



Development of High-Precision Monitoring Technology for Green House Gases

KENJI MUTA*¹ MASAZUMI TANOURA*¹ MASAKI IJIMA*²
 TOMOYUKI KIKUGAWA*³ KO NAKAYA*⁴

High-precision monitoring technology has been developed to monitor the production of greenhouse gases (CO₂, CH₄, and N₂O) in the vicinity of industrial plants and in the general atmosphere. This technology is based on tunable diode laser absorption spectroscopy, and, in combination with proprietary wavelength modulation and laser wavelength stabilization technologies, offers superior sensitivity, responsiveness, and stability.

1. Introduction

Reductions in emissions of greenhouse gases consisting of CO₂, CH₄, and N₂O are being sought in the context of practical programs aimed at securing both environmental and economic viability in response to global warming concerns. Greenhouse gas monitoring is, therefore, essential to the quantitative assessment and verification of the effectiveness of such programs.

The authors of the present report have developed gas concentration measurement systems using tunable diode laser absorption spectroscopy (TDLAS) to monitor the production of O₂, CO, NO_x, and other gases in the furnaces of large installations such as power generation boilers and large-scale incinerator plants. The effectiveness of these systems has been confirmed in the measurement of gas concentrations in the furnaces of both pilot plants and actual installations^{(1)–(3)}, as well as in the measurement of gas concentrations of CO₂ due to automotive exhaust⁽⁴⁾.

The method discussed here is not affected by coexisting gases, and enables continuous measurement of gas concentrations with high precision. This method is very close to practical application as a technology for monitoring the emission and absorption points, as well as the wide-area monitoring of greenhouse gases. This report presents the principles and characteristics of this method, together with examples of greenhouse gas measurements and discussion of possible applications of the method.

Table 1 Measurement wavelength of green house gases and air pollutants

	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9 μm
CO ₂	-	-	-	-	-	-	-	-
CH ₄						—	—	
N ₂ O	-	-	-	-	-	-	-	-
CO	-				—			
NO							—	
NO ₂							-	

2. Measurement principle and characteristics

2.1 Measurement principles

The method reported here is based on TDLAS. (Tunable Diode Laser Absorption Spectroscopy) Gaseous molecules are subject to characteristic absorption caused by molecular vibration in the in the 1–2 μm near-infrared region.

Table 1 shows the characteristic absorption bands for CO₂, CH₄, N₂O, etc⁽⁵⁾. Each absorption band is made up of many absorption lines, and when molecules are irradiated with light having a wavelength that matches one of these absorption lines, the molecules absorb the light and information on molecular concentration can be obtained from the absorption intensity.

2.2 Structure and functions of apparatus

Figure 1 presents a block diagram of the apparatus, while the photograph at the top of this page shows the appearance of the measurement apparatus, which is composed of the following components⁽⁶⁾:

- (1) Light source: Distributed-Feed Back type (MQW-DFB) InGaAs(P) laser diode (LD) developed by Anritsu Corporation for gas detection applications, featuring a strained multi-quantum well structure for the oscillation of near-infrared light at room temperature, and which emits monochromatic light in response to specific species of gas⁽⁷⁾;
- (2) Detector: InGaAs photo-diodes (PD) for the measurement of laser light intensity;
- (3) Reference cell: Used for calibration and laser wavelength stabilization, which is done through the introduction of a standard gas at a known concentration and constant pressure;
- (4) Measurement unit: Obtains information on concentration by modulating the laser wavelength and separating out signals synchronized with the frequency of the modulated wavelength from among the optical signals received; and
- (5) LD driver unit: Used to set the temperature and current of laser diode, as well as the oscillation wavelength of the laser.

*1 Advanced Technology Research Center, Technical Headquarters

*2 Plant and Transportation Systems Engineering & Construction Center

*3 Anritsu Corporation

*4 Central Research Institute of Electric Power Industry

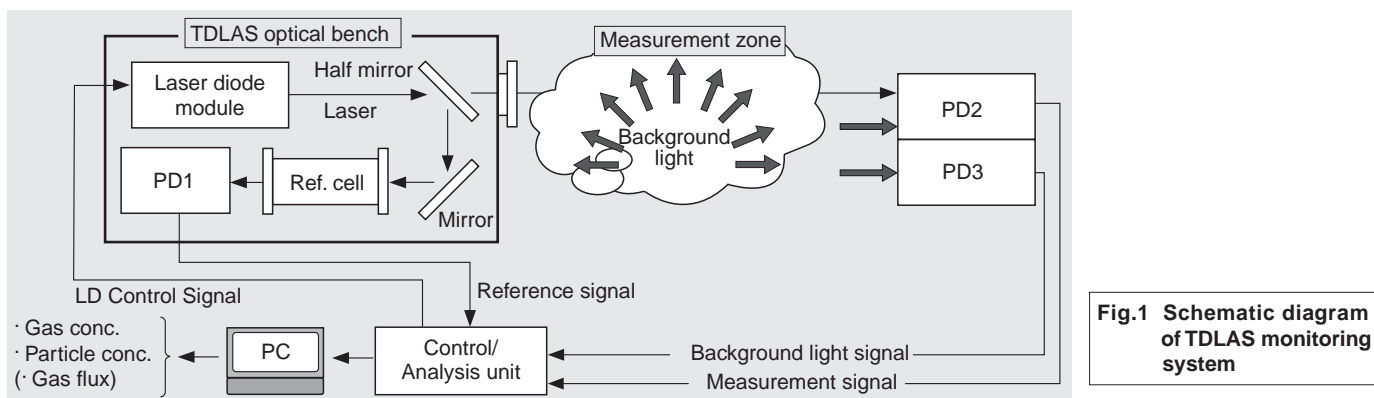


Fig.1 Schematic diagram of TDLAS monitoring system

Laser light emitted by the LD is divided in two by means of a half mirror, with one stream passing through the reference cell and received by PD1 for use in gas concentration calibration and wavelength stabilization. The other stream of laser light is fed through the measurement zone and received by PD2, with the concentration calculated from the amount of light absorbed in the zone. Meanwhile, PD3 is installed at a location removed from the optical axis of the laser light in order to cancel the influence of any light other than that originating from the laser (e.g., flame or sunlight). The measurement unit processes the signals from the three photo-diodes, and measures the gas concentration.

This technology utilizes LD characteristics that enable control of the laser oscillation wavelength by means of the temperature of LD or input current, meaning that the laser wavelength can be modulated by adjusting the input current to the LD. Only the frequency components, which are synchronized with the modulation frequencies, can be detected from among the output signal of PD using synchronous detection. Since the light absorption due to the gas depends on the light wavelength, the wavelength modulation method enables high-precision measurement of the light absorption.

In addition, using the reference cell, proprietary techniques have been developed to stabilize the measurement laser wavelength and dual modulation of two modulated frequencies, thus achieving substantially greater sensitivity than that normally realized using conventional TDLAS methods. Impressive gains have been achieved in terms of long-term measurement stability, making it possible to conduct outdoor measurements over long periods of time.

2.3 Characteristics

The TDLAS-based gas monitoring equipment possesses the following characteristics.

- (1) It has a high-sensitivity and real-time measurement capability for gas concentrations at the ppm level and lower.
- (2) It is capable of measuring gas and particle concentrations simultaneously, while remaining unaffected by coexisting substances such as gases, dust, or raindrops.
- (3) It is capable of rapid response with no need for sample intake, and no need for dust filters. It is also maintenance-free for long periods of time.

Table 2 Detection limits of gases by TDLAS method

	Species	Sensitivity*1*2	Laboratory	Furnace	Measurement Length
					30 m
Global Warming	CO ₂	3.0 ppm·m	○	○*3	30 m
	N ₂ O	3.0	○	○	
	CH ₄	{0.07}	○	—	
Combustion	H ₂ O	{0.002} (0.73)	○	○	
	O ₂	9.1	○	○	
	CO	3.6	○	○	
	NO	1.3	○	—	
	NO ₂	{0.01} (2.0)	○	—	
	HCl	{0.006} (0.56)	○	○	
	NH ₃	0.06	○	○	

*1 { } : Expected sensitivity, () : Present sensitivity

*2 Allowable concentration of dust: 10 g/m³N
(equivalent to the condition of the following:
▪ the inside of oil-fired boiler furnace
▪ the gas duct of pulverized-coal fired boiler)

*3 Measurement of automobile exhaust gas

○ : performed
— : not performed

- (4) It is a compact and low cost apparatus that allows continuous, automated measurement.

2.4 Greenhouse gases that can be measured

The species of gas that can be measured using the TDLAS method are shown in **Table 2**, together with measurement sensitivities and examples. The unit of measurement sensitivity employed (ppm·m) represents the lower limit of measurement for changes in the concentration of the target gas along the optical path with a measurement distance of one meter.

For instance, the measurement sensitivity for CO₂ is 3 ppm·m, or 3 ppm at a measurement distance of one meter, or 0.03 ppm at a measurement distance of 100 meters. As noted in the table, the representative greenhouse gases CO₂, CH₄, and N₂O can all be measured levels of several ppm·m.

3. Examples of Measurement of Greenhouse Gases

3.1 Measurement of N₂O concentrations in an incinerator

The TDLAS method was applied to measure the concentration of N₂O present in exhaust gas at the furnace outlet of an actual toxic waste incinerator.

As shown in **Fig. 2(a)**, optical windows were installed on either side in the vicinity of the furnace outlet, with the light source placed on one side and the receptor on the other, and a laser operating in between for the continuous measurement of N₂O concentrations. For the purpose of comparison, a gas sampling type N₂O meter was placed at nearly the same location. The measurement results are presented in Fig. 2(b).

Note that the results for the TDLAS method show the average concentration of N₂O across the entire furnace width (90 cm), while the results for the sampling type meter represent the local concentration at the sampling location. The average values for both sets of measurements are in agreement at about 60 ppm. In addition, it was also possible to ascertain any sudden changes in concentration that would occur due to fluctuations in the amount of fuel, etc., in real time using the TDLAS method, as opposed to a delay of about two minutes using the conventional sampling type concentration meter. The real-time capabilities of the TDLAS method were accordingly confirmed.

3.2 Measurement of CO₂ concentrations in the atmosphere

Preparatory consideration is being given to applying this technology to monitoring CO₂ in underground CO₂ processing plants, and for use in monitoring the amount of CO₂ absorption in forests. **Figure 3** shows the TDLAS measurement results obtained for CO₂ in the atmosphere at a measurement distance of 25 m. Measurement of CO₂ in the atmosphere was performed using a light source placed at ground level, and with the receptor 25 m distant. Also,

in order to verify the appropriateness of the concentration measurement values obtained, measurement was also performed using a gas sampling type CO₂ concentration meter at the center of the measurement optical path.

Examples of the measurement results are presented in Fig. 3(b). The average values recorded by the TDLAS and gas sampling methods were in agreement. It is noteworthy that the noise level associated with the TDLAS measurement data was 1/100th of the TDLAS measurement data shown in Fig. 3(b). The data in Fig. 3(b) reflects fluctuations in the actual CO₂ concentration measured.

This shows that the TDLAS method is capable of detecting atmospheric changes and the effects on the surrounding environment from passing vehicles, demonstrating the possibility of application in real-time monitoring of actual phenomena.

4. Future Application and Issues

Figure 4 shows candidate areas for the applied development of this technology. Various applications are anticipated for industrial areas, urban environments, and the natural world.

4.1 Wide area monitoring

Applications of the TDLAS-based gas monitoring method are being considered for measuring CO₂ levels in underground storage systems, the detection of CH₄ leaks in natural gas plants and pipelines, and for various other applications including urban environmental monitoring in tunnels and at intersections.

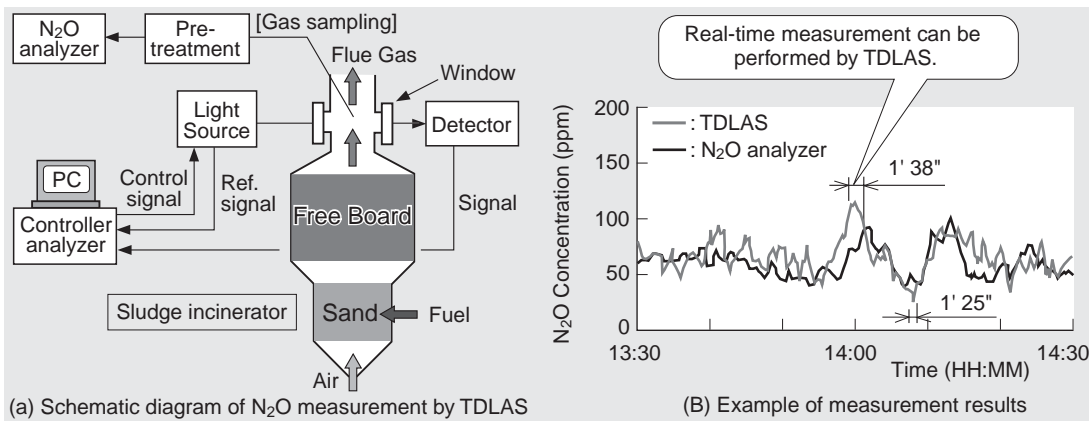


Fig. 2 In-furnace measurement of N₂O

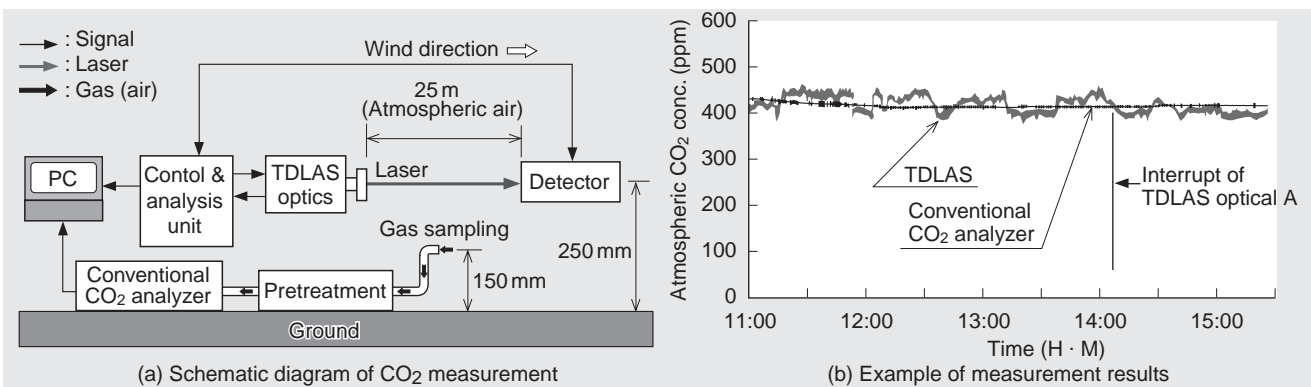


Fig. 3 Measurement of atmospheric CO₂

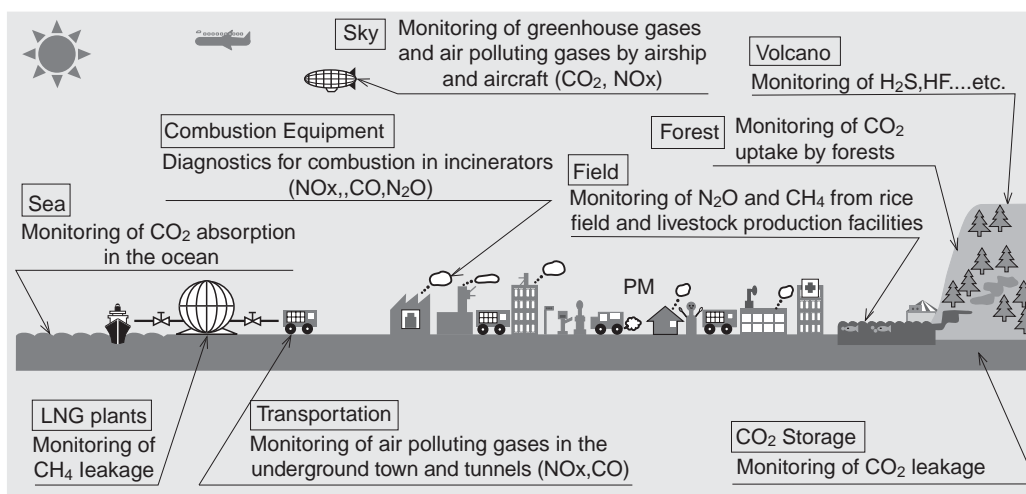


Fig. 4 Application of a wide-area monitoring of greenhouse gases and air pollutants

Longer measurement distances are required for wide area monitoring, and current development work is aimed at achieving a distance of 1 km through the development of automatic control mechanisms for the laser optical axis, used in combination with convergent optical systems. The addition of laser scanning functions would enable area measurements, and consideration is being given for plans for the application of gas leakage monitoring over wide areas of one square kilometer (Fig. 4).

4.2 Flux measurement

Technology for the measurement of gas fluxes (the amount of perpendicular shift in the measurement target gas) is being developed through deployment of TDLAS-based gas concentration measurement. When the atmosphere along a laser optical path is in a turbulent state, the refractive index along the path changes irregularly, and the laser intensity received also correspondingly fluctuates irregularly. Accordingly, the kinetic and thermal flux along the optical path can be measured from the amount of fluctuation (this is known as the scintillation method).

Technology for the measurement of gas flux is currently being developed through the combination of this method with TDLAS-based concentration measurement. The scale of this technique would be between that of the localized flux measurement method known as vortex correlation and that of remote sensing from observation satellites, such that integration and analysis of the resulting data could enable the construction of wide area monitoring networks covering several hundred square kilometers.

5. Conclusion

Technology has been developed for the high-precision monitoring of greenhouse gases such as CO_2 , CH_4 , and N_2O . Based on the TDLAS method, this technology allows automated

measurement without sampling. Moreover, as a result of the proprietary development of wavelength modulation and laser wavelength stabilization techniques, high measurement sensitivity, responsiveness, and stability have been achieved without any influence from coexisting substances.

Future applications include underground monitoring of CO_2 storage systems and gas leakages, as well as the simultaneous promotion of technologies for wide area gas concentration monitoring and gas flux measurement. Such technology could be employed for use in investigation and verification as required for emissions rights trading, including the measurement of the amount of CO_2 absorbed by forests or estimating the amount of CH_4 released by landfills.

The authors wish to express their sincere appreciation to Dr. Koichi Yamada of the Research Institute for Environmental Management Technology of the National Institute of Advanced Industrial Science and Technology (AIST), for his guidance on the evaluation of the temperature dependence of the absorption strength of N_2O molecules.

References

- (1) Matsudera et al., Application of TDLAS for Flue Gas Measurement in the Sludge Incinerator, Proceeding of 40th Meeting of Japan Sewage Works Association (2003), p.976
- (2) Muta K, et al., Simultaneous Detection of oxygen molecule and soot particles by visible diode laser absorption spectroscopy, European Sensing Symposium (1997)
- (3) Muta K, et al., In-situ Measurement of CO by Tunable Diode Laser Absorption Spectroscopy in a Large Scale Waste Test Furnace, International Laser Sensing Symposium (1999)
- (4) Tanoura M, et al., Tunable diode laser measurements of nitrous oxide and carbon dioxide at 1.5 μm , Conference on Tunable Diode Laser Spectroscopy (2001)
- (5) Tanoura M, et al., Detection of nitrogen oxides by high resolution near-infrared absorption spectroscopy, European Sensing Symposium (1997)
- (6) Tanoura M, et al., An In-situ Gas Analyzer Based on Tunable Diode Laser Absorption Spectroscopy, International Laser Sensing Symposium (1999)
- (7) Tohmon, R. et al., Distributed Feedback Laser Diodes for Laser Gas Sensing, Anritsu Technical Bulletin No.76 (1998)



Kenji Muta



Masazumi Tanoura



Masaki Iijima



Tomoyuki Kikugawa



Ko Nakaya