



# LUND UNIVERSITY

## Broadband spectroscopic sensor for real-time monitoring of industrial SO<sub>2</sub> emissions

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

*Published in:*  
Applied Optics

2007

[Link to publication](#)

*Citation for published version (APA):*

Xu, F., Zhang, Y., Somesfalean, G., Wang, H., Wu, S., & Zhang, Z. (2007). Broadband spectroscopic sensor for real-time monitoring of industrial SO<sub>2</sub> emissions. *Applied Optics*, 46(13), 2503-2506.

*Total number of authors:*

6

### General rights

Unless other specific re-use rights are stated the following general rights apply:

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

Read more about Creative commons licenses: <https://creativecommons.org/licenses/>

### Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

LUND UNIVERSITY

PO Box 117  
221 00 Lund  
+46 46-222 00 00

# Broadband spectroscopic sensor for real-time monitoring of industrial SO<sub>2</sub> emissions

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

A spectroscopic system for continuous real-time monitoring of SO<sub>2</sub> 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 SO<sub>2</sub> 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

OCIS codes: 300.1030, 300.6450, 120.0280.

## 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. SO<sub>2</sub> 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.<sup>1</sup> 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.<sup>2</sup> 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,<sup>3–6</sup> correlation spectroscopy is often employed in the petrochemical and gas industry for leak detection and remedy against explosion,<sup>7–10</sup> differential absorption lidar enables three-dimensional mapping and total flux measurements,<sup>11–13</sup> while tunable diode laser absorption spectroscopy provides miniaturization and high sensitivity detection.<sup>14</sup> 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 SO<sub>2</sub> concentrations by broadband absorption in the UV spectral range was reported.<sup>15</sup> 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 SO<sub>2</sub> 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

---

F. Xu, Y. Zhang, G. Somesfalean, and Z. Zhang (zhangzhiguo@hit.edu.cn) are with the Department of Physics, Harbin Institute of Technology, Harbin 150001, China. G. Somesfalean is also with the Department of Physics, Lund Institute of Technology, P.O. Box 118, SE-22100 Lund, Sweden. H. Wang and S. Wu are with the Institute of Combustion Engineering, Harbin Institute of Technology, Harbin 150001, China.

Received 12 July 2006; revised 12 December 2006; accepted 19 December 2006; posted 19 December 2006 (Doc. ID 72967); published 9 April 2007.

0003-6935/07/132503-04\$15.00/0

© 2007 Optical Society of America

continuous *in situ* measurements of SO<sub>2</sub> concentration.

## 2. Experiment

Figure 1 illustrates the setup of a new portable SO<sub>2</sub> 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 SO<sub>2</sub> 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

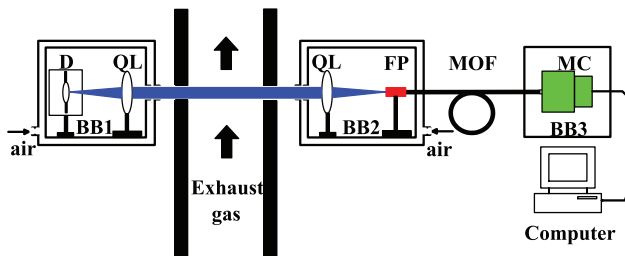


Fig. 1. (Color online) Experimental setup of the portable SO<sub>2</sub> sensor. The instrument is composed of three modular parts: BB1, BB2, and BB3. D, deuterium lamp; QL, quartz lens; FP, fiber port; MOF, multimode optical fiber; MC, monochromator and 2048 element CCD-array detector.

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 SO<sub>2</sub> concentration can be deduced from the Beer–Lambert law<sup>17</sup> 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  $\lambda_1$  and  $\lambda_2$ , 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 SO<sub>2</sub> gas concentration.

Prior to the field campaign, we simulated industrial pollution emissions in laboratory measurements of SO<sub>2</sub> gas flow at room temperature and at different concentrations. First, we considered the influence of particles in the light path on the SO<sub>2</sub> detection. Figure 2(a) shows a typical SO<sub>2</sub> transmission spectrum at ~300 nm for a gas flow of 1036 ppm SO<sub>2</sub> 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

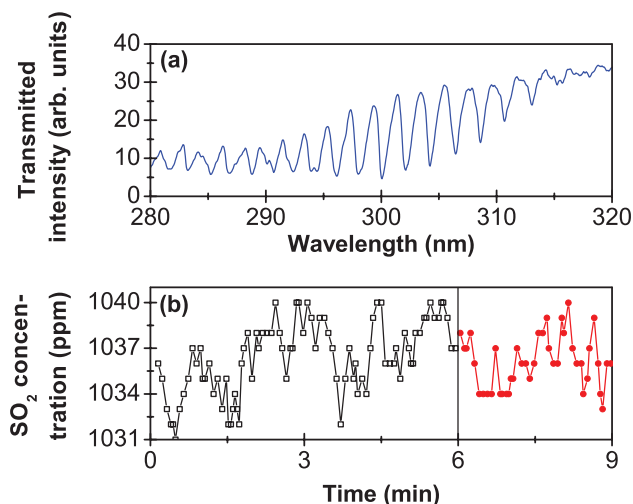


Fig. 2. (Color online) (a) Absorption spectrum of a flowing  $\text{SO}_2$  gas mixture of 1036 ppm concentration. (b) Influence of dust on the  $\text{SO}_2$  detection, evaluated by a short-time continuous recording of 126 data samples, using ten spectra averaging and 4 s integration time. For the 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  $\text{SO}_2$  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  $\text{SO}_2$  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  $\text{SO}_2$  concentrations were selected approximately equal to demonstrate the

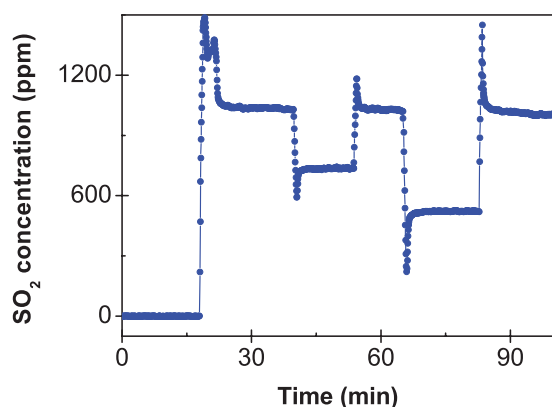


Fig. 3. (Color online) Continuous concentration recording of  $\text{SO}_2$  at normal temperature and pressure in a gas flow during laboratory simulation. Measurement of five different  $\text{SO}_2$  concentrations, i.e., 1040, 740, 1030, 520, and 1020, was performed.

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  $\text{SO}_2$  concentration are due to transients in the process of dilution of pure  $\text{SO}_2$  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  $\text{SO}_2$  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  $\sim 1$  ppm.<sup>15</sup>

A measurement campaign was carried out in early Spring 2006 in Harbin, China. The sensor was then tested for measurement of the  $\text{SO}_2$  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  $\text{SO}_2$  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  $\text{SO}_2$  concentration to be  $106 \pm 8$  ppm. To illustrate measurement details, a 1 h continuous recording is presented in the inset of Fig. 4. Using the obtained  $\text{SO}_2$  concentrations and the measured flux of the exhaust gas, which was  $50802 \text{ m}^3/\text{h}$ , we could calculate a 24 h total  $\text{SO}_2$  release of 0.24 ton/day. This value could be verified, since the coal consumption was estimated to 1.5 ton/h and the

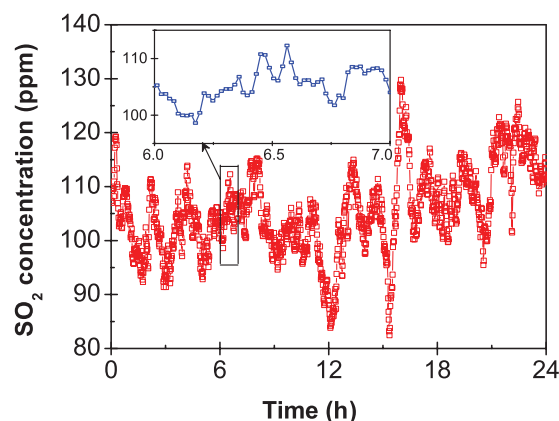


Fig. 4. (Color online) Twenty-four hours recording of the  $\text{SO}_2$  concentrations at a temperature of 411 K emitted from a coal-fired industrial boiler in China. Each point was obtained by averaging ten spectra 1.1 min integration time. The inset shows a 1 h data set measured from 6 a.m. to 7 a.m.

average sulfur content of coal in Northeast China is 0.36%.<sup>20</sup> 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 SO<sub>2</sub> 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 SO<sub>2</sub> concentration using our data evaluation method without requiring any reference spectra. Flowing SO<sub>2</sub> 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 SO<sub>2</sub> monitoring sensor. Ultimately, we carried out SO<sub>2</sub> 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.

This work was supported by the SIDA Asian-Swedish Research Partnership Programme and the 863 Hi-Tech Research and Development Programs of the People's Republic of China.

#### References

1. P. Weibring, M. Andersson, H. Edner, and S. Svanberg, "Remote monitoring of industrial emissions by combination of lidar and plume velocity measurements," *Appl. Phys. B* **66**, 383–388 (1998).
2. I. Linnerud, P. Kaspersen, and T. Jæger, "Gas monitoring in the process industry using diode laser spectroscopy," *Appl. Phys. B* **67**, 297–305 (1998).
3. H. Edner, P. Ragnarson, S. Spännare, and S. Svanberg, "Differential optical absorption spectroscopy (DOAS) system for urban atmospheric pollution monitoring," *Appl. Opt.* **32**, 327–333 (1993).
4. U. Platt, "Differential optical absorption spectroscopy (DOAS)," in *Air Monitoring by Spectroscopic Techniques*, M. W. Sigrist, ed. (Wiley, 1994), Vol. 127 of Chemical Physics Series pp. 27–84.
5. U. Platt and D. Perner, "Direct measurement of atmospheric CH<sub>2</sub>O, HNO<sub>2</sub>, O<sub>3</sub>, and SO<sub>2</sub> by differential absorption in the near UV," *J. Geophys. Res.* **85**, 7453–7458 (1980).
6. J. Mellqvist, H. Axelsson, and A. Rosén, "DOAS for flue gas monitoring-III. in-situ monitoring of sulfur dioxide, nitrogen monoxide and ammonia," *J. Quant. Spectrosc. Transfer* **56**, 225–240 (1996).
7. M. M. Millan and R. M. Hoff, "Remote sensing of air pollutants by correlation spectroscopy—instrumental response characteristics," *Atmos. Environ.* **12**, 853–864 (1978).
8. P. Weibring, H. Edner, S. Svanberg, G. Cecchi, L. Pantani, R. Ferrara, and T. Caltabiano, "Monitoring of volcanic sulphur dioxide emissions using differential absorption lidar (DIAL), differential optical absorption spectroscopy (DOAS), and correlation spectroscopy (COSPEC)," *Appl. Phys. B* **67**, 419–426 (1998).
9. C. Oppenheimer, P. Francis, and J. Stix, "Depletion rates of sulfur dioxide in tropospheric volcanic plumes," *Geophys. Res. Lett.* **25**, 2671–2674 (1998).
10. S. Svanberg, "Environmental and medical applications of photonic interactions," *Phys. Scr.* **T110**, 39–50 (2004).
11. H. Edner, K. Fredriksson, A. Sunesson, S. Svanberg, L. Unéus, and W. Wendt, "Mobile remote sensing system for atmospheric monitoring," *Appl. Opt.* **26**, 4330–4338 (1987).
12. P. Weibring, H. Edner, and S. Svanberg, "Versatile mobile lidar system for environmental monitoring," *Appl. Opt.* **42**, 3583–3594 (2003).
13. P. Weibring, J. Swartling, H. Edner, S. Svanberg, T. Caltabiano, D. Condarelli, G. Cecchi, and L. Pantani, "Optical monitoring of volcanic sulphur dioxide emissions—comparison between four different remote-sensing spectroscopic techniques," *Opt. Lasers Eng.* **37**, 267–284 (2002).
14. G. Somesfalean, Z. G. Zhang, M. Sjöholm, and S. Svanberg, "All-diode-laser ultraviolet absorption spectroscopy for sulfur dioxide detection," *Appl. Phys. B* **80**, 1021–1025 (2005).
15. F. Xu, Z. Lv, Y. G. Zhang, G. Somesfalean, and Z. G. Zhang, "Concentration evaluation method using broadband absorption spectroscopy for sulfur dioxide monitoring," *Appl. Phys. Lett.* **88**, 231109 (2006).
16. F. Xu, Y. G. Zhang, G. Somesfalean, Z. G. Zhang, H. S. Wang, and S. H. Wu, "Temperature-corrected spectroscopic evaluation method for gas concentration monitoring," *Appl. Phys. B* **86**, 361–364 (2007).
17. S. Svanberg, in *Atomic and Molecular Spectroscopy: Basic Aspects and Practical Applications* (Springer, 2004), pp. 164–165.
18. D. J. Brassington, "Measurement of the SO<sub>2</sub> absorption spectrum between 297 and 316 nm using a tunable dye laser," *Laboratory Note RD/L/N 184/79* (Central Electricity Research Laboratories, Leatherhead, UK, 1979).
19. D. J. Brassington, "Sulfur dioxide absorption cross-section measurements from 290 nm to 317 nm," *Appl. Opt.* **20**, 3774–3779 (1981).
20. Z. Y. Zhang, W. H. Li, Z. G. Xu, and S. J. Qu, in *On the Appropriate Processing and Utilization of Coal* (Chinese U. of Mineralogy, 2000), pp. 53–55.