A photocoustic spectroscopy system for gas detection based on the multi-pass cell

Luo Han[a,b], Xinglong Chen[c,d] ,Hua Xia[b], Tao Pang[b], Zhirong Zhang[b], Bian Wu[b],Pengshuai Sun[a,b], Xiaojuan Cui[b], Zhe Li[b], Yu Wang[a,b], Fengzhong Dong[*a, b]

[a]University of Science and Technology of China, Hefei China, 230026; [b]Anhui Provincial Key Laboratory of Photonic Devices and Materials, Anhui Institute of Optics and Fine Machine, Chinese Academy of Sciences, Hefei China, 230031;[c]Sieyuan Electric Co., Ltd，Shanghai，China,201108;[d]School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong university, Shanghai，China，200240

ABSTRACT

Photo-acoustic spectroscopy gas detection technology has the advantages of high sensitivity, good selectivity, small size and real time monitoring and has been widely used in environmental monitoring, industrial production, medical diagnosis, biological technology and monitoring of power facilities. In this paper, a method to improve the sensitivity of photo-acoustic spectroscopy system is presented, which is combined with the technique of Herriott type multiple pass cell. In this experimental apparatus, the design of the experimental device can make the beam pass the cell 18 times. By comparing the signal of one time pass through the photoacoustic cell and the signal of 18 times passes pass through the photoacoustic cell, we can confirm that the signal is increased and this method is feasible.

Keywords: Photo-acoustic spectroscopy   Trace gas detection   Multiple passes technology

1. INTRODUCTION

As early as nineteenth Century, the famous American scientist Bell found that the film under the irradiation of the sun can make a sound, This phenomenon is called photoacoustic effect[1]. Photoacoustic spectroscopy technology is a kind of gas detection technology based on photoacoustic effect . Because the power of light source and the sensitivity of the sound detector is low, there is no substantial progress in the photoacoustic spectroscopy technique. Until 1938, A Former Soviet scientist Viegerov developed the world's first photoacoustic spectroscopy gas concentration detection device using infrared band light source[2].

High power, good monochromatic laser light source, high sensitivity of sound detection technology, as well as good signal processing technology has greatly promoted the development of photoacoustic spectroscopy technology[3-6]. The experts at home and abroad have conducted a deep research on the theory of photoacoustic spectroscopy, the theoretical study of photoacoustic spectroscopy is becoming more and more perfect. The photoacoustic spectroscopy gas detection technology is becoming more and more mature , integrated and practical. [7-9]

Photoacoustic spectroscopy which is based on photoacoustic effect is a kind of high sensitive gas detection technology. The gas in the sealed cell can produces heat energy by means of the non-radiative transition after absorbing light energy. If the intensity or wavelength of the incident light is modulated, the gas measured will produce a temperature change with the same frequency. Then the sound pressure is generated in the sealed cell and the gas concentration can be obtained by detecting the intensity of the sound pressure. Different substances have absorption in different light wavelengths, so through the choice of different wavelengths of light source, we can detect different types of gas. Photoacoustic spectroscopy gas detection technology has advantages of high sensitivity, large dynamic range, small volume and so on it has been widely used in the environmental monitoring, industrial production, medical diagnosis, biological technology etc. [10-12]

In this paper, basing on the photoacoustic spectroscopy technology, we combine photoacoustic spectroscopy with Herriott type multiple passes cell technology. Setting two concave mirrors at both ends of the photoacoustic cell, letting the incident light back and forth through the photoacoustic cell, and the time of the reflection of the light is far less than the relaxation time of the sound. Then the generated sound signal is superimposed which makes the sound signal and the

signal to noise ratio increased. Finally, the detection limit of photoacoustic spectroscopy technology is improved, and the application range become more extensive.[13]

2 . PRINCIPLE OF PHOTOACOUSTIC SPECTROSCOPY

The intensity modulated light is incident to the photoacoustic cell，the gas molecules in photoacoustic cell absorb light radiation energy, it transitions from the vibrational state to the vibrational excited state of the molecule , and then it returns to the ground state by non-radiative way. The vibration energy of molecules is converted into kinetic energy in this process, then the temperature of the cell is rising and the pressure in the sealed photoacoustic cell is increasing. When the intensity of excitation beam is modulated , the temperature will exhibit a periodic variation with the same intensity modulation frequency and the pressure in the sealed photoacoustic cell will be modulated with the same frequency. If the frequency is in the range of sound frequency, the sound signal will be generated. The sound signal can be detected by a microphone which is installed in the cell, and then the pressure is converted into electrical signal. We can calculate the concentration of gas by electrical signal.

The expression of photoacoustic signal S:

$$S = P_0 \times M \times C_{cell} \times \alpha_0 \times C + S_b \quad （1）$$

P_0: Optical power M: Response degree of microphone C_{cell}: The constant of cell α_0:Coefficient of gas absorption   C: Gas concentration S_b: Background noise of photoacoustic cell

After the light source, the gas, the sound detector and the size of cell is determined , the parameters (M P C_{cell} α_0 S_b) in the above formula can be measured. The gas concentration in the formula is only one unknown parameter, so it can be detected. Different cells have different sound field distribution. Designing a cylindrical photoacoustic cell, the sound field distribution in the cylindrical photoacoustic cell :

$$P(\vec{r}, \omega) = \sum_j A_j(\omega)p(\vec{r}) = -\frac{i\omega}{\omega_j^2} \frac{\alpha(\gamma-1)P_0 I_j L_c P_j(\vec{r})}{V_c (1-\frac{\omega^2}{\omega_j^2}-i\omega/（\omega_j Q_j））}(2)$$

$P_j(\vec{r})$: resonant mode of sound $A_j(\omega)$:amplitude ω：modulated angular frequency α: absorption coefficient of gas molecules γ: specific heat capacity of gas P_0：optical power $I_j=\frac{1}{L_c}\int P_j^*(\vec{r}, \omega)g(\vec{r}, \omega)dV$ （$g(\vec{r},\omega)$: normalized light distribution function L_c:length of photoacoustic cell ω_j:resonant angular frequency V_c：volume of photoacoustic cell Q_j：quality factor of resonant mode

When the modulation frequency of light $\omega = \omega_j$, the photoacoustic cell works in a resonant mode state. At this time, the sound pressure at $\vec{r}_M$ of the photoacoustic cell is

$$P(\overrightarrow{r_M}, \omega)=-（\gamma-1）) \frac{Q_j}{\omega_j} \frac{L_c}{V_c} I_j P_j(\vec{r}_M)\alpha P_0 \quad （3）$$

In the above formula, the $-（\gamma-1）) \frac{Q_j}{\omega_j} \frac{L_c}{V_c} I_j P_j(\vec{r}_M)$ is related to the photoacoustic cell and the modulation frequency, but it has nothing to do with the gas absorption coefficient and the optical power, so it can be regarded as a constant: cell constant

$$C_{cell} =-（\gamma-1）) \frac{Q_j}{\omega_j} \frac{L_c}{V_c} I_j P_j(\vec{r}_M) \quad （4）$$

Bring equation 4 to equation 1,

$$S_{PA} = P(\overrightarrow{r_M}, \omega_j) \times C = C_{cell}\alpha P_0 \times C \quad （5）$$

When the microphone is selected , the response of microphone is determined. The expression of the photoacoustic signal
$$S = P_0 \times M \times C_{cell} \times \alpha_0 \times C + S_b \quad （6）$$

3.1 EXPERIMENTAL ARRANGEMENT AND PROCESSING

We designed a PA- cell. The structure of the photoacoustic cell is shown in Fig 1. The parameter of cell: basic length L=23mm, diameter ϕ=12mm，The parameter of buffer: basic length L=12mm, diameter: ϕ=36mm. The K9 mirrors are used to seal cell as the windows with Brewster angle. There is a hole in one mirror. The laser beam entry to the cell through the hole. The diameter of the hole is 2mm and the distance between the hole and the center of mirror is 5mm.
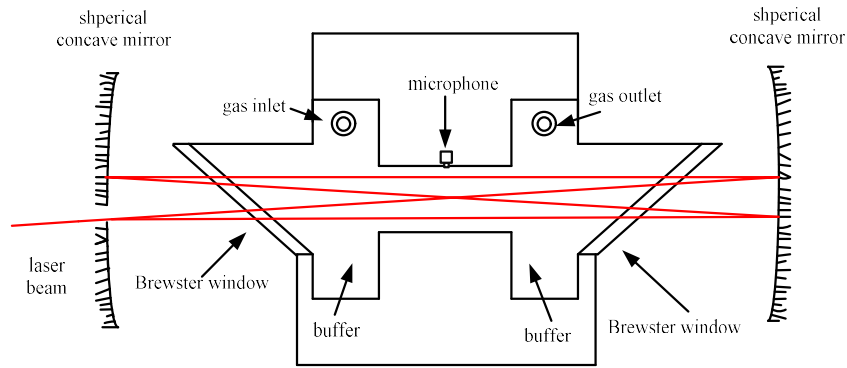
Fig 1 The structure of the photoacoustic cell

In order to get a better detection limit, we installed a Herriott multiple pass arrangement in photoacoustic cell. The diameter of the Herriott multiple pass arrangement is Φ=25mm, the radius of curvature is 683mm, the distance of two mirrors is 160mm. The spot distribution is shown in the Fig 2. Firstly, the light beam passes through the small hole ① in Fig 2 a, then the light spot arrives at ② in Fig 2 b. The light beam will be reflected in the two mirrors in the order of number shown in Fig 2 a and Fig 2 b. Finally the light beam pass out of the cell through the hole ① in Fig 2 a. This Herriott cell exhibits 18 times passes and the total light path is 2.88m.
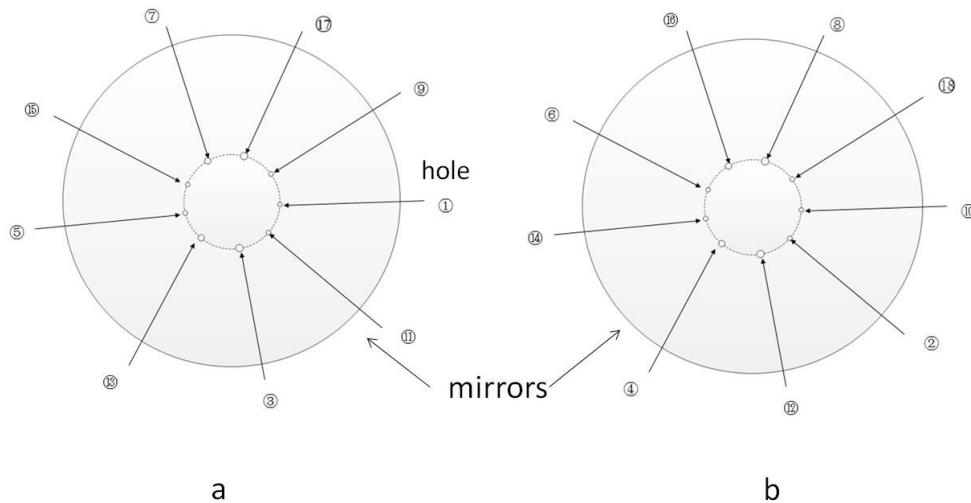

Fig 2 The spot distribution on the concave mirror

The optical path is adjusted by a collimator . We use the visible light to indicate the light path and adjust the collimator and the mirrors to satisfy the conditions of the Herriott cell. Then the light source is replaced by the selected laser light source. The results of light path completely accord with the optical simulation

Due to the small size of the photoacoustic cell, the conditions of the sound detector should meet the following aspects:(1) Smaller volume(2) Detection sensitivity of detector is relatively high(3) Wide detection response frequency. The microphone we chose is produced by a British company Knowles ,the model of it is EK-23024-000. The relationship between frequency and response of this microphone is shown in Fig 3.
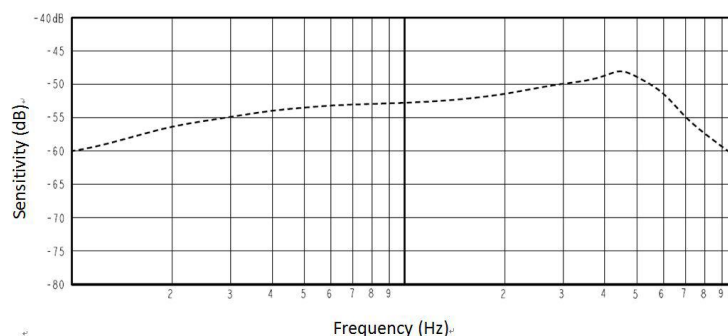
Fig 3 The relationship between frequency and response of this microphone

The working frequency of the photoacoustic spectroscopy system is about 2KHz, so we can find that the microphone sensitivity is satisfied from the Fig 3. Therefore, this model of microphone can meet the requirements of the system.

The CO_2 absorption line we selected is at λ =1608.66nm.By looking up the data from the Hitran database, the comparison result is shown in Fig 4. We found that the temperature have the influence on the absorption of CO_2 gas. Since the temperature during the experiment have little change and does not affect the content of this article , we don't consider this factor.
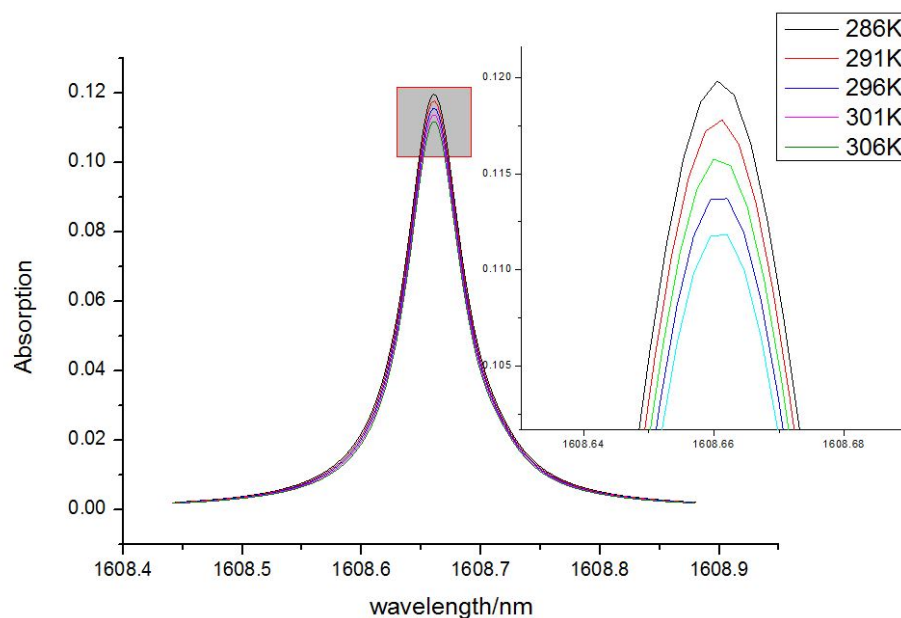

Fig 4 Relationship between the absorption of CO_2 and temperature

Photoacoustic spectroscopy system as depicted in Fig 5. In this experiment, we verify the effect of multiple passes technology through the detection of CO_2 gas absorption signal. In this experiment, the DFB laser which central wavelength is λ =1608nm is selected. The saw tooth wave signal which is generated by the signal generator is loaded onto the current controller of the laser. The wavelength of the laser is modulated at the center of the λ =1608.7nm.
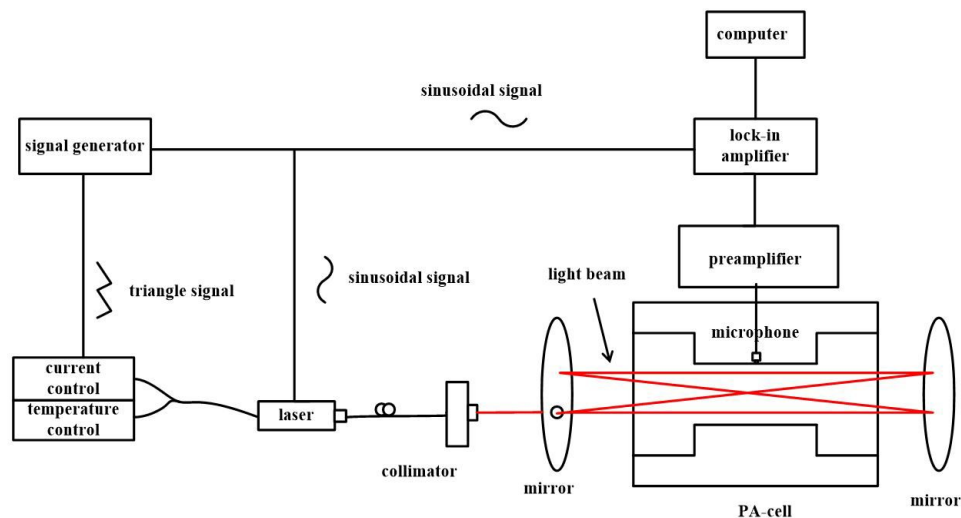
Fig 5 Photoacoustic spectroscopy system

Firstly, a certain concentration of CO2 gas is filled into the photoacoustic cell, then we seal the photoacoustic cell. The driving current of the laser is scanned and the frequency is set to 10Hz.At the same time , adding high frequency sinusoidal signal and triangle signal,then loading the result onto the laser. The frequency of the sinusoidal signal should be modulated to equal to the resonant frequency of the photoacoustic cell. Under this conditions, we will get a higher signal. Because the resonance frequency is related to the size, temperature, pressure and other factors of the photoacoustic cell, there is a deviation between the theoretical result and the theoretical result. When the temperature is 23 ℃,the humidity is 68% and the pressure is standard atmospheric pressure, we adjust the sinusoidal signal frequency gradually. When the frequency is adjusted to 2303Hz, we get the maximum value of the signal.

The sound signal from the microphone is converted to electrical signals. Firstly the signal is amplified by the amplifying circuit, then the sinusoidal signal generated by the signal generator is used as a reference signal, the signal is been locked in amplification. When the gas concentration is calibrated, the concentration of the gas can be calculated by the signal.

3.2 EXPERIMENTAL PHENOMENA

Every time the laser beam is passed through the photoacoustic cell, a sound signal is generated. And the time of the sound signal generation is much longer than the time of the light pass through the cell. Therefore, the signal detected should be the superposition of signal every time through the cell in theory.

The effective power of light is

$$\mathrm{P}_{eff} = P_0 * \sum_1^n (t_w^2 * r_m)^n \ (7)$$

P_{eff}: effective power of light, P_0: The initial optical power. The material of the window is K9, in the wavelength we choose, its transmittance is about $t_w = 0.901$. The reflectivity of aluminum film is $r_m = 0.95$. Bring value into the formula, we can get $\mathrm{P}_{eff} = 3.339$.

The relationship between the effective power and the reflection times is shown in Fig 6. We find that the growth is relatively slow when the number of reflections is more than 12 times. Therefore, we should select a higher transmittance window, a higher reflectivity mirror, and improve the number of reflection of light in order to get more effective light energy.
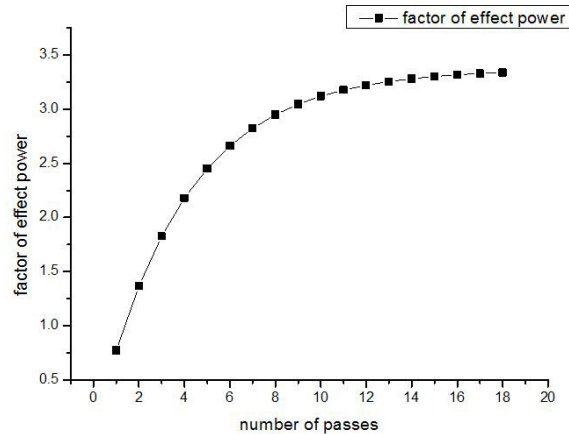
Fig 6 The relationship between the effective power and the reflection times

The signal of one pass through the photoacoustic cell and the signal of 18 times passes and the comparison of two signals is shown in Fig 6. By comparing the two sets of data in the Fig 7, we can find that the intensity of the signal is increased by 3.481 times. The experimental results agree well with the theory and the error may be due to the inaccurate measurement of the transmittance of the window and the reflectivity of the mirror.
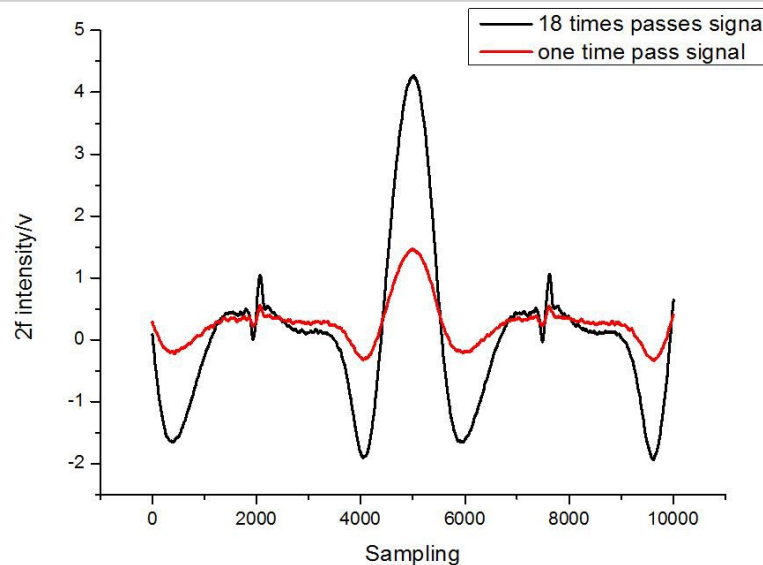

Fig 7 The comparison between one time pass and 18 times passes signal

4 . CONCLUSION

A new type of gas detection system is designed based on typical photoacoustic spectroscopy technology and multiple passes techniques According to the theoretical analysis and experimental results, we confirm that the combination of two techniques can significantly improve the signal intensity of photoacoustic spectroscopy system. So the application of photoacoustic spectroscopy technology becomes more extensive. We will do more work in this system such as selecting higher reflectivity mirrors and higher transmittance windows to improve the detection limit of photoacoustic spectroscopy technology. Moreover we will explore the influence of temperature, humidity, pressure and other factors on the signal due to the influence of many factors .

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