An optical sensor for hydrogen sulfide detection in open path using WMS-2*f*/1*f* technique*

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An optical hydrogen sulfide (H_2S) sensor based on wavelength modulation spectroscopy with the second harmonic ($2f$) corrected by the first harmonic ($1f$) signal (WMS-$2f$/$1f$) is developed using a distributed feedback (DFB) laser emitting at 1.578 μm and a homemade gas cell with 1-m-long optical path length. The novel sensor is constructed by an electrical cabinet and an optical reflecting and receiving end. The DFB laser is employed for targeting a strong H_2S line at 6 336.62 cm^{-1} in the fundamental absorption band of H_2S. The sensor performance, including the minimum detection limit and the stability, can be improved by reducing the laser intensity drift and common mode noise by means of the WMS-$2f$/$1f$ technique. The experimental results indicate that the linearity and response time of the sensor are 0.999 26 and 6 s (in concentration range of 15.2—45.6 mg/m^3), respectively. The maximum relative deviation for continuous detection (60 min) of 30.4 mg/m^3 H_2S is 0.48% and the minimum detection limit obtained by Allan variance is 79 μg/m^3 with optimal integration time of 32 s. The optical H_2S sensor can be applied to environmental monitoring and industrial production, and it has significance for real-time online detection in many fields.

For a long time, people have carried out a wide range of researches about hydrogen sulfide (H_2S) detection methods. Capillary gas chromatography (GC) is usually used to measure H_2S concentration which is down to part per billion (μg/m^3)[1], however, GC is not suitable for on-line and real time measurement. Versatile fluorescent probe[2] can be used for qualitative and quantitative detection of H_2S, yet it is greatly influenced by interference. Electrochemical method[3] is also used to detect H_2S mainly, yet it is not sensitive and selective enough to reach a low limit of detection. Nowadays, laser detection has been greatly applied to measurement of trace substance concentration[4]. Tunable diode laser absorption spectroscopy (TDLAS)[5] is widely used to detect substance concentration, gas pressure, etc. parameters. One common approach with tunable diode lasers in the near-infrared (NIR) region is applied to detect trace gases based on wavelength modulation spectroscopy (WMS)[6]. Compared with the direct detection of transmitted light intensity, the WMS method improves the sensitivity of

gas concentration detection by more than 100 times. Traditional WMS[7] needs to be calibrated by a known measurement condition, which is influenced by many factors[8]. Moreover, the efficiency of sample extraction measurement for H_2S is low and cannot meet the online detection. Furthermore, exposure to the μg/m^3 level of H_2S for a long time is harm to human. Therefore, it is necessary to improve the WMS method to realize self-calibration measurement of H_2S concentration in an open path sensitively.

In this paper, a sensor based on TDLAS is proposed for H_2S detection sensitively, which adopts calibration-free WMS technique with normalization of the second harmonic ($2f$) signal by the first harmonic ($1f$) signal (WMS-$2f$/$1f$), and it can restrain interference caused by circuit, light path, optical source and other factors.

The WMS-$2f$/$1f$ technique has been detailed previously[8,9] and a brief review will be given. The wavelength of the laser is not only scanned within a certain range, but also modulated by a high frequency sinusoidal

signal simultaneously. After laser injection current is modulated by a high frequency sinusoidal signal, the frequency modulation (FM) and light intensity modulation (IM) are produced. The TDLAS technology for the measurement of gas concentration is mainly based on Beer-Lambert law, and the transmission coefficient $\tau(v)$ is described by this law as follows

$$\tau(v) = \left(\frac{I_t}{I_0}\right) = \exp[-\alpha(v)] =$$

$$\sum_0^\infty H_k(\bar{v}, a)\cos(kwt) , \quad (1)$$

where I_t and I_0 are transmitted and incident light intensities, $\bar{v}$ is the center frequency of laser, and $\alpha(v)$ is the absorbance. I_0 can be represented as

$$I_0 = \overline{I_0}[1 + i_0\cos(\omega t + \psi_1) +$$

$$i_2\cos(2\omega t + \psi_2)] , \quad (2)$$

where $\overline{I_0}$ is the average intensity of laser at $\bar{v}$, i_0 and i_2 are the linear first harmonic and the nonlinear second harmonic IM amplitudes, respectively, Ψ_1 is the ratio of the FM and the IM phase shifts, and Ψ_2 is the corresponding ratio of nonlinear phase shifts. The laser passes through a homogeneous medium with a length of L (cm). The $H_k(\bar{v}, a)$ in Eq.(1) can be described as follows

$$H_0(\bar{v}, a) = -\frac{P\chi_i L}{2\pi}\int_{-\pi}^{\pi}\sum_j S_j\varphi_j(\bar{v} + a\cos\theta)\mathrm{d}\theta , \quad (3)$$

$$H_k(\bar{v}, a) =$$

$$-\frac{P\chi_i L}{\pi}\int_{-\pi}^{\pi}\sum_j S_j\varphi_j(\bar{v} + a\cos\theta)\cos k\theta\mathrm{d}\theta . \quad (4)$$

Based on the above formulas, the $1f$ and $2f$ signals will be demodulated by the lock-in amplifier

$$X_{1f} = \frac{G\overline{I_0}}{2}[H_1 + i_0(1 + H_0 + \frac{H_2}{2})\cos\psi_1 +$$

$$\frac{i_2}{2}(H_1 + H_3)\cos\psi_2] , \quad (5)$$

$$Y_{1f} = -\frac{G\overline{I_0}}{2}[i_0(1 + H_0 - \frac{H_2}{2})\times$$

$$\sin\psi_1 + \frac{i_2}{2}(H_1 - H_3)\sin\psi_2] , \quad (6)$$

$$X_{2f} = \frac{G\overline{I_0}}{2}[H_2 + \frac{i_0}{2}(H_1 + H_3)\cos\psi_1 +$$

$$i_2(1 + H_0 + \frac{H_4}{2})\cos\psi_2] , \quad (7)$$

$$Y_{2f} = -\frac{G\overline{I_0}}{2}[\frac{i_0}{2}(H_1 - H_3)\sin\psi_1 +$$

$$i_2(1 + H_0 - \frac{H_4}{2})\sin\psi_2] , \quad (8)$$

where G is the gain of the photoelectric detection system. In order to eliminate the background signal caused by laser parasitic amplitude modulation and obtain the only absorbed $1f$ signal (S_{1f}) and $2f$ signal (S_{2f}), the following formulas are given

$$S_{2f} = \left[\left(X_{2f} - X_{2f}^0\right)^2 + \left(Y_{2f} - Y_{2f}^0\right)^2\right]^{1/2} = \frac{G\overline{I_0}}{2}\times$$

$$\left\{\left[H_2 + \frac{i_0}{2}(H_1 + H_3)\cos\psi_1 + i_2\times\left(H_0 + \frac{H_4}{2}\right)\cos\psi_2\right]^2 +$$

$$\left[\frac{i_0}{2}(H_1 - H_3)\times\sin\psi_1 + i_2\times\left(H_0 - \frac{H_4}{2}\right)\sin\psi_2\right]^2\right\}^{1/2} , \quad (9)$$

$$R_{1f} = \frac{G\overline{I_0}}{2}\times$$

$$\left\{\left[H_1 + i_0\left(1 + H_0 + \frac{H_2}{2}\right)\cos\psi_1 + \frac{i_2}{2}\times(H_1 + H_3)\cos\psi_2\right]^2 +$$

$$\left[i_0\left(1 + H_0 - \frac{H_2}{2}\right)\times\sin\psi_1 + \frac{i_2}{2}\times(H_1 - H_3)\sin\psi_2\right]^2\right\}^{1/2} , \quad (10)$$

where X^0_{2f} and Y^0_{2f} are X and Y components of the $2f$ signal without absorption, respectively. The odd term of $H_k(\bar{v}, a)$ is 0 here. For an optically thin gas to be measured ($\alpha(v) < 5.0\%$), the $1f$ signal is mainly produced by the inherent linear IM.

The $1f$ signal measured can be used to normalize the $2f$ signal. Therefore, the $1f$ and $2f$ signals can be detected simultaneously. The peak height of the $2f$ signal normalized by the $1f$ signal can be drawn as

$$C_{2f/1f}(v_0) = \frac{S_{2f}(v_0)}{R_{1f}} = \frac{1}{i_0}H_2(v_0) =$$

$$-\frac{1}{i_0}\cdot\frac{PS(T)\chi_{abs}L}{\pi}\int_{-\pi}^{\pi}\varphi(v_0 + a\cos\theta)\cdot\cos 2\theta\cdot\mathrm{d}\theta , \quad (11)$$

where $C_{2f/1f}$ is proportional to the product of gas concentration to be measured and optical path L, when the linear function is not changed in the range of measured gas components. $C_{2f/1f}$ can eliminate the effects of laser output intensity, optical gain and transmission light intensity fluctuation. The signal peak height $C_{2f/1f}$ is a function of laser parameters (i_0, a) and gas parameters (included in the H_k item). The laser parameters can be measured in advance. Therefore, the concentration of the gas doesn't need to be calibrated and measured when the pressure P and the length L are known.

The key to the detection of H_2S in the air is to avoid the potential spectral interference of H_2O, CO_2 and other substances, and the absorption lines measured are strong enough. H_2S and air absorption lines in the range from

1 576.5 nm to 1 579.0 nm can be obtained using HI-TRAN database[10], as shown in Fig.1. The simulation results show that the H_2S absorption line located at 1 578.12 nm has interference free from that of some molecules existing normally in the atmosphere and has the strongest absorption peak. For this absorption line, the 152 mg/m^3 H_2S absorption is about 2×10^{-4} when the absorption path is 1 m. Therefore, μg/m^3 level concentration measurement can be achieved when the absorption path length is more than 100 m.
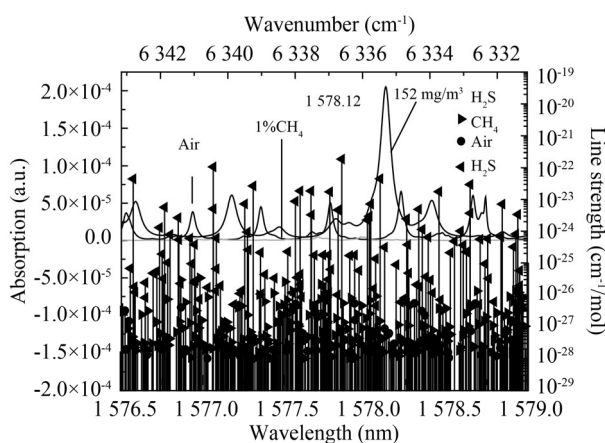

Fig.1 Absorption spectra of H$_2$S (152 mg/m^3), 1% CH$_4$ and air (*T*=296 K, *P*=1.013×10^5, *L*=1 m, HITRAN database) within 1 576.5—1 579.0 nm

The H_2S sensor architecture is depicted in Fig.2, which includes both the optical and electrical sub-systems. In the optical section, the corner-cube prism can make the gas absorption path increased by two times, and the laser is directly reflected to the multimode fiber of the transmitting end through the corner-cube prism and the off-axis parabolic mirror, which will reduce the volume of the sensor and meet open path measurement. In the electrical part, a single-mode pigtailed distributed feedback (DFB) laser with a central emission wavelength of 1.578 μm is employed. The DFB laser is on a universal laser diode mount specifically designed for 14 pins butterfly laser that integrates thermal electric cooler (TEC) and thermistor sensor. A laser diode can be operated with precise temperature control for wavelength stability by laser controllers and TEC controllers. The direct injection current is set as 40 mA and modulation current frequency is set at 2.52 kHz to perform WMS. The operating temperature of the laser is set and controlled at 20 °C. During diluting H_2S, the 100 mg/m^3 H_2S sample and 99.99% high purity N_2 are used to prepare H_2S gases with different concentrations, which are controlled by a mass flow controller IP40 (Burkert, MFC8713), while the flow velocity is adjusted by a host computer program within 0—5 L/min.

The WMS-2*f*/1*f* signals of 1.52 mg/m^3, 15.2 mg/m^3, 30.4 mg/m^3, 45.6 mg/m^3, 60.8 mg/m^3, 76 mg/m^3, 91.2 mg/m^3, 106.4 mg/m^3 and 144.4 mg/m^3 H_2S standard gases with background correction are depicted as Fig.3,

which is configured by the MFC8713. The signal shapes after background correction are basically coincident and the amplitude increases with rising concentration. Simultaneously, the WMS-2*f*/1*f* peak-peak values at 1 578.12 nm for different H_2S concentration levels are fitted in the inset. The fitting coefficient of 0.999 45 indicates that the laser gas sensor has a good linearity.
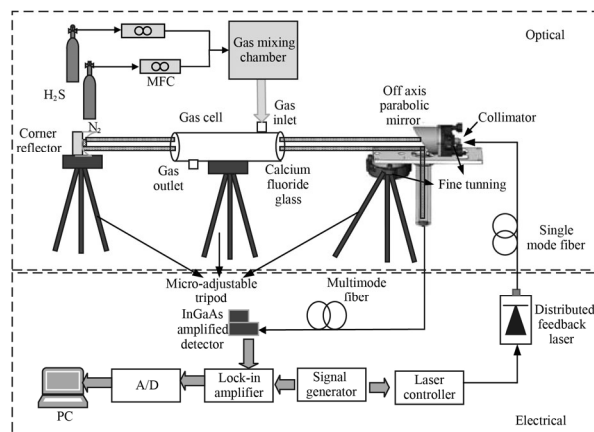

**Fig.2 Schematic setup of the H$_2$S sensor in open path**
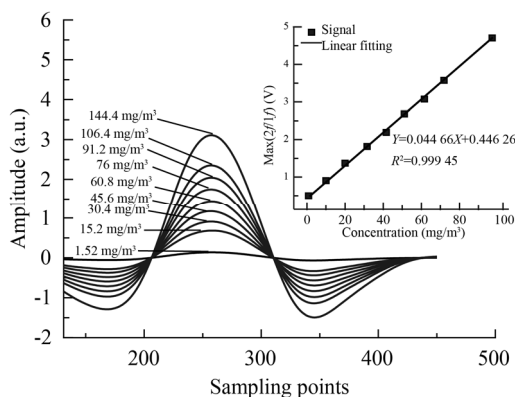
Fig.3 WMS-2*f*/1*f* signals with background correction for H$_2$S standard gases with different concentrations and 1-m-long homemade gas cell (The inset is the linearity of the H$_2$S sensor.)

The response time depends on both the sample gas cell volume and the gas inflow rate. In this test, a gas cell with 1.2 L volume and 1 m optical path is employed and the gas flow rate is 400 mL/min. Fig.4 shows that the total measurement time is 2 100 s, and the H_2S concentration initially increases from 0 mg/m^3 to 45.6 mg/m^3, 91.2 mg/m^3, 121.6 mg/m^3, 152 mg/m^3 and then decreases to 106.4 mg/m^3, finally to 0 mg/m^3. The concentration curve changes sharply, which implies that the sensor response time is shorter than the dynamic MFC8713 adjustment time. The N_2 signal levels at the beginning and the end indicate no obvious drift in the whole measurement process. From the inset, the response time of the H_2S sensor is about 6 s when switching from 15.2 mg/m^3 to 45.6 mg/m^3 H_2S standard gas. In the open path detection, the ventilation volume is larger than the cell volume, therefore, the response time is shorter and much more accurate.
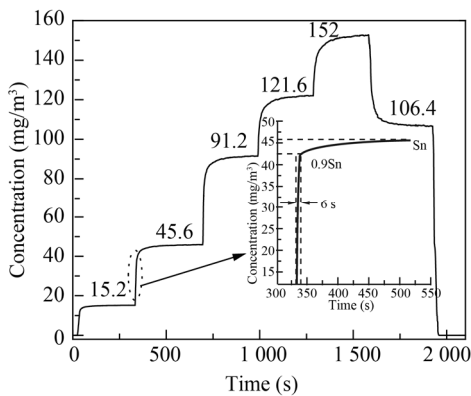
Fig.4 Concentration changes for switching from N₂ to different H₂S concentration levels (The inset is the case for switching from 15.2 mg/m³ to 45.6 mg/m³ H₂S standard gas.)

Stability and detection limit are additional parameters. In this test, the H_2S sensor was warmed up for 15 min firstly, and the 30.4 mg/m³ H_2S standard gas flowed into gas cell at 300 mL/min rate for 60 min. After data analysis, the 30.4 mg/m³ H_2S frequency distribution and Gaussian fitting result are shown in Fig.5. The maximum relative deviation for continuous measurement of 30.4 mg/m³ H_2S is 0.48%. Hence, the sensor has good stability. Allan variance[11] has been wildly used to measure the minimum detection limit of spectral analysis. The Allan variance analysis result for the 30.4 mg/m³ H_2S is recorded in Fig.6, which indicates that the minimum detection limit is 79 μg/m³ with optimal integration time of 32 s. By increasing modulation frequency, reducing white noise, and lengthening gas absorption path, the detection limit can be improved further.
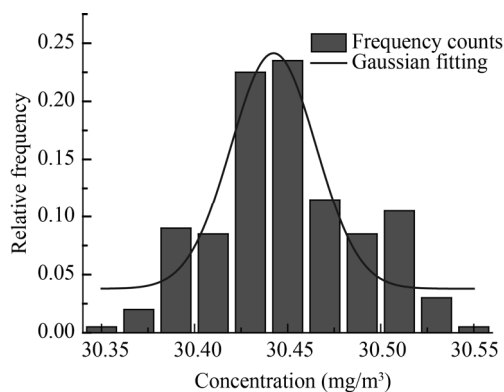
Fig.5 The frequency distribution and Gaussian fitting for 60 min continuous measurement of 30.4 mg/m³ H₂S standard gas

In this paper, a DFB laser is used as the optical source of the sensor. The $2f$ signal normalized by $1f$ signal with WMS technology is adopted, which can reduce laser intensity drift and common mode noise and realize calibration-free measurement. Under room temperature and ambient pressure conditions, the H_2S sensor performances are verified and the experimental results indicate that it
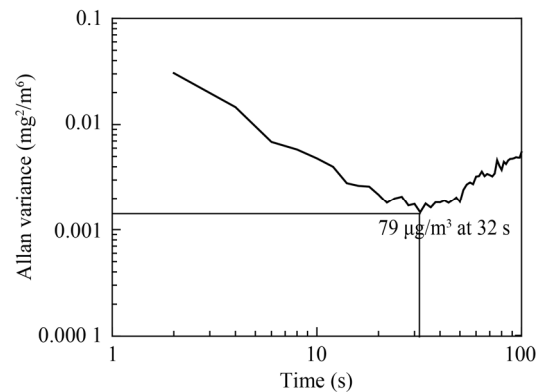
Fig.6 Allan variance for 30.4 mg/m³ H₂S standard gas

has good linearity and stability, and the response time can be as short as 6 s. The detection limit is 79 μg/m³ within 32 s integration time. Hence, the sensor built in this paper can detect the H_2S gas in an open path quickly and sensitively. Simultaneously, the proposed method can be used to detect other trace gases, such as CH_4, NH_3, CO_2, etc.

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