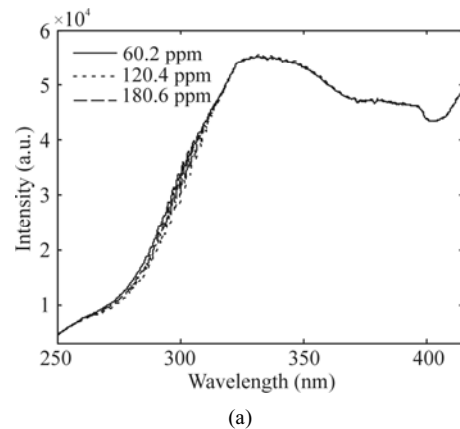
In order to enhance the stability of the light source, an improved DOAS method was put forward by Platt U^[3]. He defined the differential optical density as

$$\tau'(\lambda) = \ln \frac{I'_0(\lambda)}{I(\lambda)} = L \sum \sigma'_i(\lambda)c_i, \quad (5)$$

where $I'_0(\lambda)$ describes the slow variation of $I(\lambda)$. $\sigma(\lambda)$ of SO_2 and NO_2 , which were obtained by Bogumil et al^[14], are employed. $\sigma'_i(\lambda)$ is obtained by subtracting the slow variation from $\sigma(\lambda)$. $I'_0(\lambda)$ is calculated by Savitzky-Golay method. Thus the concentrations can be calculated from Eq.(5).

The calibration experiments are conducted with the system to test the measurement accuracy under laboratory conditions. The standard gases of SO_2 and NO_2 for 200.7 ppmv and 487.3 ppmv are used as samples, respectively. They are diluted with intervals of approximate 20.1 ppmv and 48.7 ppmv by gas separator using N_2 , as shown in Tab.1. The samples flow into a 300 mm-long gas cell. So the optical path is 600 mm-long with the retro-reflector. The caliber of the Cassegrain telescope is 150 mm, and its focal length is 1500 mm. The Cassegrain telescope folds the optical path through an ellipsoid mirror with diameter of 51 mm. Fig.2(a) shows the randomly selected absorption spectra of SO_2 samples with the concentrations of 60.2 ppmv, 120.4 ppmv and 180.6 ppmv. $\sigma'(\lambda)$ of SO_2 is calculated from Eq.(5), where c is a known parameter. We calculate the mean value of $\sigma'(\lambda)$ for the 3 samples, and then compare it with that given by Bogumil et al^[14]. The correlation coefficient is 0.9865 as shown in Fig.2(b).

The concentrations of SO_2 and NO_2 samples are calculated from Eq.(5). The calibration results are shown in Tab.1.



(a)

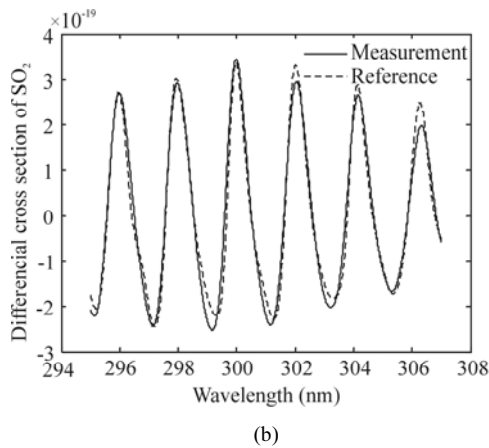


Fig.2 (a) The absorption spectra of SO₂ samples for calibration; (b) The comparison of $\sigma'(\lambda)$ between our result and that from Bogumil *et al.*^[14]

Tab.1 The comparison of the measurements and the references of SO₂ and NO₂ concentrations

SO ₂			NO ₂		
Measurement (ppmv)	Reference (ppmv)	Error (%)	Measurement (ppmv)	Reference (ppmv)	Error (%)
59.42	60.21	-1.31	146.78	146.19	0.40
80.86	80.28	0.72	196.86	194.92	1.00
101.29	100.35	0.94	243.37	243.65	0.11
120.97	120.42	0.46	290.99	292.38	0.47
141.39	140.41	0.70	338.00	341.11	0.91
162.55	160.56	1.24	386.83	389.84	0.77
181.05	180.63	0.23	433.40	438.57	1.18
202.57	200.70	0.93	493.01	487.30	1.17

Tab.1 shows that the errors for the tests of SO₂ and NO₂ are less than -1.31% and 1.18%, respectively. The high accuracy of the system is proved by the low measurement errors.

The air pollutions are measured with the prototype in Tianjin University. The distance between the retro-reflector and the system is 408 m. The optical path is 916 m. The absorption spectra are recorded once per minute. The average absorption spectra in every hour on February 29 are shown in Fig.3. It shows that the absorption peaks of O₃, SO₂ and NO₂ appear in the wavelength range of 250–270 nm, 295–307 nm and 404–414 nm, respectively.

We calculate the 24-hour average concentrations of SO₂, NO₂ and O₃. The reference data are obtained by the Tianjin Environmental Protection Bureau, China. The concentrations of NO₂ are determined by the chemiluminescence. SO₂ and O₃ concentrations are both measured by optical method. The results are shown in Fig.4.

Fig.4 shows that the variations of the measurement results from DOAS in 24-hour are substantially consistent with the reference data. The main peak of SO₂ appears at about 23:00. As we know, February is in the heating season. The main peak may be due to the coal-fired heating. And the heating pollutants can hardly disperse because of the inversion layer appearing during the night. The anti-correlation between O₃ and NO₂ concentrations caused by

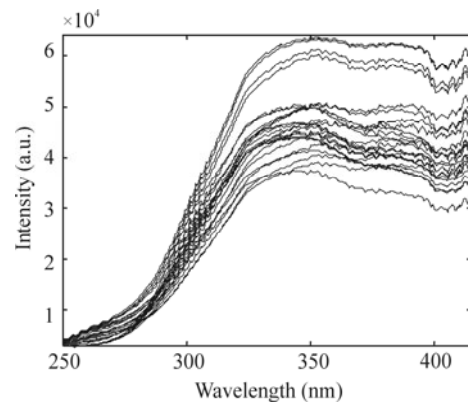
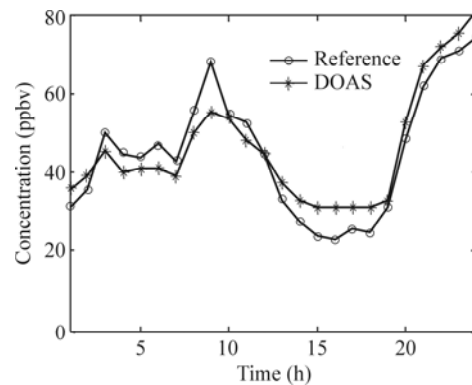
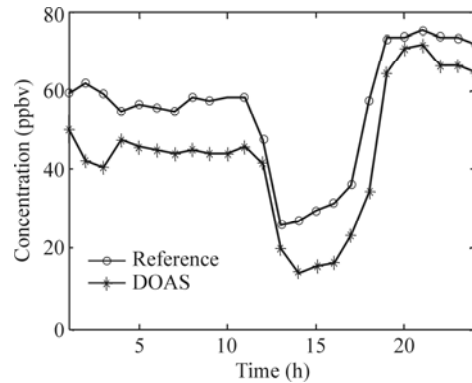


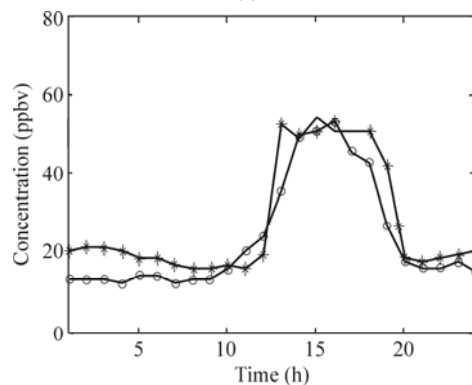
Fig.3 The average absorption spectra in every hour on February 29 in Tianjin University



(a) SO₂



(b) NO₂



(c) O₃

Fig.4 Comparisons between DOAS results and the reference data in 24 hours

atmospheric chemistry is clearly seen. The main peak of O_3 appears around 15:00, while the valley of NO_2 appears just at the same time. There are strong photochemical reactions when the sun radiation is intense. NO_2 is consumed, and O_3 is generated in the photochemical reactions^[11]. Fig.4 shows that the NO_2 reference concentrations are determined by the chemiluminescence. They are higher than those obtained by DOAS technique. The discrepancy should be primarily due to the chemical interference from nitrogen species photochemically produced in conjunction with O_3 ^[15].

Fig.5 shows the concentration correlation between the references and the DOAS. The correlation coefficients are 0.9490, 0.9614 and 0.9301 for SO_2 , NO_2 and O_3 ,

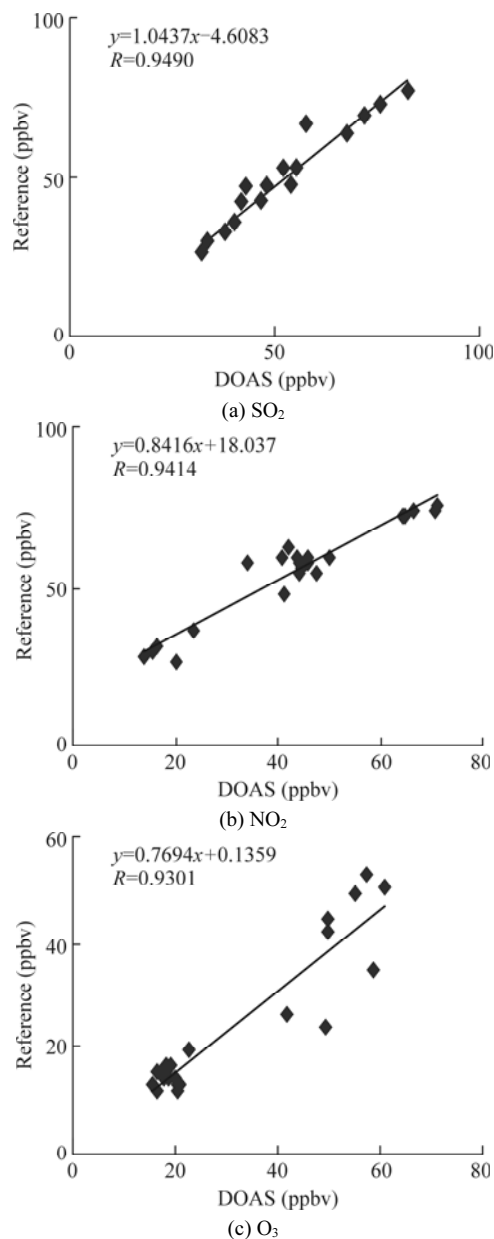


Fig.5 Concentration correlations between the references and the DOAS for three gases

respectively. The slopes of the linear fitting curves are 1.0437, 0.8416 and 0.7694. The root mean square (RMS) errors are 5.081 ppbv, 4.257 ppbv and 5.601 ppbv, respectively.

A novel measurement frame of DOAS is proposed to measure the air pollutants. It employs a Cassegrain telescope and a combined fiber bundle. Calibration results show that the errors for the tests of SO_2 and NO_2 are less than -1.31% and 1.18%, respectively. The comparison shows good consistency between measurement results and the reference data, and the correlation coefficients are 0.9490, 0.9614 and 0.9301 for SO_2 , NO_2 and O_3 , respectively. The proposed frame reduces the size, and is easier for adjustment. Meanwhile, it meets the requirements of online gas monitoring.

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