Laser Resonant Photoacoustic Spectrometer for Methane Detection

Yuxin Yun1* and Xiaoxiao Zhao2

1State Grid Shandong Electric Power Research Institute, Jinan, Shandong, 250003, China
2State Grid of China Technology College, Jinan, Shandong, 250000, China
*Corresponding author’s e-mail: 19953137128@189.cn

Abstract. A laser resonant photoacoustic (PA) spectrometer has been designed for methane detection. The design ideas and methods of the device are discussed in detail. Relevant tests are designed and done for testing and verifying the important parameters of the device. The experimental results show that the radiation wavelength of the distributed feedback (DFB) diode laser increases approximately linearly with the increase of operating temperature or injection current, and the change gradient of radiation wavelength to operating temperature is greater than that to injection current. Under the condition of low gas concentration and low laser power, the relationship between PA signal, laser power and methane concentration is linear.

1. Introduction
In recent years, with the continuous development of power system and the increasing demand of people's life for power supply reliability, the maintenance mode of electrical equipments is gradually changing from regular maintenance to state maintenance. On-line monitoring of dissolved gas in oil and the fault diagnosis technology can provide important data support and theoretical criteria for the state maintenance of power transformers, so it becomes an essential technology[1, 2]. In order to realize the on-line monitoring of dissolved gases in oil, many methods have been proposed, such as gas chromatography, gas sensor, Fourier infrared spectroscopy, but in the long-term use, these methods have some shortcomings, such as complex sampling, cross sensitivity, poor long-term stability, incomplete detection of gas components[3-5].

As an optical detection technique, photoacoustic spectrometry has some advantages including high sensitivity, high selectivity, big dynamic detection range and need not consume gas and separate gas. It has a good prospect in the application of gas detection[6-8]. Reference [9] compared the photoacoustic spectrometry with the gas monitoring techniques used in the on-line monitoring of dissolved gas in oil, and came to the conclusion that the photoacoustic spectrometry combines many advantages of on-line chromatography, on-line gas sensor and on-line Fourier infrared spectrometry and can overcome many disadvantages of them. And the measurement index of the photoacoustic spectrometry is better, so it has a good application prospect in the on-line gas monitoring or off-line gas detection.

In this paper, a portable and tunable laser resonant photoacoustic spectrometer is designed by using DFB diode laser. The design ideas and methods of the device are discussed in detail. And the relevant
tests are designed and done to test and verify the photoacoustic spectrometer. In addition, the relationship between PA signal, laser power and methane concentration is studied by using the device.

2. Design of Photoacoustic Spectrometer

The laser resonant photoacoustic spectrometer is shown schematically in figure 1. The DFB laser emits infrared radiation of a specific wavelength, which is modulated into a certain frequency beam by the chopper. And then the beam is injected along the longitudinal axis of the PA cell. At this time, the methane in the PA cell is excited by the periodic beam and produces the PA effect. The sine wave signal detected by the microphone and the square wave signal output by the chopper are respectively sent to the lock-in amplifier as the measure signal and the reference signal, respectively. The lock-in amplifier detects the PA signal intensity and send it to the computer for subsequent processing. As shown in Figure 1, the core components of the photoacoustic spectrometer is the PA cell and the laser. The designs of them are described below.

Figure 1. Schematic diagram of photoacoustic spectrometer

2.1. Design of the laser

The laser source has the characteristics of high power, monochromatic and good collimation, which can improve the sensitivity of gas detection, reduce the cross absorption interference between gases, and facilitate the optimal design of PA cells. Therefore, the laser is used in this paper. Among the existing laser sources, DFB diode lasers have the advantages of tuneable, narrow line width, long life, room temperature operation, simple operation, light volume and low price, which is suitable for the application requirements of industrial site. In this paper, the DFB diode laser of NEL company is selected as the light source of the photoacoustic spectrometer. As is known to all, each gas has its own specific infrared absorption spectrum. The emitting wavelength should be taken into more consideration in choosing the DFB laser. In this paper, the following principles are used for choosing the emitting wavelength of the DFB laser:

- For high sensitivity, the emitting wavelength of the laser should be in conformity with an absorption line of methane and the stronger the absorption, the better.

- For high selectivity, the emitting wavelength of the laser should avoid the absorption line of other gases.

The radiation wavelengths of DFB lasers in the market are all below 2 µm. Figure 2 is the near infrared spectra of methane. According to the above principles, the emitting wavelength of DFB laser is determined as 1654 nm.

2.2. Design of the PA cell

According to working modes, PA cells can be divided into two types: resonant type and non-resonant type [10-12]. Compared with non-resonant PA cells, resonant PA cells can detect flowing gas and have the advantages of low-frequency noise, high signal-to-noise ratio. Therefore, the PA cell in this paper is designed as a resonant cell. Because the cylindrical PA cell can match the axially symmetric excited sound field well, the cylindrical PA cell is designed and manufactured with brass. The PA cell is
composed of two parts: the acoustic resonator and the buffer chamber. The acoustic resonator is the place where the PA effect occurs. The buffer chamber is used to isolate the noise caused by the light absorption of the window. The inner surface of the PA cell is polished, and the two ports are sealed with quartz window with a transmittance greater than 90%. The longitudinal section is shown in Figure 3.

![Figure 2. Near infrared spectra of methane](image1)

![Figure 3. Longitudinal resonant photoacoustic cell](image2)

The geometric parameters of the PA cell are determined according to the following principles:

- In order to suppress the low-frequency noise of the device, the PA cell can work at a higher resonance frequency (above 1kHz). Generally, the smaller the length or radius of the acoustic resonator is, the higher the resonance frequency is. On the contrary, because of the use of mechanical chopper, the higher the chopper frequency is, the greater the chopper noise is, the resonance frequency cannot be too high.

- The quality factor reflects the contrast between the accumulation and dissipation of the sound energy in the PA cell. Generally, it is expected that the PA cell has a higher quality factor, but the larger the quality factor is, the greater the influence of resonance frequency drift on the PA signal is, which is not conducive to the stability of the device. Therefore, the quality factor should not be too large.

- Under the same conditions, the larger the cell constant, the stronger the PA signal. In order to increase the cell constant, the length of the acoustic resonator can be increased or its radius can be reduced, but the radius cannot be too small, which increases the difficulty of the laser collimation. Once the light beam shines on the cell wall, it will inevitably cause the absorption of the cell wall and increase the system noise.

After comprehensive analysis, the length and radius of the acoustic resonator are determined to be 10cm and 0.5cm. For the length and radius of the buffer chamber, researches show that when the length of the buffer chamber is 1 / 2 of the length of the resonator and the radius is more than 3 times of the radius of the resonator, it has better isolation effect[13-15]. Therefore, the length and diameter of the buffer chamber are 5cm and 4cm, respectively.

At the middle of the resonator, the sound wave is the strongest, and the best detection effect can be obtained, so the microphone ek3024 is placed at this position. At the ends of the resonator, the sound field is the weakest. Setting the gas inlet and outlet of the PA cell at this position can weaken the noise caused by gas flow.

3. Experimental results and analysis

3.1. Radiation characteristics of the laser

In the experiment, ltc502, a laser controller of Thorlabs company, is used to adjust the operating temperature and injection current of the DFB laser, while Q8384, a spectrum analyzer of ADVANTEST company, is used to record the radiation wavelength of the DFB laser. Figure 4 (a) and figure 4 (b) are the radiation wavelength curves of the laser at different operating temperatures and different injection currents, respectively. It can be seen that the radiation wavelength of the laser
increases approximately linearly with the increase of the working temperature or the injection current, and the change gradient of the radiation wavelength to the working temperature is greater than that to the injection current. Figure 4 (a) shows that the wavelength tuning range of the laser is about 1653-1656.3nm and the temperature tuning rate is about 0.102nm/℃ at the operating temperature of 20-40℃ under the injection current shown in the figure. Figure 4 (b) shows that the wavelength increment of the laser does not exceed 0.5nm and the current tuning rate is about 0.005nm/mA when the injection current increases from 20mA to 100mA at the operating temperature as shown in the figure 4.

In conclusion, although the DFB laser has certain tunability, its tuning range is limited; when the operating temperature or injection current is certain, the radiation wavelength basically changes linearly with the injection current or operating temperature; when the radiation wavelength of the laser is calibrated, the operating temperature can be changed for coarse tuning, while the injection current can be changed for fine tuning.

3.2. Resonance frequency and quality factor of the PA cell

The resonance frequency of the PA cell can be calibrated by a certain concentration of standard methane gas. Keeping the output power, radiation wavelength of the laser and the methane concentration in the PA cell unchanged, adjust the frequency of the chopper from 500Hz to 1700Hz slowly, record the change of the PA signal, and get the frequency response curve of the PA cell as shown in figure 5. It can be seen from figure 5 that the PA signal is greatly affected by the modulation frequency. The closer the modulation frequency is to the resonance frequency, the stronger the PA signal will be. In the modulation frequency range of the chopper, a strong and a weak resonance peak appear in figure 5. The strong resonance peak is due to the first-order longitudinal resonance of the sound wave in the PA cell. The measured resonance frequency is 1403Hz. The weak resonance peak near 755Hz is caused by the resonance of the sound wave in the buffer chamber and the pipes with sealed windows at both ends.

Quality factor Q is an important parameter of the PA cell. Its actual value can be determined according to the frequency response curve of the PA cell.

\[ Q = \frac{f_{\text{res}}}{\Delta f} \]  

where, \( f_{\text{res}} \) is the resonance frequency, \( \Delta f \) is the width of the whole line at the resonance frequency. In order to get \( f_{\text{res}} \) and \( \Delta f \), Lorentz line is needed to fit the experimental data. The Lorentz function used in this paper is as follow:

\[ S = \frac{\delta}{1 + 4((f - f_{\text{res}})^2 / \eta)} \]  

where, \( S \) is the PA signal, \( \delta \) is the resonant peak height, \( f \) is the modulation frequency, \( \eta \) is the full line width at 1 / 2 resonance frequency. The result of fitting the measured value of PA signal in the
range of 1370-1430hz of the first-order longitudinal resonance peak in figure5 with this function is shown in figure6. From figure 6, $f_{\text{res}}$ is 1403Hz, $\Delta f$ is 29.1Hz, and $Q$ is 48.2.

### 3.3. Relationship between PA signal, laser power and methane concentration

The standard methane gas with a concentration of 1000µL/L is slowly injected into the PA cell. Adjust the laser wavelength to 1654nm, keep the chopper frequency at 1403Hz, set the integration time of the lock-in amplifier at 1s, constantly change the laser power, and record the PA signal under different powers. In the range of 2 ~ 15mW, the PA signal changes linearly with laser power, as shown in figure 7. The experimental results are fitted by the linear regression method, and the goodness of fit is obtained $R^2 = 0.9982$.

A gas distribution system which is composed of high-purity nitrogen, 1000µL/L standard methane, mass flow controller, mixing coil, etc. is used to study the relationship between the PA signal and the methane concentration. Keeping the laser power at 15MW, wavelength at 1654nm, the chopper frequency at 1403Hz and integration time of lock-in amplifier at 1s, record the PA signals and the corresponding five methane concentrations. The experimental results are shown in figure 8. Obviously, the PA signal is linear with the methane concentration. The experimental results are fitted by linear regression method, and the goodness of fit is obtained $R^2 = 0.9989$.

### 4. Conclusion

Although the on-line monitoring technology of dissolved gas in oil has been studied for more than 50 years, there are still many deficiencies in the existing technology that cannot meet the field requirements. In this paper, methane is taken to study the photoacoustic spectroscopy which has a good application prospect in the on-line monitoring of dissolved gases in oil. A laser resonant photoacoustic spectrometer has been designed for methane detection. The design ideas and methods of the device are discussed in detail. Relevant tests are designed for testing and verifying the important parameters of the device. The experimental results show that the radiation wavelength of the DFB laser increases approximately linearly with the increase of operating temperature or injection current, and the change gradient of radiation wavelength to operating temperature is greater than that to
injection current. Under the condition of low methane concentration and low laser power, the relationship between PA signal, laser power and methane concentration is linear.

Acknowledgments
We would like to express our gratitude to all those helped us during the writing and publish of this paper.

References
[1] Duval M. (2002) A review of faults detectable by gas-in-oil analysis in transformers. IEEE Electr. Insul. Mag., 18: 8-17.
[2] Tapan K.S. (2003) Review of modern diagnostic techniques for assessing insulation condition in aged transformers. IEEE Trans. Dielectr. Electr. Insul. 10: 903–917.
[3] Arakelian V.G. (2004) The long way to the automatic chromatographic analysis of gases dissolved in insulating oil. IEEE Electr. Insul. Mag., 20: 8-25.
[4] Zylka P. (2005) Electrochemical gas sensors can supplement chromatography-based DGA. Electrical Engineering. 87:137–142.
[5] Liu X.Y., Zhou F.J., and Huang F.L. (2002) Research on on-line DGA using FT-IR. In: International Conference on Power System Technology Proceedings. Hangzhou. pp.1875– 1880,
[6] Miklos A., Hess P., and Bozoki Z. (2001) Application of acoustic resonators in photoacoustic trace gas analysis and metrology. Rev. Sci. Instrum. 72: 1937–1955.
[7] Pao Y. H.(1977) Optoacoustic spectroscopy and detection. Academic Press. New York.
[8] Kania P., Civiš S.(2003) Application of InAsSb/InAsSbP and lead chalcogenide infrared diode lasers for photoacoustic detection in the 3.2 and 5 μm region. Spectrochim. Acta, Part A. 59: 3063-3074.
[9] Liu X., Zhou F., Hu J., (2004). Prospect to apply photoacoustic spectroscopy in dissolved gases in oil analysis. Transformer, 41: 30~33.
[10] Li J., Gao X., Li W., (2006) Near-infrared diode laser wavelength modulation-based photoacoustic spectrometer. Spectrochim. Acta, Part A, 64: 338-342
[11] Hao L., Han J., Shi Q., (2000) A highly sensitive photoacoustic spectrometer for near infrared overtone. Rev. Sci. Instrum. 71: 1975-1980.
[12] Besson J., Schilt S., and Thevenaz L.(2004) Multi-gas sensing based on photoacoustic spectroscopy using tunable laser diodes. Spectrochim. Acta, Part A. 60: 3449-3456.
[13] Schit S., Thevenaz L., Nikdes M., (2004) Ammonia monitoring at trace level using photoacoustic spectroscopy in industrial and environmental applications. Spectrochim. Acta, Part A, 60: 3259-3268.
[14] Telles E.M., Bezerra E. and Scalabrin A. (2005) A photoacoustic spectrometer for trace gas detection. J. Phys. IV France. 125: 885-888.
[15] Song K., Cha H. K., Kapitanov V. A., (2002) Differential Helmholtz resonant photoacoustic cell for spectroscopy and gas analysis with room-temperature diode lasers. Appl. Phys. B. 75: 215-227.