

# Four-step DOAS calibration method of SO<sub>2</sub> in flue gas

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SO<sub>2</sub> monitoring in the flue gas of a coal burning boiler is important for environmental protection. The non-linearity of practical condition causes deviation from theoretical law. On the basis of the Lambert-Beer Law, a new four-step calibration method is introduced. This method includes cross section interpolation, weighting spectral region combination, acquiring the spectrum with new calibration devices, and least-square fitting. Compared with conventional methods, this new method is low cost, convenient, and accurate. In the proof test, SO<sub>2</sub> samples with different concentrations are measured. The average errors are less than 1.5%, while the maximum deviation is less than 4.5%.

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The technology of spectral measurement is the development direction of conventional online monitoring of emissions from pollution sources. The detection technology of H<sub>2</sub>S and CH<sub>4</sub> based on tunable differential laser absorption spectroscopy<sup>[1,2]</sup> and the measurement of NO<sub>2</sub> based on a differential absorption radar have got theoretical progress<sup>[3]</sup>. However, differential optical absorption spectroscopy (DOAS) is relatively mature in the field of industrialized application, which has been introduced by Platt *et al.*<sup>[4]</sup>. DOAS is a very useful technique that allows the quantitative measurement of gas concentrations by recording and evaluating the characteristic differential absorption of an ultraviolet (UV) light source over the path in the stack<sup>[5]</sup>. Anhui Institute of Optics and Fine Mechanics of the Chinese Academy of Sciences started the study of spectrum analysis of flue gas earlier in the domestic setting<sup>[6,7]</sup>. They have applied the research production of the flue gas measurement system to an industrial setting<sup>[8]</sup>.

Lambert-Beer (LB) Law is the basis of DOAS. The average theoretical density of measured gas can be calculated by this law. The optical depth (OD) is defined as  $\sigma \cdot c \cdot x$  and the total column as  $c \cdot x$ , where  $\sigma$  is the gas absorption cross section,  $c$  is the gas density, and  $x$  is the gas length.

In actual conditions, the environmental factors will affect the measurement, such as the spectral shift<sup>[9]</sup> and the scattering of multiple particles<sup>[10]</sup>. These influences which cannot be described as a linear model have great effects on real-time measurements. In this letter, a new four-step nonlinearity calibration method to modify these factors is presented.

As compared with the prerequisite of the LB Law, the nonlinearity of actual measurement is more obvious. The root cause of nonlinearity is its imperfect dynamic behavior<sup>[11]</sup>, which mainly includes the following aspects. Firstly, the OD in actual measurement is larger, which causes line broadening. Secondly, the existence of several pollutants affects the electron transition through the collision and interaction between the molecules of different kinds of gases. Thirdly, in a strict sense, the LB Law is valid for instruments with infinite resolution when the

thickness of measured gas is infinitely small<sup>[12]</sup>.

The common calibration method is conducted with a single sample pool having measured gas of different concentrations. The lower the gas concentration, the larger measurement error is induced. Using several different concentrations of gas in the calibration will result in higher costs, less calibration data points, and lower precision.

The proposed nonlinear calibration method can be divided into four parts: standard cross section interpolation, weighting spectral region combination, acquiring the spectrum with new calibration devices, and least-square fitting.

The standard cross section is necessary to get the correct result. However, it is measured in the strict condition that is not easy to establish in normal labs. Because the standard cross section from the databases and the real spectrum are discrete types with different resolutions, the wavelength is not corresponding between them. The interpolation method is used to let cross section data get the corresponding wavelength with the real spectrum.

As we all know, DOAS measurements of SO<sub>2</sub> can be performed in two UV spectral regions: 200–230 and 260–340 nm. In the region of 260–340 nm, some kinds of sulfides show the similar absorption characteristics to SO<sub>2</sub>. And in different heat-engine plants, different kinds of gases also disturb these two regions. So it is unreliable to choose one single region to perform the calculation. A weighting method is adopted to combine the calculated data of two regions into one single result. The following high order polynomial is used:

$$c = \sum_{k=0}^n a_k c_h^k c_l^{n-k}, \quad (1)$$

where  $a_k$  is the weighting factor,  $c_h$  is the concentration calculated in the region of 260–340 nm, and  $c_l$  is the concentration calculated in the region of 200–230 nm.

In the third calibration procedure, a new calibration device is designed base on the LB Law. The expression of the LB Law's formula will be changed to find a more suitable amendment. The received light intensity at the

wavelength  $\lambda_0$  is given by

$$I_d(\lambda_0) = I_0 \int_0^{\infty} \exp[-\sigma(\lambda, T, P, \dots) \cdot c \cdot x] \cdot F(\lambda - \lambda_0) d\lambda, \quad (2)$$

where  $I_0$  is the reference spectrum,  $\lambda$  is the wavelength,  $T$  is the temperature, and  $F(\lambda)$  is an instrument spectral response function. Thus, the apparent OD,  $OD_{app}$ , can be calculated from Eq. (2) as a Taylor polynomial of the theoretical total column  $(c \cdot x)_{true}$ ,

$$\begin{aligned} OD_{app}(\lambda_0) &= -\ln \left( \frac{I_d(\lambda_0)}{I_0(\lambda_0)} \right) \\ &= A_1(c \cdot x)_{true} - A_2(c \cdot x)_{true}^2 + O(3), \quad (3) \end{aligned}$$

in which  $A_i$  is the fitting coefficients, and  $O(3)$  is a higher order infinitesimal.

Evidently, the real total column  $(c \cdot x)_{app}$  is obtained by the fitting process such as the least-square method, when  $(c \cdot x)_{true}$  is derived.

The solution of Eq. (3) requires the different known total column data, whose amount is larger than that of the unknowns. From the definition of the total column and OD, they obey the association law as

$$(k \cdot c \cdot x) = (c \cdot kx), (\sigma \cdot c \cdot kx) = (\sigma \cdot kx \cdot c). \quad (4)$$

In this way, the change in gas concentration is converted to the change in gas length. Let a certain value  $L_0$  be the base of the length of measured gas, and the gas length will be changed as the integer multiple of  $L_0$  in each experiment. This is equal to standard gas with a concentration of the integer multiple of  $c_0$ , which is the original standard gas concentration.

As a result, a set of new calibration devices with variable length sample pools is designed to determine the nonlinear coefficients by least-square fitting. The calibration devices include the light source, the optical component of collimation and extender, the sample pools, the collective lens, the fiber connector, and the base. The system diagram is shown as Fig. 1.

The measurement light path is as follows. The light beam transmitted from the source is convergent to the focusing lens after passing through the measurement area. It will be subsequently sent to the spectrometer by fiber. This path can maximally reduce the unnecessary attenuation of light intensity<sup>[13]</sup>.

To provide the accurate calibration data, a group of sample pools is designed for the calibration process and the experiments. There are four sample pools whose lengths are 1, 2, 4, and 8 times of that of the first sample pool. Sixteen kinds of different lengths can be obtained by combining the sample pools in various groups. In accordance with Fig. 1, the gas path is connected with

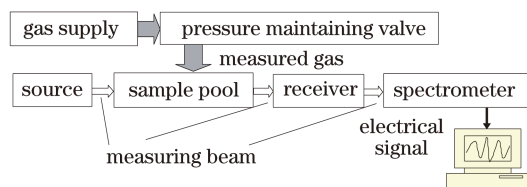


Fig. 1. Flow diagram of the calibration devices.

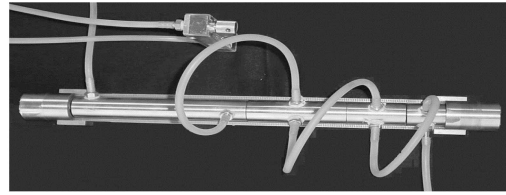


Fig. 2. Location of the sample pools and the base.

adequate gas tightness. In order to improve the utilization ratio of the measuring beam and reduce the wall effect, the central axis of the sample pools should coincide with the optical axis of the beam by the base, as illustrated in Fig. 2.

SO<sub>2</sub> samples with the concentrations of 2029 and 505 ppm were utilized in the calibration experiment. The spectrometer used was the EPP2000 portable spectrometer made by StellarNet. The reference spectrum  $I_0$  was obtained first when the sample pool on the base was empty. After collecting the spectral data, the concentrations were calculated by Eq. (2). According to Eq. (4), the nonlinear coefficients were calculated. To test these coefficients, another group of concentrations was collected for calibration and compared with the standard concentration. It should be pointed out that the sample pools had their outside portion air-filled, which would facilitate additional absorption of the beam. However, this factor can be considered by adding the reference light into the data processing. This does not affect the final results.

The strong absorption property of SO<sub>2</sub> results in the deposition phenomenon that occurs in the sample pools. This will increase the absorption of the measuring beam greatly. The influence of the deposition phenomenon is checked through the change in concentration with the increase of time. This is equal to the test of repeatability of the measured concentration. There are two steps: 1) increasing the length of the sample pools to collect the spectrum, and 2) calculating the concentration, decreasing the length of the sample pools, and recording the spectrum and the measured concentration. The deviation between these two groups shows the influence of the deposition. The data are shown as the 2029A and 2029B which stand for the uncalibrated and uncalibrated return data in Fig. 3, while the curve named 2029C and 505C represent the calibrated data for the concentrations of 2029 and 505 ppm, respectively. Most points of the uncalibrated return data are larger as compared with those of the uncalibrated data, which proves that the deposition effect of SO<sub>2</sub> increases with time. The instability of the deposition creates an impact and does not change monotonously with time. The deviation data also show that the inconsistent processing accuracy of the sample pool disturbs the beam path, so that the deviation of some data points with the same index is larger in all groups.

From Fig. 3, the calibrated data of 2029 and 505 ppm almost match with each other, which indicates that the repeatability of the calibration method is good. The maximum deviation between the calibration fitting curve and the standard concentration in 2029-ppm group is 4.3%, while the average deviation is 1.4%. The maximum

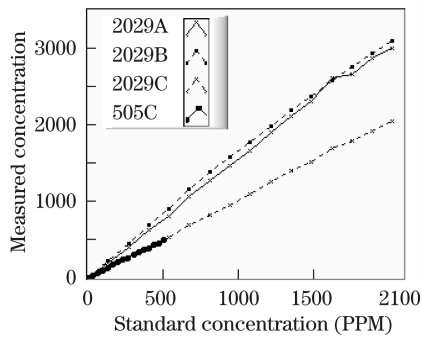
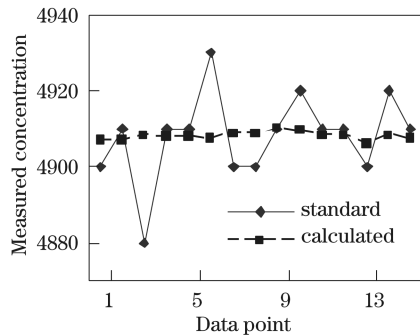
Fig. 3. SO<sub>2</sub> calibration curve.

Fig. 4. Comparison of concentration data.

deviation in 505-ppm group is 3.56%, while the average deviation is 0.12%.

A power plant in Shandong Province, China was chosen as the target in this experiment. Eighteen groups of spectral data were collected. The data of SGA94-SO<sub>2</sub> single gas analyzer was taken as the standard value, whose resolution was 1 mg/m<sup>3</sup>. As the data shown in Fig. 4, the deviation of the calculated concentrations is less than 5%. Because of the interference of other gas components, the deviation is larger. However, this also achieves better measurement accuracy. But it is also shown that this method does not have a good real-time ability.

In the industrial field, nonlinearity will be greater than that under the laboratory conditions, which may be attributed to high temperature, complex gas components, and other factors. Therefore, the proper calibration method is required to correct the deviation from the LB Law. There are four steps in the new calibration method. Cross section interpolation and weighting spectral region

combination are the pre-process procedures of the concentration calculation. A set of sample pools can provide a more convenient equipment to acquire the spectrum accurately. At last, the least-square fitting method is adopted to get the final processed data.

The average deviation of the new calibration method is less than 1.5%, and the maximum deviation is less than 4.5%. If a non-metal material is used, the deposition phenomenon will be reduced, which is ideal in obtaining stable spectrum intensity. In this case, the accuracy of the new method could be higher than that it already is. It offers a more convenient and low-cost calibration method. In the future, the real-time ability of this method is to be improved.

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