Large scale gas leakage monitoring with tunable diode laser absorption spectroscopy

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Tunable diode laser absorption spectroscopy (TDLAS) has been widely employed in atmospheric trace gases detecting and industrial control due to its high sensitivity, selectivity, and rapidity of response. An open path TDLAS system is developed for monitoring large scale methane leakage around the oil refinery. The tunable distributed feedback (DFB) diode laser emits at 1.65 μm. In order to enhance the sensitivity, a system combining long open path and second harmonic detection technique is developed. The test results show that the time resolution is less than 0.1 second and the detection limit is lower than 3.6 ppmv. This system is adapted for monitoring a large scale methane concentration changing trend instead of measuring its absolute concentration.

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The fast development of petrochemical industry has brought many safety problems, such as the leakages of inflammable, explosion hazard, and toxic gases. This has become an urgent problem and caused lots of loss and made so many people lose their lives in the accidents.

The traditional gas analyzers, such as gas chromatogram and electrochemistry sensor, cannot work continuously, cannot monitor a large scale, and cannot avoid the interference from other gases, while the tunable diode laser absorption spectroscopy (TDLAS) has been widely employed in atmospheric trace gases detecting and industrial control due to its high sensitivity, high selectivity, and rapidity of response[1−6]. In order to realize large scale continuous monitoring of the gas leakage in the refinery or the warehouse, an open path monitoring system based on TDLAS was developed. The optical source used in the TDLAS system is a tunable distributed feedback (DFB) diode laser emitting at 1.65 μm, where $R(3)$ lines of methane located at. The $R(3)$ lines are strong enough for the methane leakage detecting and free of interference from other gases. A retroreflector is used in this system to realize a long open path monitoring.

The most important part in a standard TDLAS system is a tunable DFB diode laser. High sensitivity detection is obtained by wavelength or frequency modulation spectroscopy and by monitoring first-, second-, or higher order of modulation frequency in the detected output signal. In addition increasing the absorption path length by adopting the open long path technique can also greatly enhance the detection sensitivity. The laser diode is modulated by a low frequency sawtooth waveform and a high-frequency 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 amplifier to the modulation frequency. The intensity $I_0(\nu)$ of a laser beam at frequency ν passing through a cell of length L filled with an absorption gas can be approximated as

$$I(\nu) = I_0(\nu)[1 - \alpha(\nu)CL], \tag{1}$$

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, $\alpha(\nu) \approx \alpha_0$, α_0 is the absorption coefficient at the center of the absorption line; C is the concentration of the absorption gas. For harmonic detection one is only concerned with weak absorption lines, i.e., when the value of $\alpha_0 L$ is confined to $\alpha_0 L \ll 0.05$, the second harmonic signal obtained by demodulation can be expressed as

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

The diode laser employed in this study is a commercially available near-infrared DFB laser from NEL NTT Electronic Corporation. The diode laser is driven by a current controller and a temperature controller 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 sine waveform at frequency of 5 kHz. A retroreflector is located on a bracket with 6-m distance, and the total path length is 12 m limited by the scale of the laboratory. A telescope is used in the transceiver to collimate the laser beam and a lens of 12-cm diameter is used to collect the reflected laser to the detector. A reference cell filled with 0.5% methane is used to calibrate the trace gas concentration, its equivalent integral concentration to the open path is about 41 ppmv·m. The schematic of this system is shown as Fig. 1.

The reference cell was put into the optical path at the beginning, the reference signal was obtained as shown in Fig. 2. Removing the cell, the ambient methane's second harmonic absorption signal can be got. By least squares

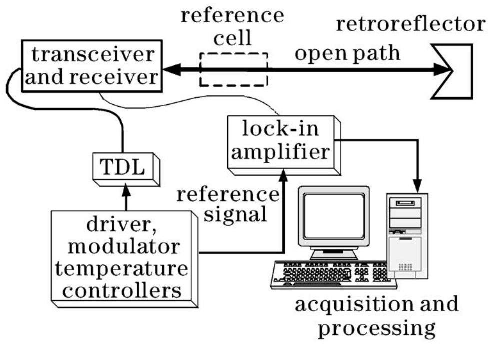

Fig. 1. Schematic of the TDLAS system.

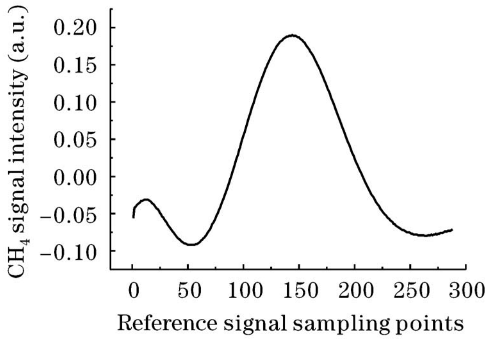

Fig. 2. Reference signal with methane concentration used in the calibration.

fitting with the reference signal, the ambient methane's integral concentration in the optical path was deduced approximately. For a long time monitoring, the ambient methane concentration's changing trend can be obtained.

TDLAS system was tested with different concentration methane gases. The vent hole from the gas container is located at 50 cm from the optical path. The baseline in Fig. 3 is more than 20 ppmv·m due to the methane concentration in the atmosphere being 1.2—1.8 ppmv. The falling parts (curve a) is due to the shading of the optical path, which can be used to monitor if the system is working well or if anyone passes through the optical path. For a man-free warehouse, the system can monitor not only the gas leakage but also the man entrance. Curve b is caused by the emission of 10% methane, the

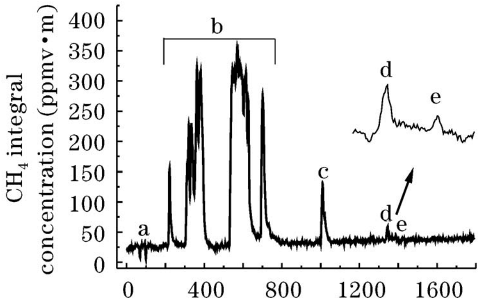

Fig. 3. Test results with different concentration methane gases. a: laser was blocked; b: 10% methane with different flowing time intervals; c: 0.5% methane; d: 100-ppm methane with flowing rate of 5 L/min; e: 100-ppm methane with flowing rate of 3 L/min.

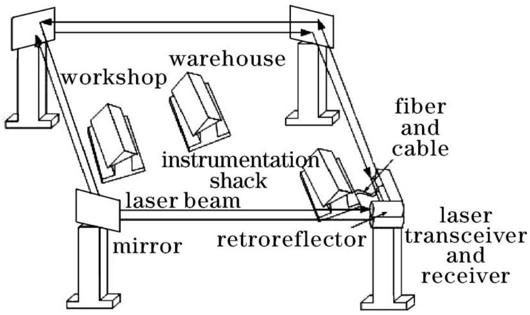

Fig. 4. Application of the open-path TDLAS in industry.

difference of these peaks is due to the different time intervals of the methane flowing out with rate of 3 L/min. Peak c is corresponding to emission of 0.5% methane with 3-L/min flowing rate. Peak d is due to the flowing out of the 100 ppmv methane with 5 L/min, and peak e is the same concentration with peak d, but with 3-L/min rate. From the test results the detection limit can be obtained by computing with the signal to noise rate; the limit is about 3.6 ppmv. The detection limit can be lower by lengthening the optical path. The optical path can be easily lengthened to as long as 500 m, and the detection limit will be lower than 0.09 ppmv. The baseline has a rising trend because when the experiment began and the high concentration methane was let out, the methane's concentration of the air in the laboratory increased.

The open path TDLAS system can be used in industry to monitor toxic or explosive gases emission, such as methane (1.65 μm)[7], carbon oxide (1.57 μm)[8], hydrogen fluoride (1.33 μm), hydrogen sulfide (1.57 μm)[9], ammonia (1.55 μm)[10], and ethane (1.68 μm)[11] in or around petrochemical refineries and aluminum smelters, as shown in Fig. 4. The laser beam transmitting along a rectangle path can be up to a few hundreds of meters in length. An optical transceiver is securely mounted at one end of the path, and a retroreflector is mounted at the opposite end. There are three mirrors in the path to change the beam direction. The laser beam makes a round trip and senses the concentration of target gas along the path.

In conclusion, TDLAS system has enough sensitivity to monitor the methane leakage in a large scale. It will become a reliable technology used in many industrial applications to monitor emissions of toxic or explosive gases in petrochemical plants, aluminum smelters, and others with its high sensitivity, fast responsibility, and large scale monitoring ability.

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