Temperature Compensation for Concentration of NO₂ Based on DOAS

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Abstract: Temperature has an effect on the accuracy of measurement results of NO₂ by using differential optical absorption spectroscopy (DOAS) technology to monitor the concentration of polluted gases in air in real time. In this paper, a new method of temperature compensation is proposed, in which the integral value of differential absorption cross section is linearly fitted with the temperature. Fitting functions in selected five wave-bands are used to respectively compensate, and the results are compared. The experimental results show that the relative error after compensation is less than 1.67%, which can significantly improve the accuracy of NO₂ concentration measurement.

1. Introduction

Combustion processes, e.g., coal burning in the power industry, generate a major source of air pollution today. Nitrogen dioxide (NO₂) is one of the most important combustion constituted pollutants. DOAS algorithm is widely applied in NO₂ measurement. NO₂ presents a main region of absorption in 350nm-400nm spectral region. Due to its differential absorption characteristics that changing dramatically with temperature and pressure, direct application of DOAS makes it difficult to accurately measure the concentration of NO₂. Thus, it is necessary both for theoretical study and engineering practice to make some research work on temperature.

Johan-Mellqvist et al. observed the qualitative relationship between temperature and differential optical cross section [1-3], without giving any specific mathematical expression. Utilizing pure SO₂ samples, C. Hermans firstly investigated its temperature effects which was considered a linear dependency with respect to temperature [4-5]. Domestic and foreign scholars have done a lot of research [6-10] on compensation for the deviation. Litang Shao put forward a compensation method utilizing the ratio between molecular density of polluted gases in 20℃ and other temperatures. With quadratic polynomial and exponential function models, Orphal J investigated the temperature dependence of the NO₂ cross sections [11]. These methods, however, are aimed at the correction of concentration inversion in high temperature environment (100℃ or above). Little research has been done at ambient temperature or slightly higher than it.

The system used in this paper will be applied to the detection of ultra-low emission (1-54 ppm). In practice, the temperature of NO₂ pretreated is below 50℃. When the concentration of NO₂ is higher (more than 100 ppm), with strong absorption of incident light and the obvious absorption spectrum, the influence of temperature is relatively small. When it decreases down to 10 ppm or less, however, its absorption decreases, signal-to-noise ratio of spectrum drops and the extraction of differential absorption cross section becomes more difficult. Therefore, the control of environmental parameters is more stringent. The temperature variation of 1℃ will have a great impact on the accuracy of measurement especially at low concentration. Therefore, this paper focuses on the establishment of temperature effect and its compensation model in the range of 30℃-50℃.

2. Basic theory of DOAS

Basic theory of DOAS is Lambert-Beer Law. Its physical meaning is that when a bundle of parallel monochromatic light passes vertically through a gas chamber filled with certain concentration gas, its absorption cross section $\sigma(\lambda_i)$ is proportional to the concentration c of the gas and the thickness L of the gas chamber, and inversely related to the transmittance $A(\lambda_i)$. Its mathematical model is defined as

$$I(\lambda_i) = I_0(\lambda_i) \exp[-L\sigma(\lambda_i) * c] * A(\lambda_i) \tag{1}$$

Gases exhibit a rapidly changing pattern in a particular absorption band and the absorption varies drastically with wavelength. The absorption cross section $\sigma(\lambda_i)$ is separated into two parts.

$$\sigma(\lambda_i) = \sigma_s(\lambda_i) + \sigma'(\lambda_i) \tag{2}$$

Where, $\sigma_s(\lambda_i)$ denotes its slow changes with wavelength; $\sigma'(\lambda_i)$ represents differential absorption cross section which varies rapidly with wavelength.

Differential optical density $OD'(\lambda_i)$ can be calculated by the above equations in case that only the rapid change $\sigma'(\lambda_i)$ is taken into consideration.

$$OD'(\lambda_i) = L * \sigma'(\lambda_i) * c = ln\frac{I_0{'}(\lambda_i)}{I(\lambda_i)} \tag{3}$$

Where, $I_0{'}(\lambda_i)$ represents absorption spectrum which varies rapidly with wavelength. In the case that differential optical density $OD'(\lambda_i)$ or differential absorption cross section $\sigma'(\lambda_i)$ is already known, gas concentration can be deduced by the least-squares method.

To get $\sigma'(\lambda_i)$, a key point is the differential calculation between absorption spectrum and incident spectrum. Besides wavelength λ, temperature and pressure also have an effect on $\sigma'(\lambda_i)$. So, it is necessary to compensate the deviation caused by gas temperature change.

3. Experimental system

Figure 1 shows the schematic diagram and experimental setup of the system. The test system mainly includes the gas distribution and measurement system. The concentration of NO_2 can be adjusted by gas distribution system, ranging from 0ppm to 100ppm. The light source is a commercial Ocean optics DH-2000-DUV deep ultraviolet deuterium lamp which has a continuously stable output band of 190-400nm. The gas chamber has 700cm optical path length. Its inner optical glass is a high temperature doped ultraviolet quartz of JGS1. The gas chamber can be heated up to 50℃ by the heating cable. The temperature of spectrometer can be maintained at about 28℃ by the PID intelligent temperature controller.

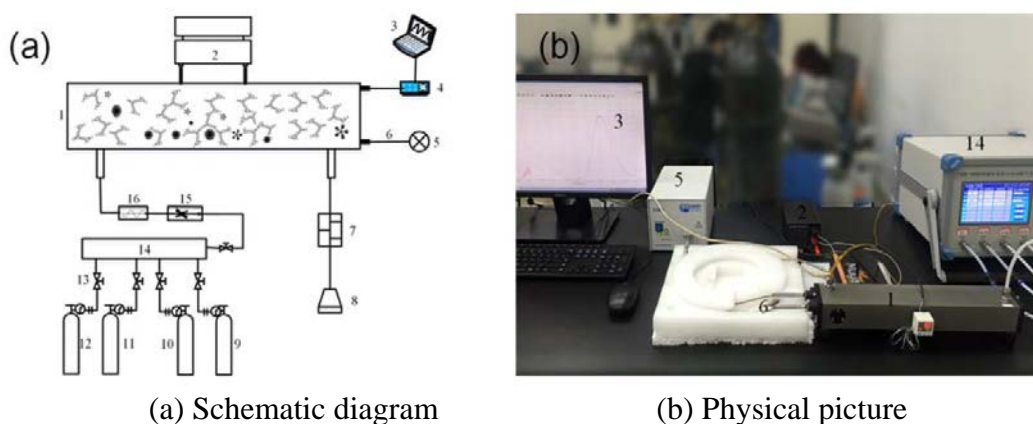(a) Schematic diagram   (b) Physical picture

Figure 1. (a) Schematic diagram: 1 gas cell; 2 control system for temperature and pressure; 3 computer; 4 spectrometer; 5 deuterium lamp; 6 optical fiber; 7 purification device for exhaust; 8 exhaust pipe; 9-12 SO2, NO2, NO and N2 standard gas; 13 control valve; 14 gas distribution system; 15 flowmeter; 16 heating belt. (b) Physical picture.

Three following factors should be considered. Firstly, spectrometer's integration time should be set as a constant value of 100ms to guarantee the consistency of the reference spectrum. Secondly, temperature variation can influence the transformation between NO_2 and N_2O_4 so that gas chamber should be heated the pre-set temperature. Its inner gas should be in the flow state. The gas flow rate is set to 600ml/min and pressure in this gas chamber is 101.33kPa. Thirdly, spectrograph's temperature should be controlled at 28 ℃ to ensure the stability of the absorption spectrum obtained by the spectrometer.

4. Temperature effect and compensation

The temperature effect was investigated by measuring the differential absorption cross sections at different temperature ranging from 30℃ to 50℃ with the step temperature of 2℃. Fig. 2(a) illustrates the temperature effect on the differential absorption cross section in the 349-359nm. Fig.2 (b)-(d) represent respectively the peak and valley value corresponding to the marked places in (a). Fig.2 shows differential absorption cross section increase with temperature in the troughs and decrease with temperature near the peaks. Its overall trend slows down and the envelope area with 0 axis decreases. This phenomenon is consistent with the conclusions of other research scholars.
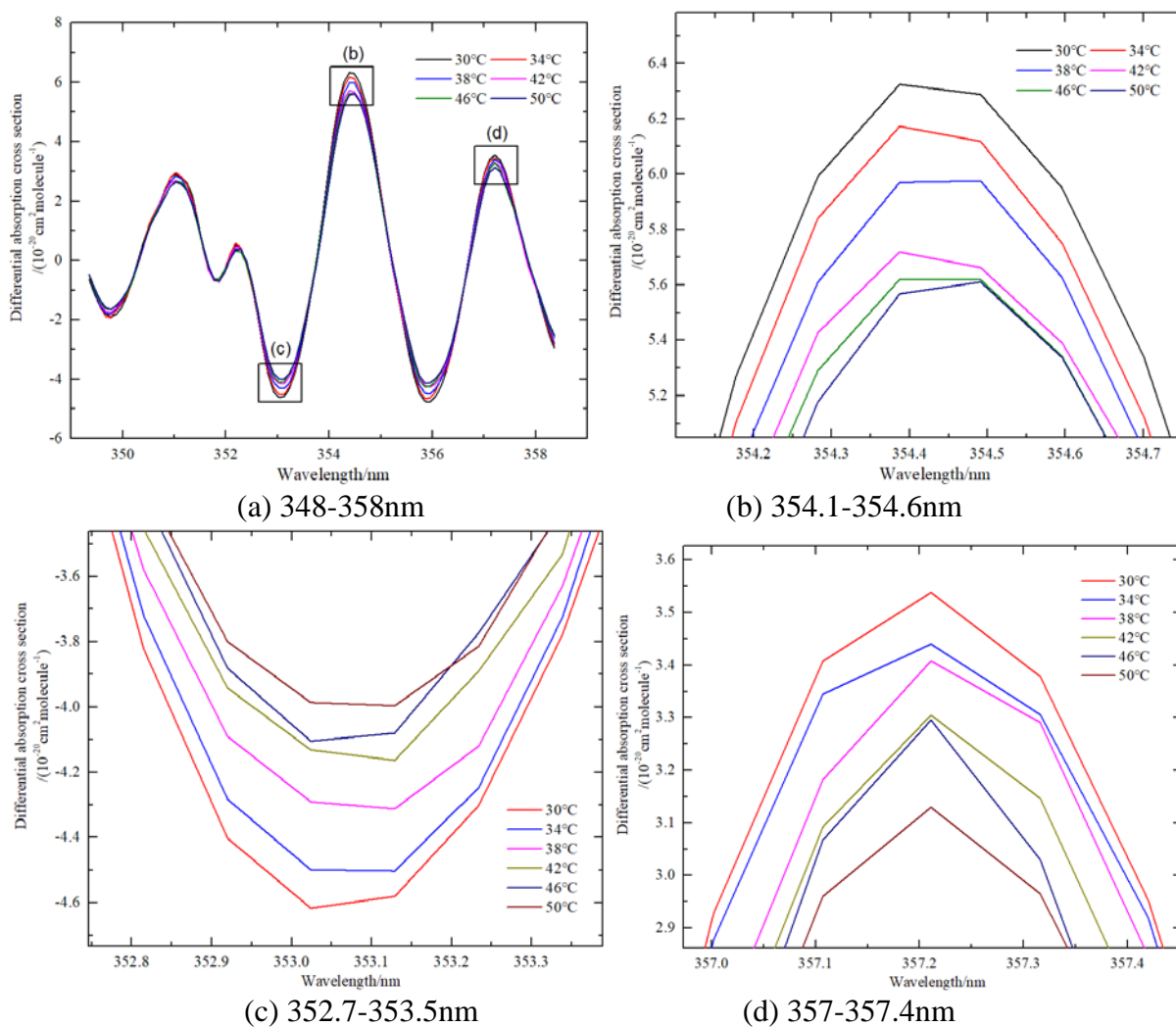

(a) 348-358nm

(b) 354.1-354.6nm

(c) 352.7-353.5nm

(d) 357-357.4nm

Figure 2. (a) Evolution of the NO_2 differential absorption cross section with wavelength from 30℃ to 50℃. (b)-(d) correspond to the marked places in (a).

Due to different variation in different wavelength band, it is unreasonable to summarize the change law of a single certain wavelength. The following expression was considered:

$$\int_{\lambda_i}^{\lambda_j} \sigma(\lambda, T) = \int_{\lambda_i}^{\lambda_j} \sigma_{303K}(\lambda, T) + K(T - 303K) \tag{4}$$

In which $\int_{\lambda_i}^{\lambda_j} \sigma_{303K}(\lambda, T)$ represents the integral value of NO_2 differential absorption cross sections obtained at 30℃. The K coefficient was obtained by linear fitting the integral value of NO_2 differential absorption cross section at different temperatures and at a given wavenumber λ.
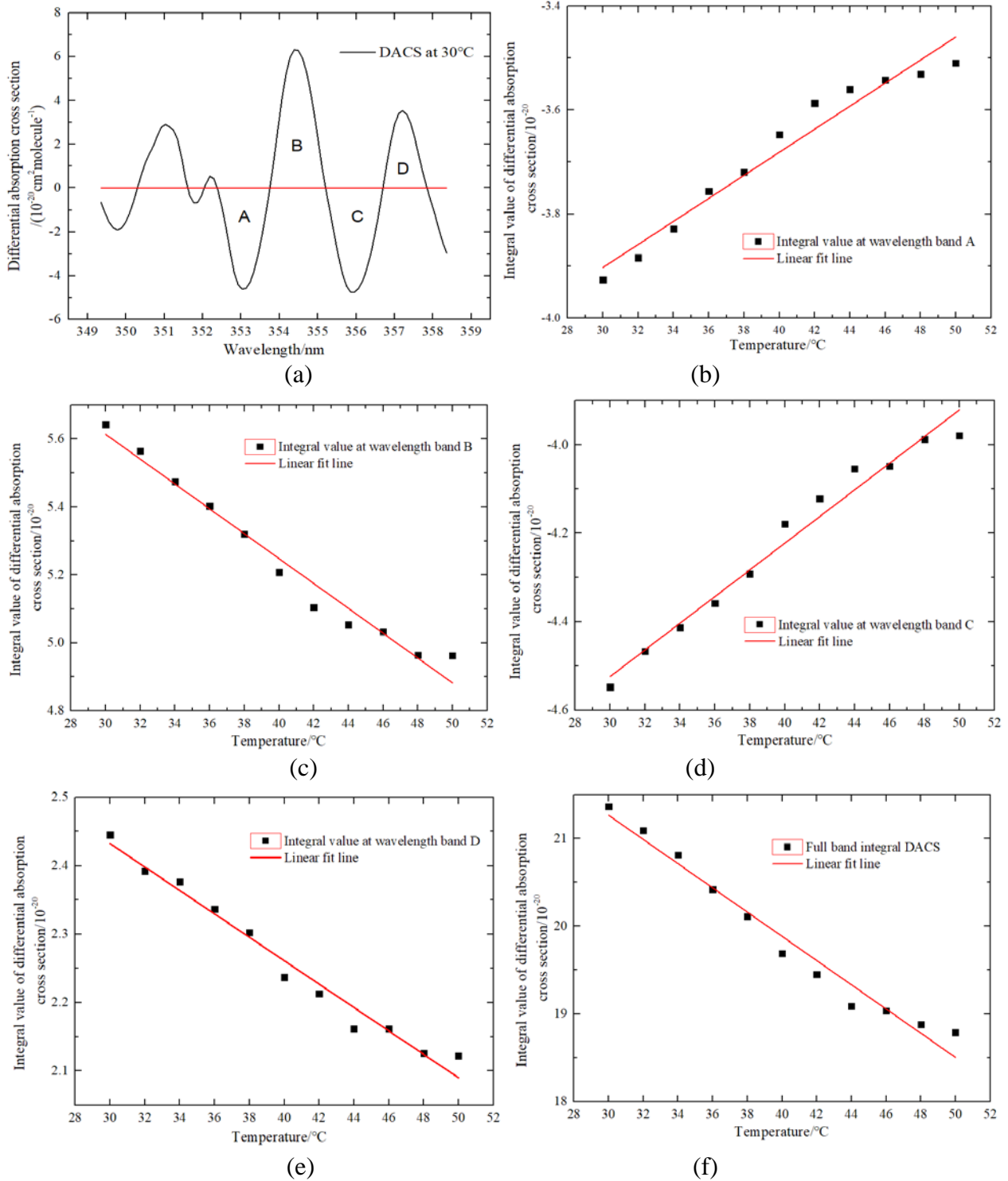

Figure 3. (a) shows the differential absorption cross section of NO_2 at 30℃. It mainly describes the selected integral wavelength band: A (351.6-353.6nm), B (353.7-355.1nm), C (355.2-356.6nm), D (355.2-356.6nm). (b)-(e) are integral value of differential absorption cross section with temperature corresponding to the marked spetral regions A-D in (a). (f) is integral value of differential absorption cross section with temperature in full wavelength band (349-359nm).

Figure 3 illustrates the linear relationship between the integral value of the differential absorption cross section and temperature in five selected wavelength bands. The linear fitting functions at A, B, C, D and full wavelength band E are shown in Table 1.

Table.1. Linear fitting functions

Wavelength band/nm	Linear fitting function
A : 351.6-353.6	$F(T) = 2.216 \times 10^{-22}(T - 303) - 4.568 \times 10^{-20}$
B : 353.7-355.1	$F(T) = -3.657 \times 10^{-22}(T - 303) + 6.711 \times 10^{-20}$
C : 355.2-356.6	$F(T) = 3.016 \times 10^{-22}(T - 303) - 5.429 \times 10^{-20}$
D : 355.2-356.6	$F(T) = -1.712 \times 10^{-22}(T - 303) + 3.659 \times 10^{-20}$
E : 354.0-358.0	$F(T) = -1.381 \times 10^{-21}(T - 303) + 2.541 \times 10^{-19}$

After compensating different spectral regions with the above linear fitting function, the compensation results are shown in Table 2. Meanwhile, control group is set up to compare the effect of compensation. Control group represents a usual method that utilizing the linear fitting between peak or valley points (353.129nm, 354.491nm, 355.957nm, 357.211nm) of each spectral regions and temperature [5].

Table.2. Relative error (%) before and after compensation

Temperature /℃	A		B		C		D		E		Control	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
30	0.68	0.56	0.67	0.55	0.78	0.67	0.06	-0.06	0.51	0.40	0.01	-0.74
32	-0.18	0.15	-0.71	0.57	-1.01	0.26	-1.73	-0.45	-0.81	0.47	0.32	0.91
34	-1.64	0.88	-2.37	0.16	-2.19	0.33	-2.40	0.13	-2.16	0.36	-2.77	-1.26
36	-4.24	-0.33	-3.87	0.03	-3.53	0.38	-4.21	-0.30	-3.98	-0.07	-3.11	-0.78
38	-5.11	0.13	-5.14	0.09	-4.84	0.39	-5.38	-0.14	-5.20	0.04	-3.68	0.94
40	-7.31	-0.79	-7.07	-0.55	-7.41	-0.89	-8.06	-1.54	-7.31	-0.79	-2.88	2.17
42	-8.77	-1.04	-8.88	-1.16	-8.89	-1.17	-8.82	-1.10	-8.80	-1.08	-6.60	-1.14
44	-10.41	-1.32	-9.81	-0.72	-10.22	-1.13	-11.13	-1.67	-10.08	-0.99	-5.96	1.37
46	-10.77	-0.30	-10.33	0.13	-10.08	0.38	-11.72	-1.26	-10.50	-0.03	-6.86	1.65
48	-10.55	1.22	-11.41	0.37	-10.92	0.85	-12.93	-1.16	-11.27	0.51	-11.36	-2.05
50	-11.45	1.52	-11.29	1.67	-11.98	0.98	-13.39	-0.43	-11.77	1.19	-11.55	-1.01

Table 2 shows the relative errors before and after compensation in five spectral regions. Concentration calculation is carried out by using the differential absorption cross section at 30℃ as the standard differential absorption cross section. Each relative error is calculated by the average of three groups data acquired separately in three days. It demonstrates that the accuracy can be effectively improved by using the above-mentioned fitting function to compensate. The maximum relative error is not more than 1.67% compared with control group.

5. Conclusion

Temperature has an effect on the differential absorption cross section of low concentration NO_2 monitored by ultraviolet differential absorption spectroscopy (DOAS). In order to improve the accuracy of gas monitoring, it is necessary to summarize the law of temperature variation and make temperature compensation. A new compensation method based on the linear fitting function of integration value of differential absorption cross section and temperature is proposed in this paper. The gas chamber temperature ranges from 30℃ to 50℃, and its pressure is 101.624 kPa. Five spectral regions (A: 351.6-353.6nm B: 353.7-355.1nm C: 355.2-356.6nm D: 355.2-356.689nm E: 354-358nm) are selected to fit the function and calculate the concentration (35ppm) of NO_2. The relative error is below 1.67% and superior than usual method. The higher temperature, the more obvious the compensation effect is. Meanwhile, measurement results perform superior stability in 72h. This model supplements the deficiency of temperature compensation model at room

temperature (30℃-50℃) and provides the possibility for further accurate measurement of ultra-low concentration.

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