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Broadband spectroscopic sensor for real-time monitoring of industrial SO₂ emissions

Feng Xu, Yungang Zhang, Gabriel Somesfalean, Huashan Wang, Shaohua Wu, and Zhiguo Zhang

A spectroscopic system for continuous real-time monitoring of SO₂ concentrations in industrial emissions was developed. The sensor is well suited for field applications due to simple and compact instrumental design, and robust data evaluation based on ultraviolet broadband absorption without the use of any calibration cell. The sensor has a detection limit of 1 ppm, and was employed both for gas-flow simulations with and without suspended particles, and for *in situ* measurement of SO₂ concentrations in the flue gas emitted from an industrial coal-fired boiler. The price/performance ratio of the instrument is expected to be superior to other comparable real-time monitoring systems. © 2007 Optical Society of America

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1. Introduction

Large amounts of industrial pollutants are emitted into the environment, especially in developing countries. Gas pollutants released by industry can damage human health and cause huge economic losses. SO₂ is among the most common of industrial gas pollutants, with well-documented toxicity and the ability to produce acid rain. Today, a majority of industrial plants are responsible for monitoring and controlling their own emissions by accurate measurement of the released pollutant gas concentration and flux. This is important not only from an environmental point of view, but also for economical reasons, since a portion of the taxation may depend on emission values.¹ Therefore, there is an increased need for the development of powerful techniques for pollutant emission measurement.

A practical monitoring sensor for industrial pollution emissions should allow for on-site, continuous, and unattended operation over a long period of time,

preferably achieved by an instrument with a simple and robust design.² Optical remote sensing techniques have obvious advantages for gas pollutant detection, e.g., they enable fast operation over large distances, and in hostile environments with large fluctuations of temperature and pressure. Differential optical-absorption spectroscopy provides realistic and reliable multispecies average concentration measurements,^{3–6} correlation spectroscopy is often employed in the petrochemical and gas industry for leak detection and remedy against explosion,^{7–10} differential absorption lidar enables three-dimensional mapping and total flux measurements,^{11–13} while tunable diode laser absorption spectroscopy provides miniaturization and high sensitivity detection.¹⁴ Generally, optical techniques have experienced tremendous development in the past decades, largely stimulated by the information technology revolution and advances in laser technology.

Recently a novel spectroscopic evaluation method for SO₂ concentrations by broadband absorption in the UV spectral range was reported.¹⁵ Laboratory tests on static and flowing gas displayed a measurement precision of 4% and long-term reproducibility under varying pressure and temperature conditions.

Here we present simulations and real-world tests of a new portable SO₂ sensor for monitoring industrial pollutant emissions, based on the above-mentioned evaluation method. Experimental data collected under a field campaign carried out at a coal-fired industrial boiler in Harbin, China, together with laboratory simulations, demonstrate the possibility of performing

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continuous *in situ* measurements of SO₂ concentration.

2. Experiment

Figure 1 illustrates the setup of a new portable SO₂ sensor composed of three independent benches. The first bench (BB1) includes a deuterium lamp (Beijing Union Optics-Electronic Co. 5601) operated as an UV light source with a lifetime of approximately 2000 h. A quartz lens of 10 cm focal length fixed on a two-dimensional sliding stand was adjusted to collimate the exiting light. The light beam was passed through two side holes of an exhaust chimney, across the flowing flue gas, to a second bench (BB2), where the transmitted light was focused by a second quartz lens of 10 cm focal length into a multimode optical fiber (Ocean Optics OFLV-200-1100). The lenses were chosen to match the numerical aperture of the source and the fiber and had relatively short focal lengths for compactness of the sensor. The UV light output from the multimode optical fiber was sent into a high-resolution spectrometer (resolution of ~0.1 nm) composed of a monochromator and a 2048-element CCD array detector (Ocean Optics HR2000), which were mounted on a third breadboard (BB3). The CCD signal was transmitted to a personal computer, where continuous instrument settings and spectra acquisition (maximum rate of 0.5 Hz) were performed using VISUAL BASIC code. All the mechanical components were made of corrosion-resistant stainless steel and were designed to enable on-site substitution of damaged optics without any need for realignment.

The temperature of the SO₂ gas was measured with an accuracy of 0.1 K using a K-model thermocouple placed directly in the gas sampling area. To avoid problems related to external disturbances, such as air turbulence, particle contamination, stray light, and excessive temperatures, all three benches were placed in protective boxes, leaving two circular openings in front of the two quartz lenses to permit emission and reception of UV light. To avoid long-time contamination by dust of the quartz lenses, which could reduce the received light intensity and the signal-to-noise ratio (SNR), external covers were added to the BB1 and BB2 boxes, allowing clean airflow at slight overpressure to pass through the interspace and out through the two

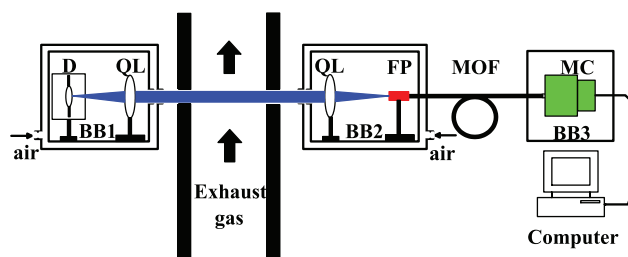


Fig. 1. (Color online) Experimental setup of the portable SO₂ sensor. The instrument is composed of three modular parts: BB1, BB2, and BB3. D, deuterium lamp; QL, quartz lens; FP, fiber port; MOF, multimode optical fiber; MC, monochromator and 2048 element CCD-array detector.

openings located in front of the lenses. This design was utilized in the field measurements over long time periods and ensured unattended and undisturbed operation of the sensor.

3. Measurement Evaluation and Results

The evaluation principle used by the gas sensor is based on direct absorption spectroscopy, as described in Refs. 15 and 16. The concentration evaluation can be briefly reviewed as follows: An average SO₂ concentration can be deduced from the Beer–Lambert law¹⁷ according to

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

where N is the gas concentration, $C(T)$ is the temperature corrected coefficient at temperature T , L is the absorption path length, $P_t(\lambda_1)$ and $P_t(\lambda_2)$ are the received radiation intensities, and $\sigma(\lambda_1)$ and $\sigma(\lambda_2)$ are the absolute absorption cross sections at the on–off absorption wavelengths of $\lambda_1 = 300.02$ nm and $\lambda_2 = 301.39$ nm, respectively. A thorough analysis of the temperature effect on the proposed concentration evaluation method was presented in Ref. 16, where $C(T)$ was determined experimentally.

The recorded spectra were transmitted to a personal computer at a sampling rate adjusted to optimize the SNR. The spectral integration was allowed to continue until the transmitted intensity was slightly below the CCD threshold value, which ensured a good SNR without overflowing its measurement range. The received radiation intensities $P_t(\lambda_1)$ and $P_t(\lambda_2)$ at the on–off resonance wavelengths of λ_1 and λ_2 , respectively, were read out from the transmitted spectra. The values of the absolute absorption cross sections $\sigma(\lambda_1)$ and $\sigma(\lambda_2)$ were acquired from Refs. 18 and 19, while the absorption path length L was measured on site. To obtain accurate $C(T)$ values, the temperature was carefully sampled by the thermocouple. Finally, the gas concentration could be calculated directly using Eq. (1) at a maximum acquisition rate of 0.5 Hz and by averaging ten spectra to increase the SNR. The above sampling and computation processes were performed automatically using VISUAL BASIC code, allowing straightforward determination of the SO₂ gas concentration.

Prior to the field campaign, we simulated industrial pollution emissions in laboratory measurements of SO₂ gas flow at room temperature and at different concentrations. First, we considered the influence of particles in the light path on the SO₂ detection. Figure 2(a) shows a typical SO₂ transmission spectrum at ~300 nm for a gas flow of 1036 ppm SO₂ mixture in dry air. Figure 2(b) presents the 126 data samples continuously evaluated from ten spectra averages acquired using 4 s integration time—although the actual response time of the system is of the order of 100 ms. The first 6 min in Fig. 2(b) were recorded in the presence of dust in the light path (squares), showing

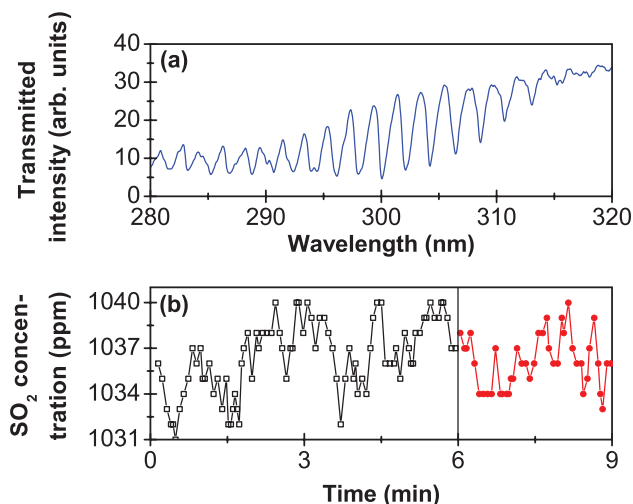


Fig. 2. (Color online) (a) Absorption spectrum of a flowing SO_2 gas mixture of 1036 ppm concentration. (b) Influence of dust on the SO_2 detection, evaluated by a short-time continuous recording of 126 data samples, using ten spectra averaging and 4 s integration time. For the first 6 min (squares) dust was present in the light path; during the last 3 min (circles) there was no interference from dust.

a mean value of 1036 ppm and a standard deviation of 2.4 ppm. The last 3 min of recording were detected without interference of dust (circles), yielding an average value of 1036 ppm with a standard deviation of 1.7 ppm. This test demonstrates that, although fluctuations increased, dust in the sampling volume reduces the SNR only slightly and does not change the accuracy of the concentration measurement. Due to difficulties in stabilizing the SO_2 gas flow for a long time, the measurement time was relatively short, yet enough to quantify the influence of particles on the accuracy of the method.

Long-term monitoring of SO_2 at room temperature is shown in Fig. 3, where a series of five gas concentrations, i.e., 1040, 740, 1030, 520, and 1020 ppm were sequentially detected. Three of the SO_2 concentrations were selected approximately equal to demonstrate the

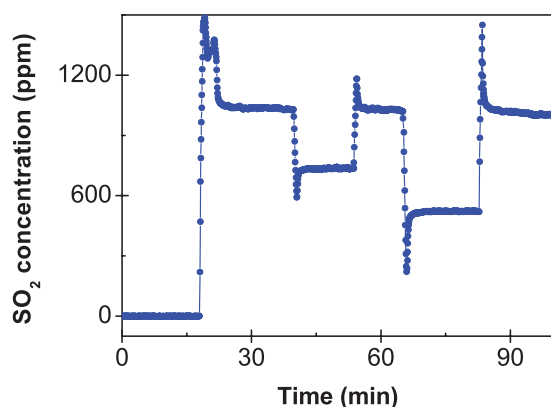


Fig. 3. (Color online) Continuous concentration recording of SO_2 at normal temperature and pressure in a gas flow during laboratory simulation. Measurement of five different SO_2 concentrations, i.e., 1040, 740, 1030, 520, and 1020, was performed.

repeatability of the measuring instrument. The slight slant of the concentration curve displayed in the figure can be attributed to the difficulty of perfectly stabilizing the gas flow during recording. The gas flow was slow and the pressure inside the measurement cell was approximately one atmosphere. The artifacts present at each change in SO_2 concentration are due to transients in the process of dilution of pure SO_2 gas in dry air, which takes place in the limited volume of the gas-mixing manifold. These anomalies are not encountered in real-world industrial emission measurements and are therefore not considered further.

It can be inferred from Eq. (1) that for very high SO_2 concentrations, present in strongly polluted emissions, the absorption path length L should be correspondingly shortened. In contrast, for very low gas concentrations, long-time averaging (>10 s) or path length increase (e.g., 1–3 m, which is feasible in single-pass cross-stack monitoring) can enhance the absorption measurement sensitivity. The extrapolated minimum detectable concentration of the instrument was previously estimated to ~ 1 ppm.¹⁵

A measurement campaign was carried out in early Spring 2006 in Harbin, China. The sensor was then tested for measurement of the SO_2 in flue gas emitted from an industrial coal-fired boiler. The gas concentration was measured through the chimney flue using an absorption path length of 1.6 m. A continuous 24 h recording of the SO_2 concentration is shown in Fig. 4, where every point represents the value obtained from averaging ten spectra at 1.1 min integration time. The temperature of the flue gas remained approximately constant at 411 K during data recording. From Fig. 4 we estimated the average SO_2 concentration to be 106 ± 8 ppm. To illustrate measurement details, a 1 h continuous recording is presented in the inset of Fig. 4. Using the obtained SO_2 concentrations and the measured flux of the exhaust gas, which was $50802 \text{ m}^3/\text{h}$, we could calculate a 24 h total SO_2 release of 0.24 ton/day. This value could be verified, since the coal consumption was estimated to 1.5 ton/h and the

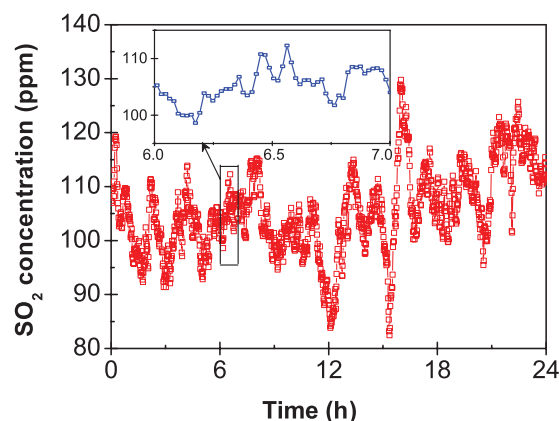


Fig. 4. (Color online) Twenty-four hours recording of the SO_2 concentrations at a temperature of 411 K emitted from a coal-fired industrial boiler in China. Each point was obtained by averaging ten spectra 1.1 min integration time. The inset shows a 1 h data set measured from 6 a.m. to 7 a.m.

average sulfur content of coal in Northeast China is 0.36%.²⁰ These data yield a total expected 24 h release of 0.26 ton/day. The slight discrepancy in the results could be explained by incomplete combustion of the fuel. However, this measurement campaign demonstrated the sturdiness and the real-time applicability of our novel broadband spectroscopic sensor to accurately monitor the variation of the SO₂ gas concentration.

4. Discussion and Conclusions

The design of the new sensor was found to be suitable for measurement of gas emissions in industrial environments. The sensor enabled direct recording of the absorption spectrum and acquisition of the SO₂ concentration using our data evaluation method without requiring any reference spectra. Flowing SO₂ at room temperature and at different concentrations was continuously monitored in simulations of industrial pollution emissions. The influence of dust in the light path on the concentration evaluation was studied in order to prove the accuracy and robustness of the SO₂ monitoring sensor. Ultimately, we carried out SO₂ concentration measurements in an industrial environment, where the selected target was a coal-fired boiler in Harbin, China. The field campaign yielded 24 h continuous recording and demonstrated the practicability of the sensor and the rationality of the data evaluation method. It should also be noted that the cost of the gas sensor is expected to be lower than for other real-time detection techniques having the same performance.

In the future, the measuring system will be further miniaturized and optimized, e.g., by replacing the computer by a single chip circuit, simplifying the mechanical and optical parts, and improving the performance of the CCD array to obtain higher SNR.

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