

A high sensitivity spectrometer with tunable diode laser for ambient methane monitoring

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Tunable diode laser absorption spectroscopy (TDLAS) has been widely employed in atmospheric trace gases detection. In the measurement of these trace gases, harmonic detection combined with a multi-pass white cell could remarkably enhance the detection sensitivity. In this paper, a portable TDLAS system built specifically for long time monitoring methane in the atmosphere is introduced. The detection limit is below 100 ppb that is enough for the monitoring of ambient methane, and the long time monitoring results obtained in Beijing are given, which is well coincident with that of the Fourier transform infrared (FTIR) spectroscopy.

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Methane is strongly affected by human activities. It is the second most important greenhouse gas after CO₂. Methane concentration in the atmosphere is about 1.6 ppm and much lower than CO₂, however, it is responsible for 26% of the total greenhouse effect, as its capability as a greenhouse gas is 22 times larger than that of CO₂.

Tunable diode laser absorption spectroscopy (TDLAS) has been widely employed in detecting atmospheric trace gases due to its high sensitivity, high selectivity, and fast time response^[1-7]. High sensitivity detection is obtained by wavelength or frequency modulation spectroscopy and by monitoring the first, second, or higher order of the modulation frequency in the detected output signal. In addition increasing the absorption path length by adapting a multi-pass technique could also greatly enhance the detection sensitivity^[1-5,8]. To monitor methane concentration in the atmosphere is of particular importance for the study of radioactive process and climate trends. To achieve such high detection sensitivity, it is desirable to use an absorption line as strong as possible. Methane has strong absorption line in the ν_3 and ν_4 bands at around 3.3 and 7.7 μm , respectively. At the present time, however, it is still difficult to get a tunable distributed feedback (DFB) laser operating at wavelength over 2.2 μm at room temperature. The strongest absorption of methane below 2.2 μm is the $2\nu_3$ band located at 1.6–1.7 μm . There are several lines labeled as *P*, *Q*, and *R* lines being free of interference from other atmospheric gases in this band. Among these lines *R*3 line at wavelength of 1.654 μm with line strength about 5.3×10^{-21} cm/molecule is found to be free of interference and suitable for the high sensitive detection as shown in Fig. 1.

TDLAS in conjunction with harmonic detection has been extensively used to measure many trace-gases. To achieve high detection sensitivity, the laser diode is modulated by a low frequency sawtooth waveform and a high frequency f sine waveform, the laser wavelength is slowly scanned across an absorption line by the sawtooth; the signal from the detector is processed by a lock-in am-

plifier referenced to the modulation frequency f . The intensity $I(\nu)$ of a laser beam at frequency ν passing through a cell of length L filled with a absorption gas can be approximated as

$$I(\nu) = I_0(\nu)[1 - \alpha(\nu)CL], \quad (1)$$

where $I_0(\nu)$ and $I(\nu)$ are the laser beam intensities before and after passing through the absorption gas, respectively. $\alpha(\nu)$ is the absorption coefficient of the gas at frequency ν , $\alpha(\nu) \approx \alpha_0$; C is the concentration of the absorption gas. For harmonic detection one is only concerned with weak absorption lines, i.e., we can assume that the value of $\alpha_0 L$ is confined to $\alpha_0 L \ll 0.05$. The second harmonic signal obtained by demodulation could be expressed as^[9]

$$I_{2f} \propto I_0(\nu)\alpha_0 CL. \quad (2)$$

TDLAS system includes diode laser, electronic elements, and optical elements as shown in Fig. 2, in which the most important part is a tunable DFB diode laser. The key features of the DFB lasers are 1) the very narrow linewidth, typically less than 50 MHz, and thus much

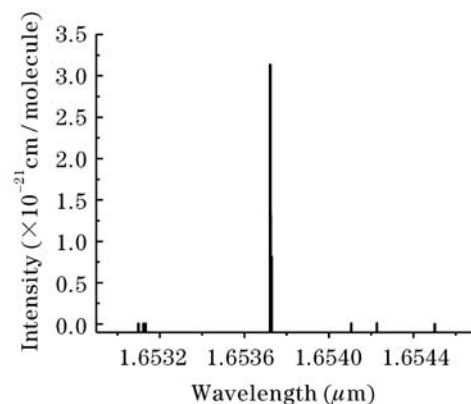


Fig. 1. Methane absorption lines around 1.654 μm .

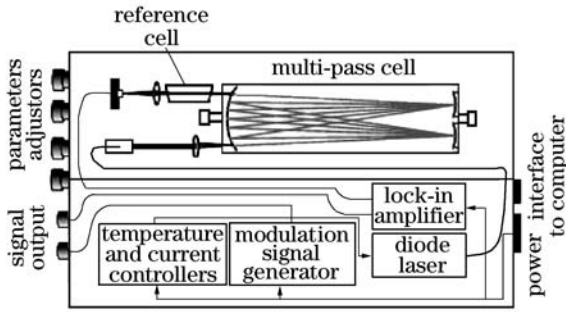


Fig. 2. Schematic of the TDLAS system.

less than the linewidth of single rotational transition absorption line, and 2) the ability to modulate the wavelength of the laser output through the injection current.

The DFB diode laser used in this TDLAS system is made by NTT Electronics Corporation in Japan. The output wavelength is $1.6537 \mu\text{m}$ and the fiber output power is about 10 mW when it operated at 25°C . The diode laser is driven by the temperature and current controllers as shown in Fig. 2. These controllers are made by ILX lightwave. The laser output wavelength can be tuned coarsely by the temperature controller and tuned finely by the current controller. The laser wavelength is slowly scanned through the absorption line from 1653.61 to 1653.83 nm by a sawtooth waveform at frequency of 50 Hz and simultaneously modulated by a sinusoidal waveform at frequency of 5 kHz. The harmonic detection technique is used in this TDLAS system. The modulation sinusoidal with frequency f and sawtooth signals for the laser and the reference signal with double frequency $2f$ for the lock-in amplifier are produced by a signal generator.

In order to enhance the sensitivity, a little volume (1.6 L) multi-pass cell based on White mode was used in this system. The laser output from a grin lens was focused on the focal plane of the field mirror and lengthened the path length to about 25 m with 23-cm base length. The laser output from the multi-pass cell after 108 times reflections then passed through a reference cell and was focused on a detector by a lens. The reference cell was full of the mixture of nitrogen and methane. All the optical elements were fixed on a 55×18 (cm) optical table to maintain the stability of the optical path.

The gas sample was pumped through the 1.6-L multi-pass cell used in the TDLAS system to lengthen the path length to 25 m. The operation sequence is shown in Fig. 3. The cell was separated from outside by two valves at the two ports. One is connected to a pump with 1.6-L/s pumping speed, the other is connected to a filter which was used to remove the dust and water vapor in the air that was pumped from outside through a pipe. The temporal resolution is one minute to get a concentration value. During the running, firstly, open the two valves and send a trigger signal to turn on the pump to pump the outside air through the cell, after 30 seconds pumping, the air in the cell has been exchanged inside out; then close the valve 1 and delay 10 second to let the gas in the cell be stabilized; and then start the data acquiring. 50 pieces of the second harmonic absorption spectrum were acquired in one second; in the long time

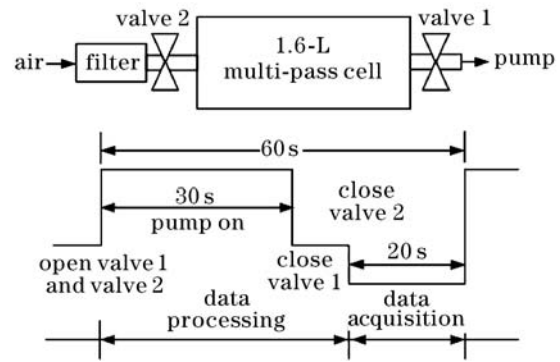


Fig. 3. Sampling parts and operation sequence of the TDLAS system.

continuously monitoring the average time was set to 1000 times. In order to make full use of the computer's CPU to ensure the one minute temporal resolution, the data was processed in the duration of gas exchanging. The concentration was obtained by the fit of the averaged spectrum with the standard spectrum, and the correlation coefficient of the two spectra indicated the background changing. When the correlation coefficient is lower than 0.8, the system will give a warning that it should be recalibrated and obtain the new standard spectrum.

This $2f$ signal output from the lock-in amplifier was digitized with a data acquisition card with a computer. The card can acquire as many as 16 k samples/s with 12-bit resolution.

Using traditional calibrating methods, a background signal \dot{S}_{bg} was acquired by filling the cell with nitrogen or was ignored^[9,10], and a rude reference signal \dot{S}_{ref} was acquired by filling the cell with reference gas with known concentration, a standard signal \dot{S}_{cal} was obtained by subtracting \dot{S}_{bg} from \dot{S}_{ref} . The sample concentration can be obtained by fitting the sample signal deducted \dot{S}_{bg} to \dot{S}_{cal} , a reference cell was used only to lock the absorption line. A traditional TDLAS system is only fit for short time monitoring, due to letting out a mass of methane into the ambient air.

In order to design a TDLAS system for long time continuous ambient methane monitoring, it must be able to calibrate itself without letting out methane into ambient air. So we used a reference cell with high concentration methane in this system to realize the self-recalibration.

Firstly, fill the multi-pass cell with nitrogen to obtain the signal (S_1) (see Fig. 4), including the absorption of the reference gas (S_{cal}) and the background (S_{bg}) signals,

$$S_1 = S_{cal} + S_{bg}. \quad (3)$$

Secondly, pump the sample gas with any concentration in the measurement range to obtain the signal, including the absorption of reference gas (S_{cal}), sample gas (S_{samp}) and the background (S_{bg}) signals,

$$S_2 = S_{cal} + S_{bg} + S_{samp}. \quad (4)$$

Then, a standard $2f$ signal of S_{samp} was obtained obtained from Eqs. (3) and (4).

Supposing that the background signal is noncorrelated with standard $2f$ signal, then the S_{ref} equals S_{samp} multiplied by a factor which can be obtained through least

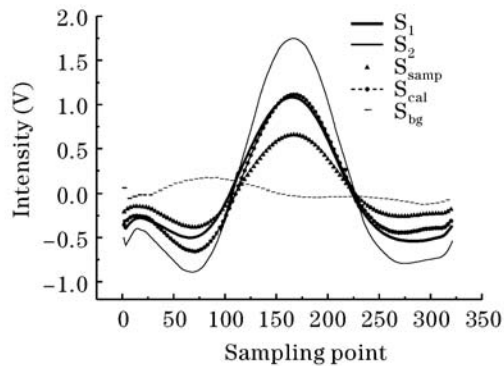


Fig. 4. Signals used in the calibration. $S_1 = S_{cal} + S_{bg}$, measured when the cell filled with nitrogen; $S_2 = S_{cal} + S_{bg} + S_{samp}$, measured when the cell filled with sample gas; S_{samp} , obtained by subtracting S_1 from S_2 ; S_{cal} , obtained by least squares fit with S_{samp} ; S_{bg} , obtained by subtracting S_{cal} from S_1 .

squares fitting

$$S_{cal} = a \times S_{samp}. \quad (5)$$

From the above equation, a reference $2f$ signal with known concentration and a background signal have been obtained, which can be used in the concentration deducing. When a $2f$ signal with background of a sample S_x was obtained, its concentration can be obtained by subtracting S_1 from S_x and fitting to S_{cal} .

Compared with traditional method which used nitrogen and standard sample gas, the new calibrating method does not let out sample gas into the atmosphere and more suitable for long time continuous monitoring. The two methods were compared by detecting several sample gases with different concentrations of 20, 15.074, 10.099, 5.075, 2.036, 1.019, and 0.764 ppmv. The concentration values measured by the new method are a little higher than that of the traditional method, as shown in Fig. 5.

Though the concentration values obtained by the new calibrating method are about 0.034 ppmv higher than those by the traditional method, the linearity is comparable with the traditional. The average deviation about 0.034 ppmv may be caused by the difference of the background signal, and the fluctuation in the range of ± 0.007 ppmv should be caused by the fluctuation of the background and other noises. In this new calibrating

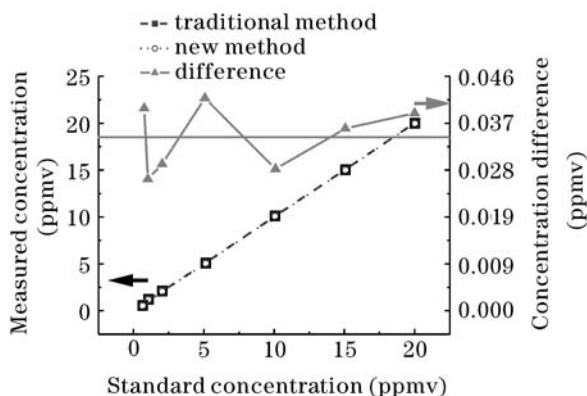


Fig. 5. Comparison of new and traditional calibrated methods.

method, the average deviation has some thing to do with the optical path, once the optical path is fixed, whether the deviation is larger or smaller, it will be constant. So before the long time monitoring, we can obtain the constant deviation and compensate this deviation to the final calibrated concentration values in the course of continuous monitoring. The deviation will be constant without obvious optical path changing.

The concentration was obtained by the fit of the averaged spectrum with the standard spectrum, and the correlation coefficients of the two spectra indicated the background changing. When the correlation coefficient is lower than 0.8 (will cause about 0.070-ppmv deviation), the system will recalibrate and update the new standard spectrum by itself.

Fengtai stadium ($39^{\circ}52'N$, $116^{\circ}17'E$) in the southern Beijing, there are many heavy industries in this region and the air pollution is very serious, has brought the attention of Beijing government. It is the uptake of Beijing for the monsoon from south, so the control of air pollution in this region is very important to improve the air quality of Beijing and it was selected for the investigation.

The long time continuous monitoring result by TDLAS was shown in Fig. 6 together with that of a MR154 type Fourier transform infrared (FTIR) spectrometer made by BOMEM. The temporal resolutions were one minute and five minutes respectively. The TDLAS was sampled from the roof of the building by a pump and the FTIR measured the average concentration along a 200-m optical path. The result by the TDLAS is in well agreement with that by the FTIR in the trend with the relative coefficient R of 0.84. The difference between the two results can be explained by Fig. 7. The two systems

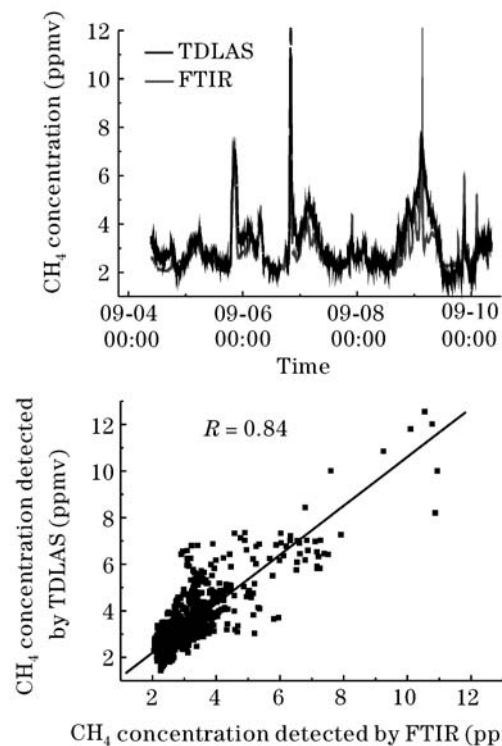


Fig. 6. Relevancy of the TDLAS and FTIR monitoring results.

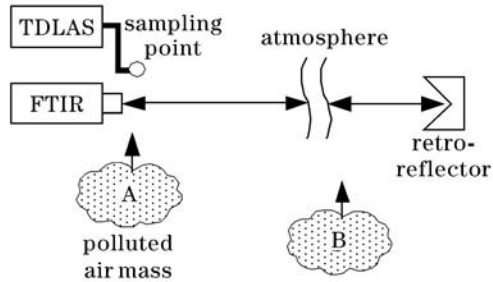


Fig. 7. Explanation for the difference between TDLAS and FTIR.

are in the same ambient air environment, so the trends of the trace gas variation are similar. But the polluted gas masses from the vehicle and hotel about fifty meters away cause the difference of the results. When a gas mass A transfers across the optical path, the TDLAS system measures its concentration, but the FTIR averages the concentration in the whole optical path, so it causes the concentration obtained by the TDLAS a little higher than that of the FTIR. Inversely when a gas mass B appears, it results in that of the FTIR higher than the TDLAS. Because of the 250-m path length of the FTIR, the chance of event of B happening is much higher than that of A, the fluctuation of FTIR is larger than that of TDLAS.

A new TDLAS system with self-recalibration was developed for long time continuously monitoring ambient methane. This system does not need additional calibrated gas and is most suitable for long time continuously

monitoring; and the comparison with FTIR demonstrates the well long time monitoring result.

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