P2-6 An In-situ Gas Analyzer Based on Tunable Diode Laser Absorption Spectroscopy

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ABSTRACT

An in-situ gas analyzer based on near-infrared Tunable Diode Laser Absorption Spectroscopy (TDLAS) has been developed.

The features of this system are as follows:

(1) In-furnace gases can be directly measured in a large-scale test plant or field plant.
(2) Simultaneous measurement of gases and solid particles can be performed.
(3) Laser wavelength can be automatically stabilized.
(4) The effect of background emission can be eliminated.

The detection limit of NO was estimated to be 1.3 ppm-m/$Hz^{1/2}$.

1. INTRODUCTION

For combustion diagnostics and controls, it is necessary to develop in-situ and real-time measurement techniques for gases in combustion processes. Recently, the performance of visible and near-infrared diode lasers has improved, achieving sufficient spectroscopic-quality to be used as light sources for high-resolution spectroscopy. Therefore, we expect to be able to develop new gas analyzers featuring high-sensitivity and non-interference by coexisting gases, and allowing in-situ and real-time measurement. Accordingly, we are developing a technique known as Tunable Diode Laser Absorption Spectroscopy (TDLAS).

In the near-infrared TDLAS system, InGaAs distributed-feedback (DFB) diode lasers at wavelengths lower than 2 μ m are used as radiation sources. The diode lasers operate at room temperature, and oscillate in a single longitudinal mode with over 1mW of power. This wavelength region corresponds to the vibrational overtone or combination bands of molecular species, and a number of molecules relevant to combustion, such as H_2O, CO, CO_2, CH_4 and NH_3, have been investigated by means of near-infrared TDLAS.[1] The near-infrared absorption spectra of nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O) have been investigated using a high-resolution Fourier-transform infrared spectrometer (FTIR), and the TDLAS spectra of NO and N_2O have been observed using InGaAs-DFB diode lasers designed to access their absorption lines[2]. We verified that nitrogen oxides (NO, NO_2, N_2O, i.e., NOx) which make up one of the most important species in combustion, could be detected in the near-infrared region. In-situ gas analyzers using near-infrared Tunable Diode Laser Absorption Spectroscopy (TDLAS) are accordingly being developed for combustion diagnostics and controls.

2. EXPERIMENTAL

Figure 1 shows the schematic diagram of the experimental setup of the TDLAS system which was used for our measurements. For light sources, we used InGaAs diode lasers having a strained multi-quantum-well (MQW) distributed feedback (DFB) structure. These are new custom devices available through Anritsu Corp. and are superior because they are specifically designed to access the near-infrared bands of NOx[3]. The typical characteristics of 1.8 μ m DFB diode lasers are output power of 4mW at operating current of 100mA at 25℃, lasing peak wavelength of 1.797 μ m for NO , and spectral bandwidth less than 2MHz.

The laser wavelength can be roughly tuned by varying the laser temperature (tuning rate of 100 pm/℃) , while high-resolution tuning is accomplished by variation of the laser diode injection current (tuning rate of 10pm/mA). The diode laser was set in an LD module with a Pertie element and controlled by means of an LD driver unit including temperature and current controllers.

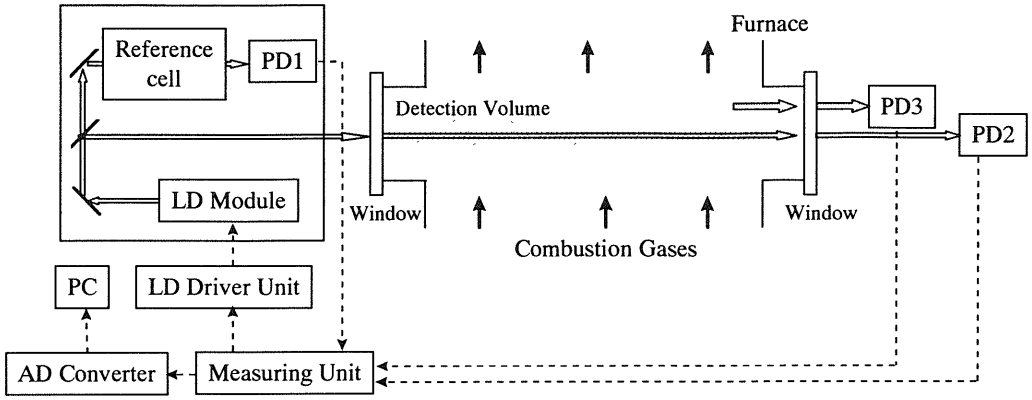

Fig. 1 Schematic Diagram of the Experimental Setup of the TDLAS system

The output beam from the diode laser was split into two beams by an half mirror. One was used for the absorption experiment, and the other was used for calibration of gas concentration and wavelength locking using the reference cell. The laser wavelength was calibrated with a Michelson interferometer wavelength meter (Burleigh Instruments Inc., WA-1000). The beams transmitted through the detection volume were detected by an InGaAs PIN photodiode detector (Hamamatsu Photonics K.K., G5051-01) followed by a measuring unit.

In our system, one of two measuring methods can be selected. For the observation of the absorption spectrum, the laser wavelength was slowly swept by a current ramp (0.5 or 0.01Hz) applied to the injection current. For the observation of the long-term trend of concentration, the laser wavelength is locked at a fixed wavelength.

The concentration of gas in the detection volume is calibrated by the concentration of reference gas, the path length of the reference cell, and the path length of the detection volume, as calculated using a PC.

Figure 2 shows the schematic diagram of the measuring unit in Figure 1.

(1) Dual modulation

As a dual modulation technique is adopted, two additional sinusoidal modulations (f=10kHz and w=500Hz) were superimposed on the injection current. The laser wavelength was modulated at frequencies of 10kHz and 500Hz and the resulting signal was demodulated by a phase sensitive detector

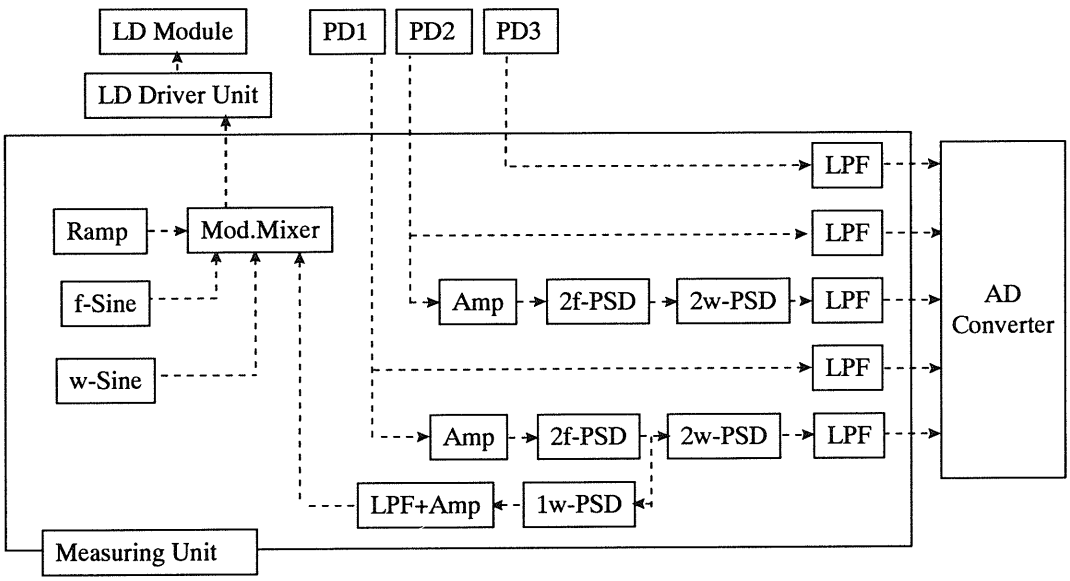

Fig. 2 Schematic Diagram of the Measuring Unit

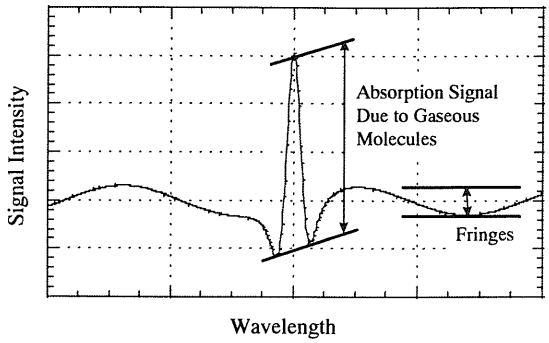

Fig.3 Absorption Signal Accompanied by Fringes

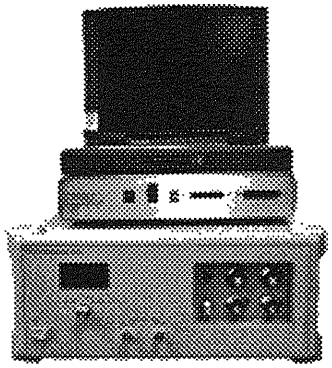

Fig.4 Photograph of the TDLAS Apparatus (Measuring Unit, AD Converter, and PC)

at 20kHz and 1kHz.

Interference fringes in the absorption spectrum which are caused by reflection at the optic components were a problem. Even after careful removal of the fringes, small-amplitude fringes often remained. In particular, amplitude fluctuation was accompanied by temperature fluctuation of optics set in the open air near the test plant, with peak absorption intensity also tending to fluctuate. However, the dual modulation technique has resolved this problem. Figure 3 shows the schematic spectrum which contains the second derivatives of Gaussian-shaped absorption signal due to gaseous molecules, and sinusoidal-shaped fringes are overlapped in the spectrum. The second derivatives of absorption detected by PD2 are obtained by demodulation by 2f-PSD and the peak-to-peak absorption intensity is obtained by demodulation by 2w-PSD. Therefore, the peak intensity can be measured whether or not fringes exist. The dual modulation technique enabled us to perform highly sensitive and long-term stable measurement

(2) Simultaneous measurement of the concentration of gas and particles

Absorption due to gaseous molecules depends on laser wavelength. However, the absorption or scattering of solid particles, such as soot, is independent of laser wavelength. Consequently, if we measure both the modulated component and the DC component of transmitted laser intensity, it is possible to simultaneously measure the concentration of gas and particles[4].

In Figure 2, detected laser intensity (output of PD2) is split into the modulated component (to amplifier followed by phase sensitive detector (2f-PSD), and the DC component (to low pass filter (LPF) in order to simultaneously measure the concentration of gas and particles.

(3) Wavelength locking

In order to perform long-term stable measurement, the laser wavelength is locked at the absorption center of the reference gas.

The de-modulated signal of output of PD1 by 2f-

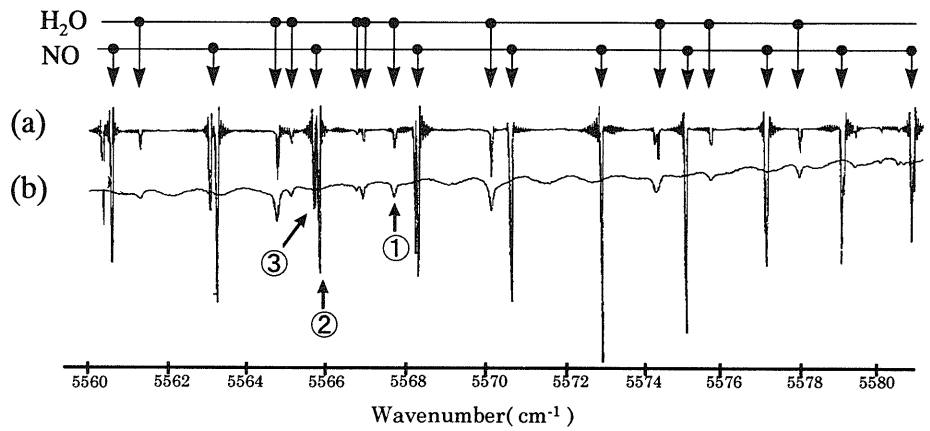

Fig.5 Near-Infrared Absorption Spectra of NO and H_2O

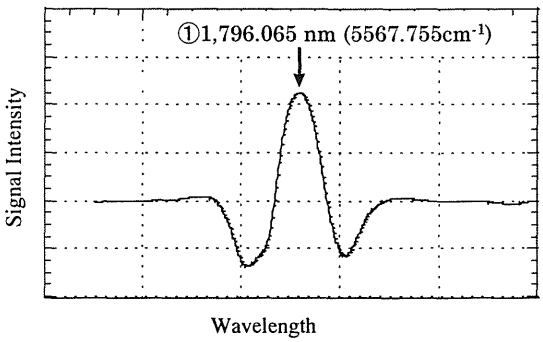

Fig.6 TDLAS Spectrum of H_2O

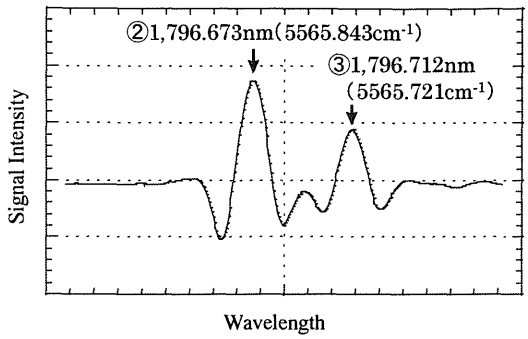

Fig.7 TDLAS Spectrum of NO

PSD and 1w-PSD is the third derivative of the absorption signal of the reference gas. This signal is proportional to the difference between the center of absorption and the laser wavelength around the center of absorption.

(4) Elimination of background emission

Since the output of the phase sensitive detector is proportional to the gas concentration and laser intensity, it must be divided by the laser intensity in order to obtain the gas concentration. The intensity detected by photodiode PD2 contains both the transmitted laser intensity and background emission from the flame in the furnace. Therefore, background emission intensity is detected by the photodiode PD3 which is set on the off-axis of laser, and background emission is eliminated, and the transmitted laser intensity is obtained by subtraction of the output of PD3 from output of PD2.

Figure 4 shows a photograph of the TDLAS apparatus, consisting of the measuring unit, AD converter and PC.

3. RESULTS AND DISCUSSION

Figure 5 shows the near-infrared absorption spectra observed by Fourier transform spectroscopy[2]. Trace (a) represents the absorption of NO gas, and trace (b) represents the background spectrum which is due to the water vapor in the optical path.

Figure 6 shows the absorption spectrum of water vapor in the optical path by the TDLAS method. The trace in this figure represents the fourth derivative of the absorption line shape, which was obtained by dual modulation, and the absorption is assigned to line No.① in Figure 5, which is shown in the HITRAN 96 database.

For the detection of nitric oxide (NO), a sample gas was held in a single-path absorption cell made of stainless steel and having wedged windows, and with an effective path length of 150mm. Commercial premixed and calibrated NO (2.93%) gases were used as samples.

The result of measuring the absorption spectrum of NO at 1.7967 μ m is shown in Figure 7. The absorption lines in this spectrum were assigned to the rotational structure named R(6.5) of the vibrational third overtone band of NO in the electronic state of $^2\pi_{1/2}$ and $^2\pi_{3/2}$, respectively. From this spectrum the detection limit of NO was estimated to be 1.3 ppm-m/$Hz^{1/2}$.

4. CONCLUSION

An in-situ gas analyzer using near-infrared Tunable Diode Laser Absorption Spectroscopy (TDLAS) was developed. The detection limit of NO was estimated to be 1.3 ppm-m/$Hz^{1/2}$.

Research is underway to further develop TDLAS techniques and apply this analyzer system to the direct measurement of real furnaces and the analysis of phenomena in combustion situations.

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