Hindawi Publishing Corporation
Journal of Spectroscopy
Volume 2015, Article ID 737635, 7 pages
http://dx.doi.org/10.1155/2015/737635

*Research Article*

# Detection of Dissolved Carbon Monoxide in Transformer Oil Using 1.567 $\mu$m Diode Laser-Based Photoacoustic Spectroscopy

**Qu Zhou,[1,2] Chao Tang,[1] Shiping Zhu,[1] Weigen Chen,[2] and Xiaojuan Peng[2]**

[1]*College of Engineering and Technology, Southwest University, Chongqing 400715, China*
[2]*State Key Laboratory of Power Transmission Equipment & System Security and New Technology, Chongqing University, Chongqing 400030, China*

Correspondence should be addressed to Qu Zhou; zhouqu@swu.edu.cn and Weigen Chen; 15541342@qq.com

Received 6 August 2014; Revised 10 October 2014; Accepted 11 October 2014

Academic Editor: Wen Zeng



Carbon monoxide (CO) is one of the most important fault characteristic gases dissolved in power transformer oil. With the advantages of high sensitivity and accuracy, long-term stability, and short detection time, photoacoustic spectroscopy (PAS) has been proven to be one promising sensing technology for trace gas recognition. In this investigation, a tunable PAS experimental system based on a distributed-feedback (DFB) diode laser was proposed for recognizing dissolved CO in transformer oil. The molecular spectral line of CO gas detection was selected at 1.567 $\mu$m in the whole experiment. Relationships between the photoacoustic (PA) signal and gas pressure, temperature, laser power, and CO gas concentration were measured and discussed in detail, respectively. Finally, based on the least square regression theory, a novel quantitative identification method for CO gas detection with the PAS experimental system was proposed. And a comparative research about the gas detection performances performed by the PAS system and gas chromatography (GC) measurement was presented. All results lay a solid foundation for exploring a portable and tunable CO gas PAS detection device for practical application in future.

## 1. Introduction

Large power transformers are costly and essential apparatus in power transmission and distribution system [1, 2], and their running conditions have important influence on the safety and reliability of the whole power system [3, 4]. Carbon monoxide is a critical fault characteristic gas dissolved in oil-filled power transformers, which can timely and effectively reflect the insulation performance of transformer insulating paper and paperboard [5]. And it has been widely used in assessing the insulation state of running transformers. Online monitoring and analyzing the gas concentration and generation rate of dissolved CO gas in transformer oil plays a quite significant role in transformer condition assessment and fault diagnosis [6]. In recent years, interest in CO gas detection has been extremely simulated and many researchers have been immersed into this field [5–9]. And metal oxide semiconductors, palladium gate field effect transistors, catalytic combustion sensors, and fuel cell sensors are the main conventional methods used to detect and analyze dissolved gases in transformer oil [5, 7].

As a novel gas sensing technology, photoacoustic spectrometry (PAS) has obtained great development and reported effectively for recognition of both reducing and oxidizing gases [10, 11]. For instance, Spagnolo et al. [10] reported a NO trace gas sensor based on quartz-enhanced photoacoustic spectroscopy and external cavity quantum cascade laser. Lewicki et al. [11] designed a 2 $\mu$m diode laser-based quartz-enhanced photoacoustic spectroscopy system for carbon dioxide and ammonia detection. Due to the advantages of high sensitivity and accuracy, rapid detection speed, long-term stability, and no gas separation and consumption [12, 13], PAS would be a promising detection technology for dissolved fault characteristic gases in transformer oil, such as hydrogen, carbon monoxide, methane, ethane, ethylene, and acetylene [3].

And with the advantages of narrow line width, tunable wavelength, and so forth, diode laser has developed as

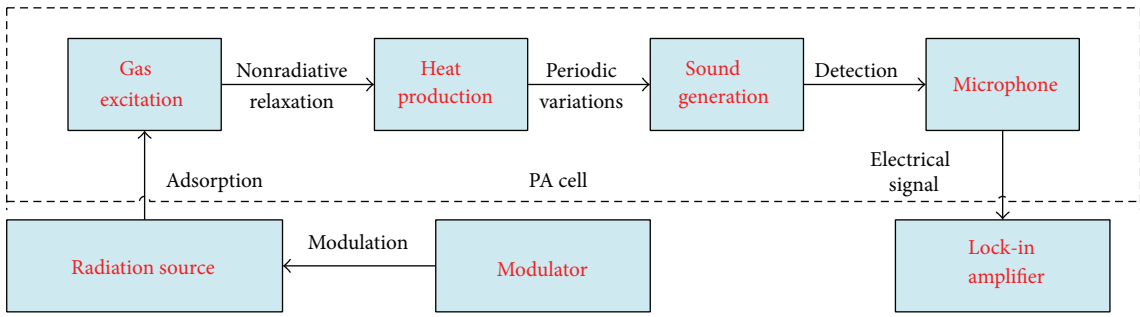


Figure 1: The principle of gas photoacoustic effect.

an ideal light source, which can be used to analyze molecular absorption lines and obtain good selectivity, large dynamic range, excellent portability, and adjustability [14]. In this study, a distributed-feedback (DFB) diode laser-based PAS experimental system was proposed, and the molecular spectral line was selected at 1.567 $\mu$m for CO detection. CO response characteristics between the PA signals and gas pressure, temperature, laser power, and gas concentration were performed and discussed. Furthermore, the least square regression method was applied to quantitatively recognize the gas concentrations from the measured PA signals.

## 2. Experimental Setup

*2.1. The Principle of Gas Photoacoustic Spectroscopy.* Photoacoustic spectrometry is a kind of calorimetric spectroscopy technique with high sensitive and dynamic range based on the gas photoacoustic effect [6]. The basic principle of gas photoacoustic effect is represented in Figure 1. Generation and detection of photoacoustic signal is a complex energy conversion process, which combines with light, heat, sound, and electricity.

Firstly, light generated from the radiation source is modulated by a modulator and passes into a PA cell container. Some gas molecules will absorb certain wavelengths of modulated light and excite to the upper energy state from its ground states. Then the absorbed energy is released to the PA cell and heats the gas molecule periodically to generate the same frequency thermoacoustic waves with the modulation light. Finally, the generated acoustic waves are sensed by high sensitivity of microphone and translated into electrical signals.

On the basis of the fluid mechanism and thermodynamics law, the gas PA signal $S_{PA}$ can be expressed as follows [6, 15]:

$$S_{PA} = C_{cell}\alpha P_0. \quad (1)$$

As shown in (1) $S_{PA}$, $C_{cell}$, $\alpha$, and $P_0$ denote the gas PA signal, the PA cell constant, the gas absorption coefficient, and the incident laser power, respectively, where the gas PA signal, $S_{PA}$, is proportional to the product of gas absorption coefficient and incident laser power. And the PA cell constant $C_{cell}$ reflects the conversion from light energy to acoustic energy.

*2.2. The Photoacoustic Spectroscopy Experimental Setup.* In this investigation, a tunable PAS experimental setup for gas recognition with a DFB diode laser was proposed [15] and the structure diagram of the gas PAS detection system was shown in Figure 2. It can be clearly seen in Figure 2 that the main experimental platform consists of several components including laser controller, laser source, lock-in amplifier, frequency modulator, modulating chopper, pressure sensor, temperature sensor, microphone, and laser power meter.

As shown in Figure 2 a certain wavelength of infrared radiation light generated by the diode laser is modulated to a particular frequency of intermittent beams by a modulating chopper firstly and then is injected into the PA cell to excite the PA effect. Finally, the excited acoustic waves are detected by a microphone for gas recognition. For the purpose of minimizing the acoustic noise generated by wall absorption, a collimator is installed at the end of the laser so that the beams could be aligned with the longitudinal axis of the PA cell.

A butterfly shape DFB diode laser (NLK1L5GAAA, NEL Corporation, Japan) was selected as the laser source, which was mainly fabricated with InGaAsP material. The central wavelength of the DFB diode laser is 1.567 $\mu$m with a maximum power output of 20 mW, a narrow linewidth of 2 MHz, and a side-mode suppression ratio of 43 dB. The deviation of its radiation wavelength is not bigger than 1 nm under room temperature. The diode laser is operated at an amplitude-modulation mode, and its working temperature and injection current are controlled by a laser controller (ITC502, THORLABS Corporation, USA) to tune the emission wavelength. A mechanical modulating chopper (SR540, Stanford Research System Inc., Sunnyvale, CA, USA) was applied to obtain a particular frequency of intermittent beams and a microphone (EK-3024, Knowles Corporation, USA) was used to acquire the PA signal with a sensitivity of 22 mV/Pa. Finally the PA signal was measured using a lock-in amplifier (SR830, Stanford Research System Inc., Sunnyvale, CA, USA).

The PA cell is the core of the gas PAS detection system, and its performance has a significant influence on the sensitivity and stability of the experimental system [16]. In our test the PA cell is made of stainless steel which has a high heat conduction coefficient. And it is designed as a first longitudinal resonant mode and the physical figure and the longitudinal section drawing of the PA cell are shown in Figures 3 and 4. One can clearly see from Figures 3 and 4 that the PA cell mainly contains five departments: a cylindrical resonator cavity, two Brewster windows, and two buffer volumes.

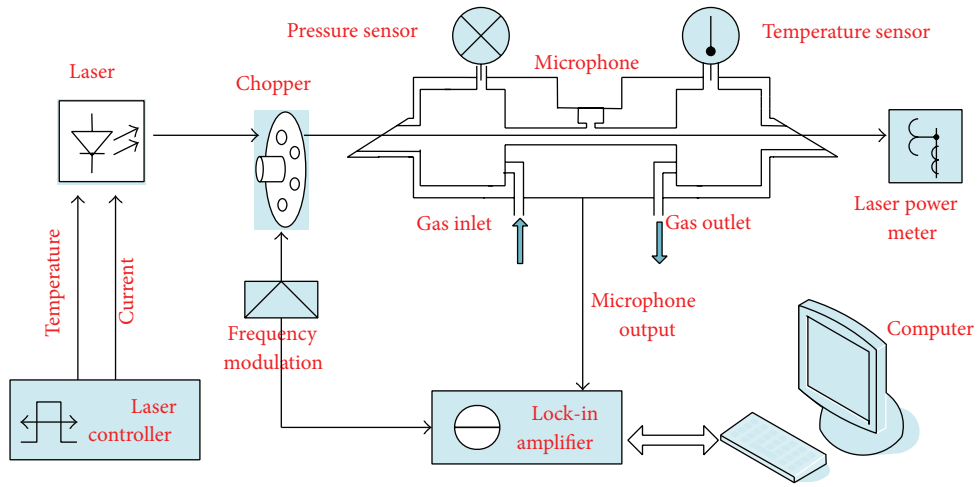


Figure 2: The structure diagram of the gas PAS detection system.

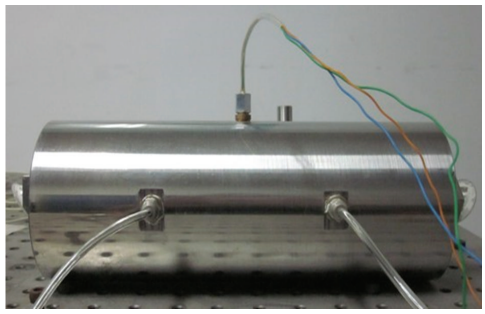

Figure 3: The physical figure of the fabricated PA cell.

The length and width of the resonator cavity are 120 mm and 6 mm, respectively, and 60 mm and 30 mm for the length and radius of the buffer volume, separately. The theoretical resonance frequency, quality factor, and cell constant of the PA cell in our experiment are calculated to be about 1395.7 Hz, 32.8, and 3775.35 Pa·cm/W.

## 3. Results and Discussion

*3.1. The Molecular Spectral Line of Carbon Monoxide.* Gas detection with the PAS system mainly depends on the wavelength of the radiation light source; thus the radiation wavelength of the DFB diode laser should be well-matched with the characteristic spectrum line of the target gas [6]. The basic principles [14] for choosing the characteristic wavelengths of CO gas are as follows.

All characteristic wavelengths should be covered in the spectrum output range of the radiation source. Cross-interference between CO gas and the potential interface gases (other characteristic fault gases dissolved in transformer oil and impurity gases) should be avoided or decreased as much as possible. And the characteristic wavelength should be chosen at a stronger adsorption place.

Combined with the HITRAN 2008 molecular spectroscopic database [17], we calculated the near infrared spectra of CO gas using the line-by-line integral method. Figure 5 shows the calculating result of CO gas with the temperature of 300 K, the pressure of 0.1 MPa, and concentration of 1000 $\mu$L/L.

According to the selecting guidelines of gas characteristic absorption lines, the line at 6380.3012 $cm^{-1}$ (1.567 $\mu$m) with an intensity of $2.138 \times 10^{-23}$ $cm^{-1}$ (molecule·$cm^{-2}$) was chosen as the characteristic absorption line of CO gas in the following experiments. Meanwhile, no obvious spectral absorption has been observed at 1.567 $\mu$m for other fault gases dissolved in transformer oil, implying an excellent selection absorption line for CO detection.

*3.2. The PAS Performances of Carbon Monoxide.* Since the PA cell is sealed during the whole measurement, a variation of the CO gas pressure will directly change the gas PA signal immediately. The influence of gas pressure to PA signal is mainly by means of the change of gas molecular absorption coefficient. Figure 6 shows the PA signal of CO gas as a function of gas pressure ranging from 0.03 MPa to 0.12 MPa, where the power of the DFB diode laser was operated at 13.7 mW with a radiation wavelength of 1.567 $\mu$m, atmospheric temperature of 300 K, and CO gas concentration of 10000 $\mu$L/L. As shown in Figure 6, the PA signal increases rapidly first in linearity with increasing the gas pressure below 0.08 MPa and nearly reaches saturation at 0.10 MPa. This is mainly due to the variation of the gas molecular absorption spectrum broadening under different pressure. Therefore, if the gas pressure could be controlled and maintained equal to and higher than 0.1 MPa, the influence of the gas pressure to PA signal will be eliminated nearly. The saturated PA signal to 10000 $\mu$L/L of CO gas under the current condition is about 28.56 $\mu$V.

Temperature is another significance influence factor to the PA signal. A standard concentration of CO gas was injected into the PA cell slowly in a dynamic flow way under various operating temperature to investigate the PA signal versus operating temperature. In the whole test period, the gas pressure was kept at 0.1 MPa, the integration time of the lock-in amplifier was set as 1 s, and the power of the DFB diode laser was maintained at 13.7 mW. As shown in

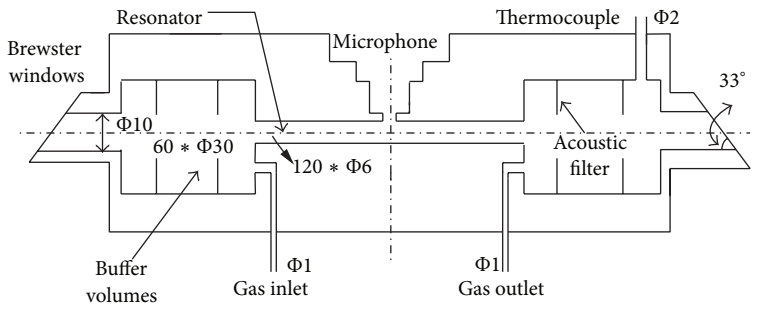


Figure 4: The longitudinal section drawing of the PA cell.

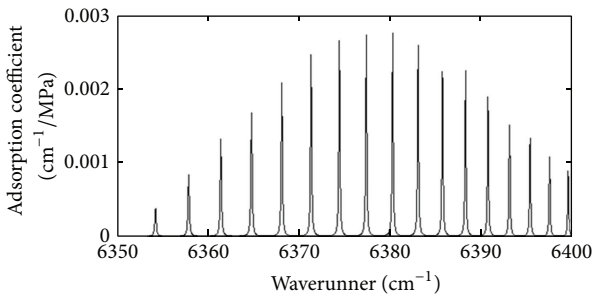


Figure 5: The characteristic absorption lines of CO in the spectral range of 6350~6400 cm$^{-1}$.

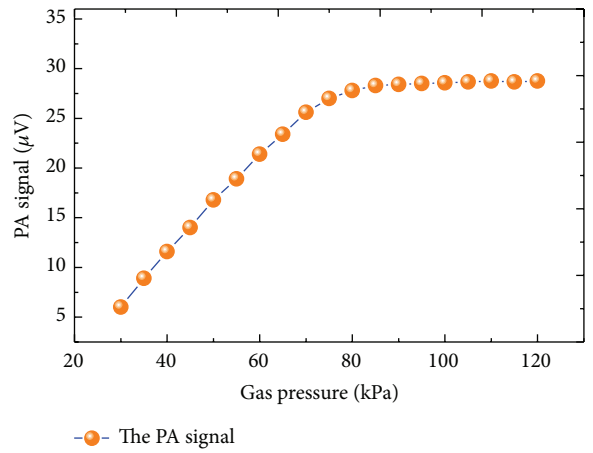


Figure 6: The PA signal versus CO gas pressure ranging from 0.03 to 0.12 MPa.

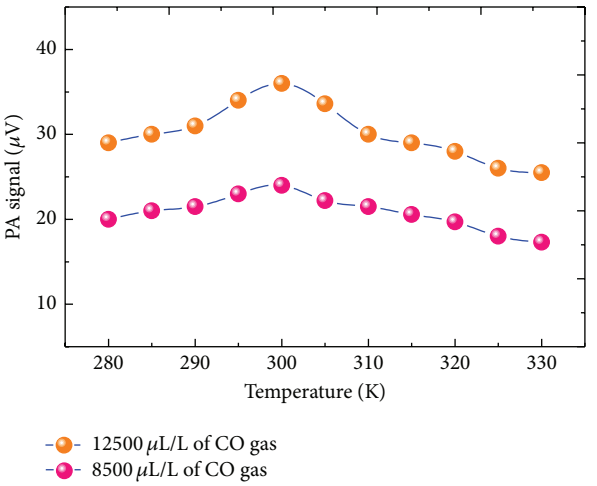


Figure 7: The PA signal versus operating temperature ranging from 280 to 330 K.

Figure 7, the PA signal increases firstly and reaches its maximum value and then decreases rapidly with the further increasing operating temperature. These results indicate that the chopping frequency should be adjusted timely according to operating temperature during the PAS experiment to obtain the maximum PA signal.

A standard concentration of 5000 $\mu$L/L of CO gas was injected into the PA cell slowly. The chopping frequency at 1305 Hz referred to the measured first-order longitudinal resonance frequency was regulated and maintained. The PA response of CO gas versus different levels of laser power ranging from 3 to 14 mW was investigated through adjusting the laser output power. It is noted that when adjusting the laser output power, there would exist an inevitable migration between the laser radiation wavelength and the characteristic absorption line of CO gas at 1.567 $\mu$m. Therefore, a seasonable calibration of the laser radiation wavelength is necessary and should be employed immediately. In this study an effective calibration method was performed as follows. The laser output power was set at the expected value first and then fine-tuned the laser temperature until the PA signal reached its maximum, where the laser radiation wavelength could be supposed to adjust back to the characteristic absorption line of CO gas.

Figure 8 shows the PA signal and linear fit curve of CO gas to laser power ranging from 3 to 14 mW, where the gas pressure was maintained at 0.1 MPa, the integration time of the lock-in amplifier was set as 1 s, and the operating temperature was 300 K. As shown in Figure 8, a good quasilinear relationship between the laser power and the PA signal has been measured, which is well consistent with (1). That is to say the number of the excited gas molecules increases with an increasing laser output power at a certain concentration of target gas, and it should be pointed out that the PA signal

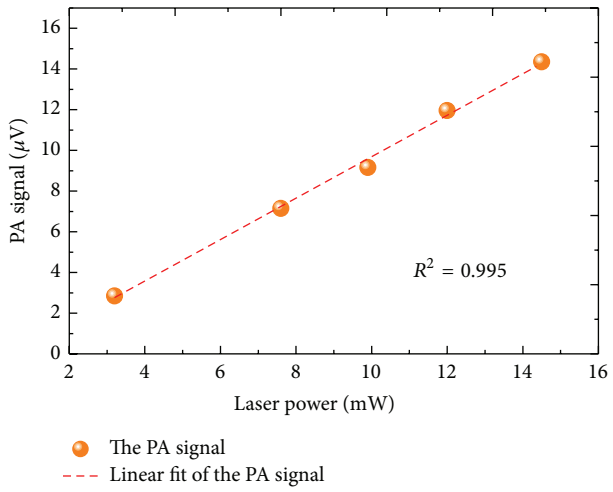


FIGURE 8: The PA signal versus laser power in the range of 3 to 14 mW.

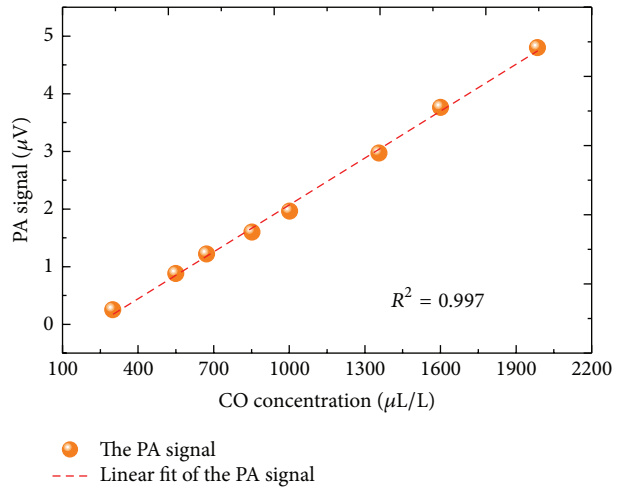


FIGURE 9: The PA signal versus CO concentration ranging from 300 to 2000 μL/L.

will not increase consistently and turn to be saturated at a threshold power.

The gas responses of the PAS detection system to various concentrations of CO gas were measured and represented in Figure 9. In our experiment different concentrations of CO gas were obtained using a RCS2000-A computer controlled automatic gas distribution system with high purity nitrogen as the carrier gas. The measurement was performed under the optimum condition, namely, a gas pressure of 0.1 MPa, a laser output power of 13.7 mW, an integration time of 1 s, a laser radiation wavelength of 1.567 μm, a chopping frequency of 1305 Hz, and an operating temperature of 300 K. It can be seen clearly in Figure 10 that a good linearity between the PA signal and CO gas concentration was found, well consistent with (1) as well, and the linear regression coefficient $R^2$ is as high as 0.997. Similarly with the relationship between the PA signal and the laser power, it should be pointed out that the PA signal will not increase unceasingly, and a saturation phenomenon would appear at the corresponding threshold concentration.

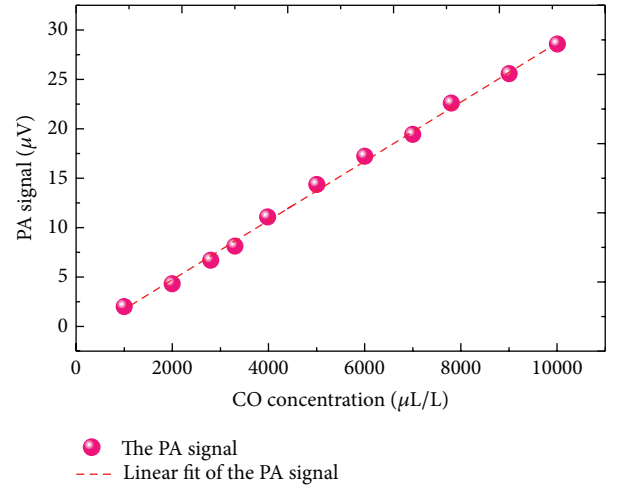


FIGURE 10: The regression relationship between CO concentration and PA signal with the least square regression method.

*3.3. The PAS Quantitative Analysis of Carbon Monoxide.* Based on the least square regression principle [15, 18], a novel quantitative identification method was proposed for CO gas recognition with the PAS experimental system. The relationship between the measured PA signal and the known CO concentration is established using the least square regression method first. Then according to the established regression relationship, the concentration value of an unknown CO gas can be derived from the PA signal value measured by the PAS detection system. This proposed method can effectively avoid the measurement errors introduced by the PA cell constant, gas absorption coefficient, laser power, and so on. Various concentrations of CO ranging from 1000 to 10000 μL/L have been obtained with the RCS2000-A gas distribution system and measured by our experimental device.

As shows in Figure 10 the PA signal exhibits a good linear relationship with CO gas in the whole concentration range. The regression relationship is

$$y_{CO} = 0.003x_{CO} - 1.3241. \quad (2)$$

A comparison study about the PAS detection results with the gas chromatography (GC) test results was performed to investigate the detection accuracy of PAS system. Detection error ($e$) is defined as the deviation percentage of $C_{PAS}$ compared with $C_{GC}$, where $C_{PAS}$ and $C_{GC}$ denote the PAS detection value and the GC detection value, respectively:

$$e = \frac{|C_{PAS} - C_{GC}|}{C_{GC}} \times 100\%. \quad (3)$$

One can clearly see in Table 1 that detection error from the PAS measurement result compared with the GC method is quite small, that is, not greater than 2%. Considering

Table 1: Measurement results detected by PAS and GA.

| CO concentration | PAS ($\mu$L/L) | GA ($\mu$L/L) | Detection error (%) |
|---|---|---|---|
| Sample 1 | 5019.4 | 5003.8 | 0.31 |
| Sample 2 | 2012.7 | 2000.6 | 0.61 |
| Sample 3 | 1011.5 | 1002.3 | 0.92 |
| Sample 4 | 860.9 | 851.7 | 1.08 |
| Sample 5 | 682.1 | 673.9 | 1.22 |
| Sample 6 | 559.8 | 550.2 | 1.75 |

the error induced by gas chromatograph, gas distribution system, and other laboratory equipment and human factors, the regression results are acceptable. All results indicate that the proposed gas analysis method based on the DFB diode laser PAS system and combined with the least square regression approach is feasible and effective.

## 4. Conclusion

In this investigation, we proposed a tunable distributed-feedback (DFB) diode laser-based PAS system for the purpose of recognizing dissolved CO in transformer oil. According to the HITRAN 2008 molecular spectroscopic database, the characteristic absorption line at 6380.3012 $cm^{-1}$ (1.567 $\mu$m) was selected as the molecular spectral line of CO gas. Gas response characteristics were measured with the proposed PAS system, and relationships between the sensing performances and gas pressure, temperature, laser power, and gas concentration were investigates in detail. Moreover, the least square regression approach was applied to quantitatively recognize the CO gas concentration from the measured PA signal. Compared with the GC measurement, error from the PAS system is not bigger than 2%. All results indicate the proposed method is an effective and feasible way for CO gas recognition, laying a solid foundation for exploring PAS online monitoring device for practical application.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgments

This work has been supported in part by Fundamental Research Funds for the Central Universities (nos. SWU-114051 and XDJK2014B031) and National Special Funds for Major Research Instrumentation Development (no. 2012YQ-160007).

## References

[1] M. Duval, "A review of faults detectable by gas-in-oil analysis in transformers," *IEEE Electrical Insulation Magazine*, vol. 18, no. 3, pp. 8–17, 2002.

[2] M. Wang, A. J. Vandermaar, and K. D. Srivastava, "Review of condition assessment of power transformers in service," *IEEE Electrical Insulation Magazine*, vol. 18, no. 6, pp. 12–25, 2002.

[3] W. Fu, Q. Zhou, J. Zou, Z. Gu, W. Chen, and C. Wang, "Using a sensitive optical system to analyze gases dissolved in samples extracted from transformer oil," *IEEE Electrical Insulation Magazine*, vol. 30, no. 5, pp. 15–22, 2014.

[4] M. Duval and J. J. Dukarm, "Improving the reliability of transformer gas-in-oil diagnosis," *IEEE Electrical Insulation Magazine*, vol. 21, no. 4, pp. 21–27, 2005.

[5] W. Chen, Q. Zhou, F. Wan, and T. Gao, "Gas sensing properties and mechanism of Nano-$SnO_2$-based sensor for hydrogen and carbon monoxide," *Journal of Nanomaterials*, vol. 2012, Article ID 612420, 9 pages, 2012.

[6] Y. Yun, W. Chen, Y. Wang, and C. Pan, "Photoacoustic detection of dissolved gases in transformer oil," *European Transactions on Electrical Power*, vol. 18, no. 6, pp. 562–576, 2008.

[7] W. Chen, Q. Zhou, and S. Peng, "Hydrothermal synthesis of Pt-, Fe-, and Zn-doped $SnO_2$ nanospheres and carbon monoxide sensing properties," *Advances in Materials Science and Engineering*, vol. 2013, Article ID 578460, 8 pages, 2013.

[8] H. Teichert, T. Fernholz, and V. Ebert, "Simultaneous in situ measurement of CO, $H_2O$, and gas temperatures in a full-sized coal-fired power plant by near-infrared diode lasers," *Applied Optics*, vol. 42, no. 12, pp. 2043–2051, 2003.

[9] R. Wang, D. Zhang, W. Sun, Z. Han, and C. Liu, "A novel aluminum-doped carbon nanotubes sensor for carbon monoxide," *Journal of Molecular Structure: THEOCHEM*, vol. 806, no. 1–3, pp. 93–97, 2007.

[10] V. Spagnolo, A. A. Kosterev, L. Dong, R. Lewicki, and F. K. Tittel, "NO trace gas sensor based on quartz-enhanced photoacoustic spectroscopy and external cavity quantum cascade laser," *Applied Physics B: Lasers and Optics*, vol. 100, no. 1, pp. 125–130, 2010.

[11] R. Lewicki, G. Wysocki, A. A. Kosterev, and F. K. Tittel, "Carbon dioxide and ammonia detection using 2 $\mu$m diode laser based quartz-enhanced photoacoustic spectroscopy," *Applied Physics B*, vol. 87, no. 1, pp. 157–162, 2007.

[12] C. Popa, M. Patachia, S. Banita, and D. C. Dumitras, "Exertion in kangoo jumps aerobic: evaluation and interpretation using spectroscopic technique determinations," *Journal of Spectroscopy*, vol. 2013, Article ID 602434, 6 pages, 2013.

[13] M. A. Gondal, A. Dastageer, and M. H. Shwehdi, "Photoacoustic spectrometry for trace gas analysis and leak detection using different cell geometries," *Talanta*, vol. 62, no. 1, pp. 131–141, 2004.

[14] T. Laurila, H. Cattaneo, V. Koskinen, J. Kauppinen, and R. Hernberg, "Diode laser-based photoacoustic spectroscopy with interferometrically-enhanced cantilever detection," *Optics Express*, vol. 13, no. 7, pp. 2453–2458, 2005.

[15] W. Chen, B. Liu, H. Zhou, Y. Wang, and C. Wang, "Diode laser-based photoacoustic spectroscopy detection of acetylene gas and its quantitative analysis," *European Transactions on Electrical Power*, vol. 22, no. 2, pp. 226–234, 2012.

[16] V. A. Kapitanov, V. Zeninari, B. Parvitte, D. Courtois, and Y. N. Ponomarev, "Optimisation of photoacoustic resonant cells with commercial microphones for diode laser gas detection," *Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy*, vol. 58, no. 11, pp. 2397–2404, 2002.

[17] L. S. Rothman, I. E. Gordon, A. Barbe et al., "The HITRAN 2008 molecular spectroscopic database," *Journal of Quantitative Spectroscopy and Radiative Transfer*, vol. 110, no. 9-10, pp. 533–572, 2009.

[18] H. Sun and Q. Wu, "Least square regression with indefinite kernels and coefficient regularization," *Applied and Computational Harmonic Analysis*, vol. 30, no. 1, pp. 96–109, 2011.