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F. XU[1]
Y.G. ZHANG[1]
G. SOMESFALEAN[1,2]
Z.G. ZHANG[1,✉]
H.S. WANG[3]
S.H. WU[3]

Temperature-corrected spectroscopic evaluation method for gas concentration monitoring

[1] Department of Physics, Harbin Institute of Technology, Harbin 150001, P.R. China
[2] Department of Physics, Lund Institute of Technology, P.O. Box 118, 22100 Lund, Sweden
[3] Institute of Combustion Engineering, Harbin Institute of Technology, Harbin 150001, P.R. China

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ABSTRACT Combustion exhaust monitoring was simulated by measurement on a sulfur dioxide flow at different temperatures using broadband absorption spectroscopy and electrochemical analysis. A linear relationship with varying rates of slope for different temperatures was found between the gas concentrations obtained using the two methods, attributed to the influence of gas volume increase and absorption line broadening. By utilizing the differential absorption at an on/off pair combined with an experimentally determined temperature correction coefficient, the sulfur dioxide concentration was evaluated with the spectroscopic method yielding a measurement precision of 4%.

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1 Introduction

Combustion processes, e.g., coal burning in the power industry, constitute a major source of air pollution today. Sulfur dioxide (SO_2) is one of the most important combustion generated pollutants since it easily dissolves in atmospheric water and produces sulfuric acid, which contributes to the acidification of water and soil (acid rain) with huge negative economical impact. Many techniques have been developed for monitoring SO_2 pollution emissions. At present, commercial instruments commonly employed in industry are based on electrochemical sensing, which is a rather inexpensive technique, however, with the disadvantage of being fairly slow and insensitive, having complex operation and requiring continuous maintenance. Alternative measurement methods using optical techniques have the advantage of being fast, sensitive, and offer the possibility of remote sensing. For example, differential optical absorption spectroscopy (DOAS) [1–3] is a line-of-sight integration method that acquires the average gas concentration, correlation spectroscopy (COSPEC) [4, 5] is especially suitable for leak detection and remedy [6], differential absorption LIDAR (DIAL) [7–9] uses pulsed laser sources and permits a three-dimensional mapping of atmospheric pollutants [2], and tunable diode laser absorption spectroscopy (TDLAS) [10] achieves miniaturization and high sensitivity by employing small and robust diode laser components.

Recently, we reported on a novel approach for SO_2 concentration monitoring using broadband absorption spectroscopy in the UV spectral range [11]. Our simple scheme is based on differential absorption, and employs the direct absorption signals for data evaluation without requiring any reference spectrum and fitted polynomials. The laboratory measurements in [11] were performed at room temperature, and the detection limit of the current implementation was found to be 1 ppm with 3-s integration time.

In many real-world applications, however, gases are monitored at elevated temperatures. Hence, a thorough analysis of the pressure and temperature effects is necessary for a correct evaluation of the gas concentration. Our present experiments simulated cross-stack flue gas emission monitoring, and were performed on slowly flowing SO_2 gas in an open cell, yielding a pressure of one atmosphere inside the sample cell. In the following we, therefore, only consider the influence of temperature on the SO_2 monitoring, expressed as a broadening of the absorption line and an increase of the gas volume. In the analysis we introduce a temperature correction coefficient which is empirically evaluated. Finally, we present results for a temperature series from 293–368 K, and we forecast the temperature correction coefficients for other temperatures based on these experiments.

2 Experimental

The schematic of the setup used in this study is shown in Fig. 1. A deuterium lamp (Beijing Union Optics-Electronic Co 5601, power of 30 W) was operated as a broadband UV light source. The exiting light beam was collimated with a quartz lens of 75 mm focal length and passed through a 80 cm-long gas cell equipped with quartz windows. Another quartz lens of 145 mm focal length focused the transmitted light into an multimode optical fiber (Ocean Optics Inc OFLV-200-1100) coupled to a high-resolution spectrometer (resolution of ~ 0.1 nm) composed of a monochromator and a 2048-element CCD-array detector (Ocean Optics Inc

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✉ Fax: +86-451-86 41 28 28, E-mail: zhangzhiguo@hit.edu.cn

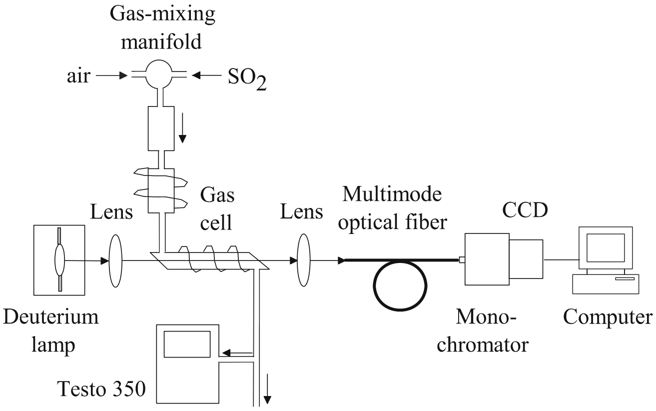

FIGURE 1 Experimental setup for spectroscopic measurements of SO_2 at elevated temperatures

HR2000). The signal from the CCD detector was transmitted to a personal computer for analysis of the integrated spectrum. The real-time data collection and evaluation, and the control of the spectrometer were performed automatically using software written in Visual Basic®.

In the experiments, dry air was passed by a compressor via a glass rotameter into a gas-mixing manifold, where it was used to dilute the pure SO_2 gas. The SO_2 gas mixture was flown in turn through two premixing chambers, and an 80 cm-long measurement cell, as illustrated in Fig. 1. The gas flow was slow and the pressure inside the cells was approximately one atmosphere. Since SO_2 is highly corrosive and the experiments were performed at elevated temperatures, the gas cells were made of stainless steel, which is a corrosion-resistant material with good heat conduction characteristics. For simulating the high temperatures in an after-combustion environment, the SO_2 gas was heated by a wire enwound around the last premixing chamber and the 80 cm-long measurement cell, as shown in Fig. 1. The voltage input to the heating wire was regulated with an accuracy of 0.1 K by a digital temperature controller (Xiamen Yuguang Electronic Technology Co AI-518T) connected to a K-model thermocouple which measured the temperature of the flowing SO_2 gas. The accurate determination of the sample gas temperature was crucial, since the temperature-corrected concentrations were calculated directly using the recorded absorption spectra.

The gas measurements performed at various temperatures were validated against a commercial fume analyzer (Germany Testo AG, Testo 350), which uses an electrochemical method for detection of the SO_2 concentration, and is not affected by temperature variations. The measurement precision of the fume analyzer was specified by the manufacturer to be ±5%.

3 Evaluation principles

Our evaluation method is based on recording of the direct absorption profiles of the gas. An average SO_2 concentration can be deduced from Beer–Lambert's law [12] in a procedure described in detail elsewhere [11]. The ratio between the received radiation intensities at two close-lying wavelengths can straightforwardly be simplified assuming negligible variation of the source radiation intensity, no dissipation of light, and no interference from other gases within the selected narrow wavelength range. The evaluated concentration can be briefly reviewed as

$$N = -\frac{\ln\left[\frac{P_t(\lambda_1)}{P_t(\lambda_2)}\right]}{\left[\sigma(\lambda_1) - \sigma(\lambda_2)\right] L}, \tag{1}$$

where λ_1 and λ_2 are the on/off wavelengths selected at 300.02 nm and 301.39 nm, $P_t(\lambda_1)$, $P_t(\lambda_2)$, $\sigma(\lambda_1)$ and $\sigma(\lambda_2)$ are the received radiation intensities and the absolute absorption cross-sections at the above two wavelengths, respectively, N is the concentration of the gas, and L is the absorption path length (here, 80 cm).

Since the sample cell was open and the gas flow slow, the pressure inside the cell was constant and approximately equal to one atmosphere. No corrections with regard to pressure were, therefore, necessary. The influence of temperature is an integrated effect of both the volume increase and the absorption line broadening. Hence, we introduce into (1) a temperature correction coefficient $C(T)$, which condenses the temperature dependence due to the changes of both gas density and spectral signature, and obtain

$$N = -C(T)\frac{\ln\left[\frac{P_t(\lambda_1)}{P_t(\lambda_2)}\right]}{\left[\sigma(\lambda_1) - \sigma(\lambda_2)\right] L}. \tag{2}$$

The values of the coefficient $C(T)$ at different temperatures were determined experimentally as described in the measurements and results section below.

4 Measurements and results

The measurements were performed on flowing SO_2 gas, which was heated to simulate real-world exhaust gas measurements for applications in, e.g., the power industry. To be able to determine the correct gas concentrations, it is very important that the temperature of the SO_2 gas is measured accurately. In order to achieve a well-defined gas temperature in the 80 cm-long sample cell, both the preceding premixing chamber and the 80 cm-long measurement cell were heated. The conditions of the SO_2 gas mixture were considered stable when the temperatures at the entrance and the exit of the 80 cm-long gas cell were identical.

The recorded SO_2 spectra in the 280–320 nm spectral region for a gas concentration of 730 ppm at two different temperatures (293 K and 333 K, respectively) are shown in Fig. 2. To better illustrate the influence of a temperature increase, we present the normalized transmitted spectra around 300 nm in the insert of Fig. 2. This was obtained by averaging the signals in the 299–302 nm range and subsequently dividing the raw spectra by the mean values. As expected, for the same gas concentration, the influence of temperature on the spectra increases with higher temperatures, due to, e.g., a shift in thermal population of the energy levels involved in the transitions.

The concentration of the SO_2 gas which passed through the 80 cm-long cell was recorded simultaneously using both the spectroscopic technique and the fume analyzer. The non-temperature-corrected results obtained for a temperature of 346 K are shown in Fig. 3. The graphic spans over SO_2 concentrations from tens to hundreds of ppm, and a straight line

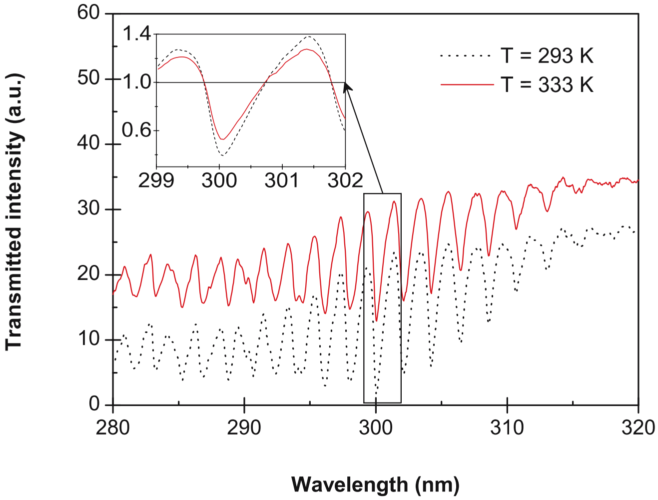

FIGURE 2 SO_2 spectra recorded at the temperatures 293 K (*dotted line*) and 333 K (*solid line*), respectively, for the same concentration of 730 ppm. The *insert* shows the normalized spectra in the range of 299–302 nm. Obviously, the spectral broadening increases with the temperature

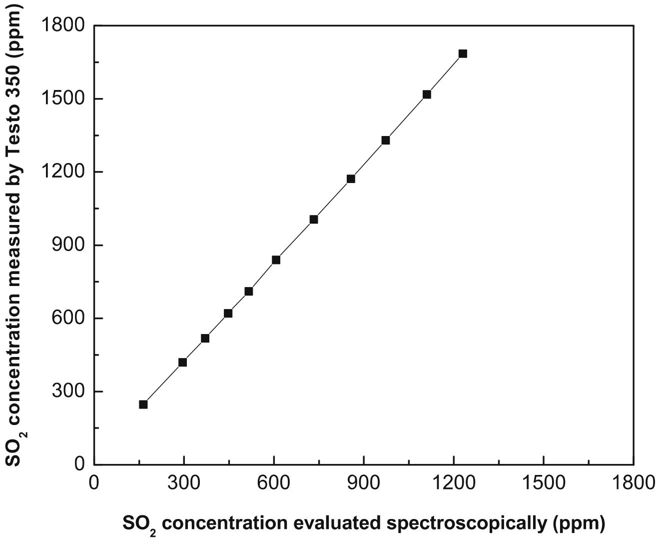

FIGURE 3 SO_2 concentrations simultaneously recorded using the proposed spectroscopic method and a non-optical fume analyzer (Testo 350). A straight line could be fitted to the recorded values (*squares*), which were measured at a sampling temperature of 346 K and the path length of 80 cm

could be fitted to this measurement values. This proofs that the temperature correction coefficients are constant at a given temperature and for different concentrations.

The temperature correction coefficient, $C(T)$, acquired experimentally for a series of different temperatures, are shown as rectangles in Fig. 4. It should be noted that at room temperature (here defined as $T = 293$ K) the temperature correction coefficient equals to one, and (1) and (2) coincide. A linear dependence of the temperature correction coefficient on the temperature was empirically found, expressed as the fitted line in Fig. 4

$$C(T) = -1.31 + 7.82 \times 10^{-3}\, T \,, \tag{3}$$

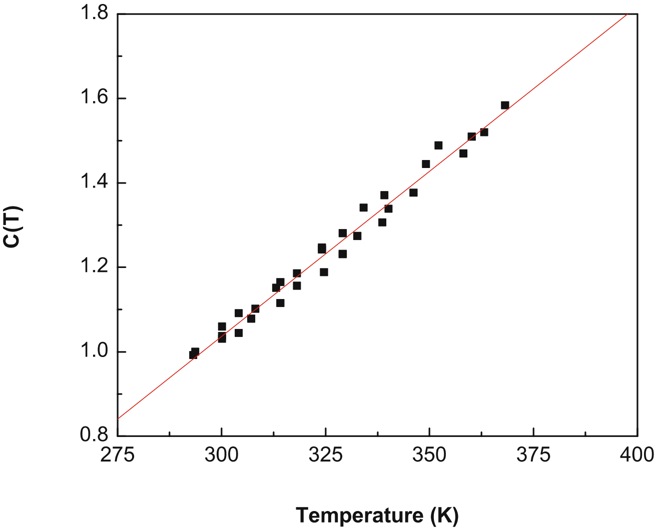

FIGURE 4 Temperature correction coefficients (*squares*) obtained experimentally from repeated gas measurements at temperatures between 293 and 368 K. The *linear fit* representing $C(T)$ was used for temperature-correction

and these values were used for the evaluation of the temperature-corrected concentration according to (2). The temperature correction coefficients can be estimated in a wider temperature range by extrapolating the straight fitted line.

A series of SO_2 concentrations simultaneously recorded using our temperature-corrected spectroscopic method and the fume analyzer at the temperatures 300 K, 333 K, and 363 K are plotted in Fig. 5. The consistency of the concentration values obtained using the two techniques (rate of slope near one) illustrates the robustness of our evaluation method. The measurement precision of the temperature-corrected method was estimated from Fig. 5 to be 4%, by computing the standard deviation compared to a fitted line with a rate of slope equal to one. Comparison can be done with the non-temperature-corrected values of the spectroscopic measurement, shown as an insert of

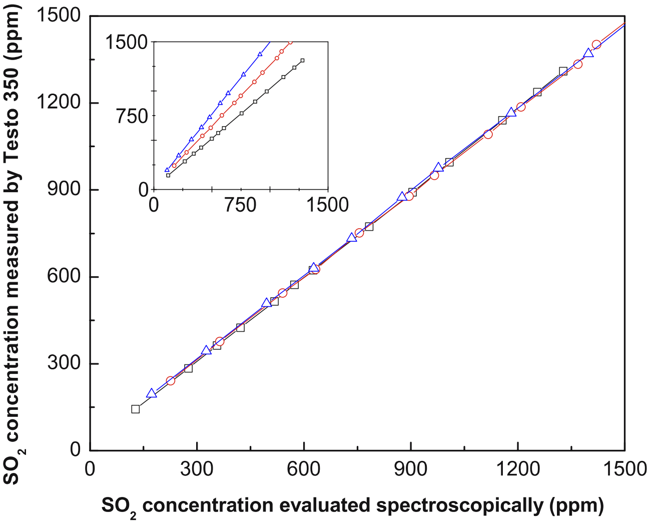

FIGURE 5 SO_2 concentrations evaluated with the proposed temperature-corrected method, compared with the simultaneously recorded values from a fume analyzer at the temperatures of 300 K (*squares*), 333 K (*circles*), and 363 K (*triangles*). The *insert* shows the plot obtained without temperature-correction

Fig. 5. The larger rates of slope of the fitted lines obtained at higher temperatures, indicate the increasing influence of the temperature on the measured spectra and gas volume.

Pressure broadening can also affect the absorption spectrum of the gas. In [11], we have measured the absorption spectral features at atmospheric and at low (1.2 mbar) pressure for the same SO_2 concentration. As expected from theoretical considerations [13], we found that for the present detector resolution of 0.1 nm the high and low pressure spectra overlap.

5 Discussion and conclusions

We have demonstrated the feasibility of a method for evaluation of a temperature-corrected gas concentration by using broadband absorption spectroscopy applied to SO_2 monitoring. Our detection scheme uses the strong differential absorption lines of the transmitted SO_2 spectrum in the wavelength region around 300 nm. In the experiments, the integral influence of volume increase and line broadening was considered when temperature correction was performed. In a series of experiments, the temperature correction coefficients for a temperature range of 293–368 K were estimated and used to evaluate the corrected gas concentration. The results were validated against a fume analyzer, which is a standard non-optical instrument that is not affected by changes in the gas temperature. After temperature correction, the concentration values obtained with the two instruments agreed within a maximum standard deviation of 4%.

Due to practical constrains in the present experimental setup, only a limited temperature span could be monitored. However, by extrapolating the straight line fitted to the experimentally recorded temperature correction coefficient values, temperature correction in a wider temperature range is possible.

In our experiments the sampling time of the CCD detector was adjusted in order to obtain a good signal-to-noise ratio and high resolution integrated spectra. No additional attempt to minimize the influence of the noise was done so far. The evaluation of the temperature-corrected concentration was in our case limited by the measurement precision and the insensitivity of the fume analyzer. These could be improved by using a reference instrument with higher precision. Additionally, the dynamic range of the spectrometer CCD currently used was 2×10^8 (system) (2000:1 for a single scan). The signal-to-noise ratio and the accuracy of this technique may be improved further by employing a CCD-array with higher dynamic range.

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