An approach of open-path gas sensor based on tunable diode laser absorption spectroscopy

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Tunable diode laser absorption spectroscopy (TDLAS) is a new method to detect trace-gas qualitatively or quantificationally based on the scan characteristic of the diode laser to obtain the absorption spectroscopy in the characteristic absorption region. A time-sharing scanning open-path TDLAS system using two near infrared distributed feedback (DFB) tunable diode lasers is designed to detect CH_4 and H_2S in leakage of natural gas. A low-cost Fresnel lens is used in this system as receiving optics which receives the laser beam reflected by a solid corner cube reflector with a distance of up to about 60 m. High sensitivity is achieved by means of wavelength-modulation spectroscopy with second-harmonic detection. The minimum detection limits of 1.1 ppm·m for CH_4 and 15 ppm·m for H_2S are demonstrated with a total optical path of 120 m. The simulation monitoring experiment of nature gas leakage was carried out with this system. According to the receiving light efficiency of optical system and detectable minimum light intensity of detection, the detectable optical path of the system can achieve $1-2$ km. The sensor is suitable for natural gas leakage monitoring application.

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Tunable diode laser absorption spectroscopy (TDLAS) technology has been widely employed in detecting atmospheric trace gases due to its high sensitivity, high selectivity, and fast time response. High sensitivity detection is obtained by wavelength or frequency modulation spectroscopy. In addition, it could also greatly improve the detection sensitivity by adopting a long-path technique[1]. Compared with the long-path system with multiple-reflection cell, the long open-path system can accurately represent a large spatial area, particularly in poorly mixed atmosphere[2], and can directly provide accurate, simultaneous measurements of the average concentration of a number of trace gases over long open paths. Moreover, long open-path system contains the information of atmospheric flow during the measuring process of gas concentration, so it can also monitor the gas emission flux[3].

The leakage of natural gas leads to the waste of energy sources and pollution of environment, resulting in a fatal economic loss. The conventional approach to low-level (ppm) leak detection is based on flame ionization detectors[4], and to a lesser degree on Fourier transform infrared (FTIR) spectrometers, but such technology measures concentration at only a single point. Such point measurements can suffer from wall and reaction effects due to sample-handling if there are highly reactive species in trace concentrations, such as HNO_3, H_2S or NH_3, to be detected. In addition, all point-sampling methods can be easily affected by neighboring pollutant sources. This makes the results only locally representative and not suitable for application with numerical models.

In this paper, a time-sharing scanning open-path TDLAS system with long optical path is reported for natural gas detection. Two pigtailed InGaAs distributed feedback (DFB) diode lasers emitting at 1.65 and 1.58 μm are used to probe a single absorption line of CH_4 and H_2S separately. A low-cost Fresnel lens is used in this system as receiving optics. Combining with wavelength modulation spectroscopy and second-harmonic detection technology, the minimum detection limits achieved with this system are 1.1 ppm·m for CH_4 and 15 ppm·m for H_2S.

Figure 1 shows a schematic of the time-sharing scanning open-path natural gas sensor based on TDLAS. The system can be divided into two parts: electronics module and optics part. The electronics module contains the laser, laser temperature and current controller, signal generator, lock-in amplifier, preliminary amplifier, and data processing components. The optics consists of an integrated transmitter/receiver telescope and retroreflector array. The main component of the transmitter/receiver system is the Fresnel lens. Compared with the common lens, the cubage and weight of Fresnel lens are much smaller. Moreover, the focal spot of Fresnel lens is smaller than that of common lens with the same caliber, and its aperture is easier to be scaled up.

Both diode lasers are commercially available near-infrared (NIR) DFB lasers from NEL NTT Electronics. They are driven by independent current controller and temperature controller. The two diode lasers are simultaneously modulated by the same sinusoidal waveform at frequency of 5 kHz, and slowly scanned through the each absorption line by two-way intermittent sawtooth waveform at frequency of 50 Hz generated by self-developed time-sharing scanning circuit board. Figure 2 shows the scanning signal of two lasers and time sequence of the system. On a scan periodicity T, one laser wavelength is scanned through the absorption line of measured gas, such as CH_4 spectral regions at T_1, and the other is modulated at fixed wavelength offsetting the absorption line.

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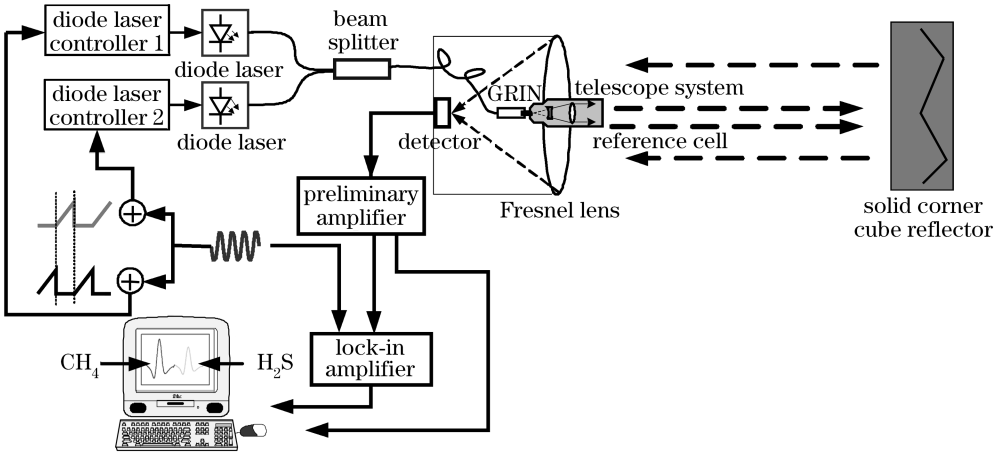

Fig. 1. Schematic of the time-sharing scanning open-path TDLAS system.

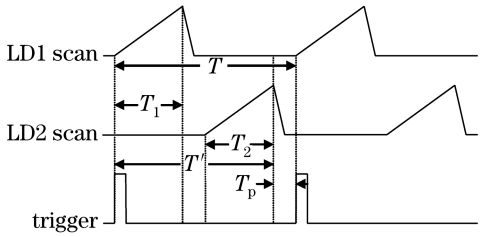

Fig. 2. Scanning signal of two lasers and time sequence of the system. T: system periodicity; T': data acquistition periodicity; $T_{\rm p}$: data processing time; T_1: CH_4 spectral region; T_2: H_2S spectral region.

The scanning of the two lasers is alternate, and the time-lag $T_{\rm p}$ of the two-way sawtooth is the time of data processing. The two laser lights are first coupled in a 2:1 beam splitter and then transmitted into telescope system through a standard single-mode optical fiber with a self-focusing lens. The laser beam is magnified ten times by a telescope system and the divergence angle is about 0.4 mrad; the space, namely 10 cm between the two lenses of the telescope, is used as a reference cell. The laser emitted from the telescope is reflected by a retro-reflector with 100-mm diameter and the reflected laser beam is focused onto the detector by Fresnel lens with 200-mm diameter. The electronic signal from the detector is sent to the preliminary amplifier, and the amplified signal is then divided into two parts, one is sent to the lock-in amplifier to get the $2f$ absorption signal, and the other passes through a low-pass filter and is linearly fitted to obtain an equalizing value for the laser intensity. The detected signal is then normalized by the fitted laser intensity to eliminate the influence of the laser intensity fluctuation arriving at the detector[5,6]. Every 50 of the normalized $2f$ signals are averaged to give a measurement absorption spectrum.

In an open-path TDLAS system, the laser beam propagates in the open atmosphere over an adequate absorption path length and is absorbed *in situ* by the molecules of interest. The absorption of laser energy is related to the molecular absorption based on the Beer-Lambert law and a molecular model[7]. Beer-Lambert law can be expressed as

$$I(\lambda) = I_0(\lambda) \exp\left[-A(\lambda)\right], \tag{1}$$

$$A(\lambda) = \sigma(\lambda) CL, \tag{2}$$

where $I_0(\lambda)$ is the transmitted intensity in the absence of absorbing species; $I(\lambda)$ is the laser intensity after passing through the object gas; $A(\lambda)$ is the absorption rate; $\sigma(\lambda)$ is the molecule absorption coefficient in standard state, $\sigma(\lambda) \approx \sigma_0$; C is the concentration of the absorbing species in molecules per unit volume; L is the optical path length. For harmonic detection, one is only concerned with weak absorption lines, i.e., we can assume that the value of $\sigma_0 L$ is confined to $\sigma_0 L \ll 0.05$. The second harmonic signal obtained by demodulation could be expressed as[8]

$$I_{2f} \propto I_0(v) \sigma_0 CL. \tag{3}$$

From Eq. (3), we can see that the product of concentration and light intensity signal I_0 is proportional to I_{2f}. The $2f$ signal collected by data collector is fitted by standard concentration signal with least square fitting to gain the original concentration. Then the original concentration is processed to eliminate the influence of the laser intensity fluctuation arriving at the detector.

The calibration of the system is achieved through the reference absorption cell filled with standard high concentration CH_4 and H_2S gas sample in the optical beam path, and then, filled with 1-atm nitrogen as background. Certainly, invariant concentration in the air is presumed during the calibration. Figures 3(a) and (b) show the single CH_4 and H_2S $2f$ signals when the two lasers operate separately, and Fig. 3(c) shows the $2f$ signal simultaneously detected by the same detector. From this figure we can see that harmonic signals of simultaneous measurement maintain the basic characteristics of those at single measurements, and the possibility of cross-interference due to the time sequence of the absorption signal is eliminated. In addition, we can see the obvious traces of noise superimposed after using the time-sharing method.

The time-sharing scanning system performance was tested by filling the 10-cm reference cell flushed with standard CH_4 and H_2S gas sample. Figure 4 shows the normalized $2f$ signals at different CH_4 and H_2S gas

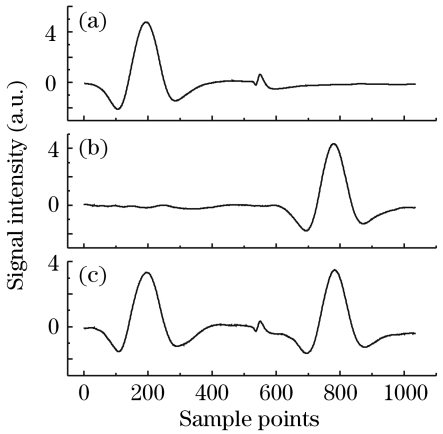

Fig. 3. Harmonic signals before and after multiplexing. (a) Single CH_4 absorbing signal; (b) single H_2S absorbing signal; (c) CH_4 and H_2S absorbing signal of simultaneous measurement.

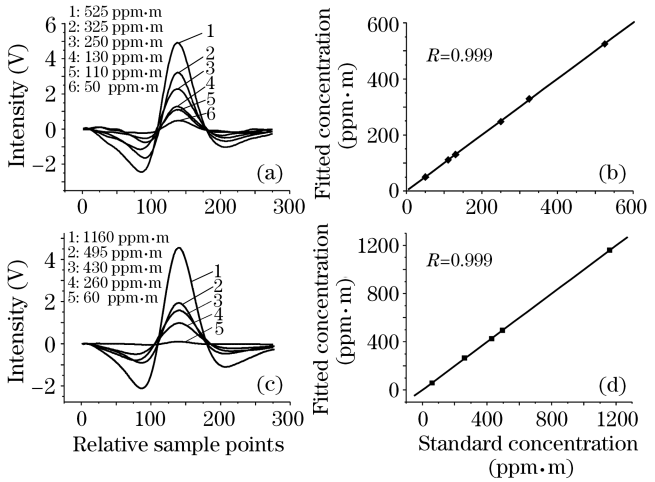

Fig. 4. (a) $2f$ absorption spectra and (b) fitted concentration as a function of standard concentration for CH_4; (c) $2f$ absorption spectra and (d) fitted concentration as a function of standard concentration for H_2S.

Table 1. Fitted CH_4 Concentrations and Corresponding Correlation Coefficients

Curve in Fig. 4(a)	1	2	3	4	5	6
C (ppm·m)	525	328.67	247.58	130.26	110.75	49.76
R	0.999	0.998	0.994	0.993	0.984	0.956

Table 2. Fitted H_2S Concentrations and Corresponding Correlation Coefficients

Curve in Fig. 4(c)	1	2	3	4	5
C (ppm·m)	1160	493.99	425.79	265.24	59
R	0.999	0.992	0.983	0.982	0.917

concentrations and the fitted linear relation between the measured and actual gas concentrations using least square fitting method[9], and the fitted concentrations and corresponding correlative coefficients are shown in Tables 1 and 2. The good linear characteristics show the time-sharing open-path system with Fresnel lens as receiving optics can detect CH_4 and H_2S concentrations simultaneously.

In order to describe the superimposed noise quantificationally for the time-sharing scanning system, the variation of noise was monitored through detecting the concentration fluctuation at the fixed gas concentration. Figure 5 shows the concentration changes relative to the averaging concentration. As can be seen, time-sharing scanning method produces significantly larger concentration fluctuation than the single detection technique by the average factors of 2.8 for CH_4 and 1 for H_2S. At the same time, although the mean square deviation detection limits (1σ)[10] calculated from Fig. 5 are 1.1 ppm·m for CH_4 and 15 ppm·m for H_2S in simultaneous measurement, the time-sharing scanning system can satisfy the need to detect the natural gas leakage.

To demonstrate the time response of the system, the experiment was conducted to simulate the gas leakage monitoring. A cylinder containing 1% CH_4 was attached to a hand-held welder's nozzle. The nozzle was mounted 30 cm below the optical path. The measured concentration curve is shown in Fig. 6. The baseline is about $1.2 - 1.4$ ppm (curves a and g) due to the CH_4

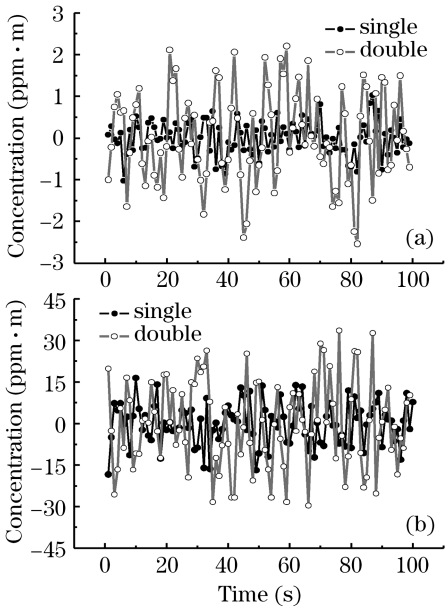

Fig. 5. (a) CH_4 and (b) H_2S relative concentrations before and after multiplexing.

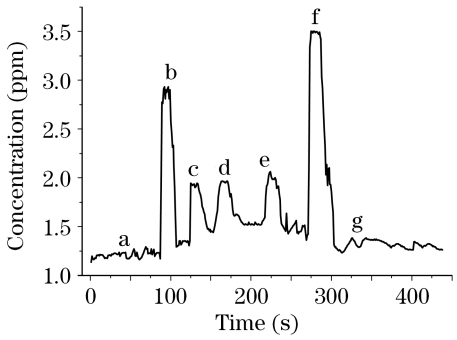

Fig. 6. Experimental results of different CH_4 concentrations. a, g, concentrations of methane in the air; b, 0.1% methane with flowing rate of 3 L/min; c, d, and e, 0.1% methane with flowing rate of 1 L/min at different positions; f, 0.1% methane with flowing rate of about 3.5 L/min.

concentration in the air being $1.2 - 1.8$ ppm. The curve g is higher than the curve a, because the high concentration methane was let out when the experiment began, thus the CH_4 concentration of the air in the laboratory increased. Curves b and f are caused by the emission of 0.1% methane with the flowing rate of 3 and 3.5 L/min, the time of release is about 3 s. We release the 0.1% methane at different positions of the optical path with the same flowing rate of 1 L/min, and let the parallel distances between the nozzle and receiving optical system being about 1, 15, and 30 m, respectively, thus the peaks c, d and e are collected correspondingly. As can be seen, the system can detect the gas leakage whose concentration is under 3 ppm. In this system, the emission power of the laser is 5 mW and the received power on the detector is greater than 2 mW. According to the receiving light efficiency of optical system and detectable minimum light-intensity of detection and the receiving areas of Fresnel lens and corner reflector, the detectable maximal optical-path of the system can achieve $1 - 2$ km. It shows that the system can satisfy the need to detect the pipe leakage continuously.

Based on NIR TDLAS technology, Fresnel lens used as receiving optics, we set up a time-sharing scanning long open-path TDLAS system combined with second harmonic detection technology, and simulate the natural leakage monitoring adopting above approach in our laboratory. Results show that this open-path TDLAS system can be used in industry to monitor the multi-component gas leakage. Moreover, it will become an effective tool in many other industrial applications to detect toxic or explosive emission and monitor concentration of trace gases. It also supplies an effective method for the monitoring of the area emission flux of ecosystem and a feasible ground calibration means for the satellite remote sensing.

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