Multi-component Gas Photoacoustic Detection

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Abstract. Based on the basic principles of photoacoustic spectrometry, this paper uses methane and acetylene as examples to conduct a research for the multi-component gas photoacoustic detection. The photoacoustic spectrometer designed in this paper has the advantages of good selectivity and large detection range, and the proposed multi-component gas photoacoustic quantification method based on least squares regression does not require cell constants and gas absorption coefficient parameters, thus avoiding errors introduced by these parameters. The method proposed in this paper provides a method reference for the engineering application of photoacoustic spectrometry.

1. Introduction

Dissolved gas in oil is one of the important characteristic quantities to characterize the early latent faults of operating power transformers [1]. The online monitoring technology of dissolved gas in oil has a good application prospect in the field of online evaluation of transformer operation status and prediction of its remaining life [2,3]. At present, the gas detection methods used in online monitoring devices of dissolved gas in transformer oil are mainly gas chromatography [4], gas sensor method [5], Fourier infrared spectroscopy [6], etc., but in long-term use, there are disadvantages such as complicated sampling, cross-sensitivity, poor long-term stability, and insufficient detection gas components in these methods.

Photoacoustic (PA) spectrometry, as an optical detection technology, which does not need to consume and separate gas, and shows unique advantages in terms of sensitivity, selectivity, and dynamic detection range [7-9], so it has huge application potential in the field of transformer oil dissolved gas online monitoring technology. Based on the basic principles of photoacoustic spectroscopy technology, this paper targets at the earliest methane gas produced by the deterioration of the insulating oil and acetylene gas which is often accompanied by discharge faults inside the transformer, and studies the photoacoustic spectrum detection methods of various faulty characteristic gases in transformer oils, so as to provide a theoretical basis for the design of multi-component fault characteristic gas photoacoustic spectrometers.

2. Principle and experimental device for multi-component gas photoacoustic detection

Photoacoustic spectrometry is a spectral calorimetric technology based on photoacoustic effects that generates thermal energy by directly measuring the absorption of light energy by a substance [10]. In the photoacoustic effect of gas, gas molecules absorb the modulated specific wavelength infrared light energy and are excited to a high-energy state. Because the high-energy state is extremely unstable, the molecules then convert the absorbed light energy into thermal energy in the form of non-radiative transitions and return to the ground state; because the light energy is
periodically modulated, this causes the thermal energy of the gas molecules enclosed in the gas pool to change periodically, which is macroscopically expressed as a change in pressure, that is, to generate sound waves [11]. For multi-component mixed gas, because the gas has selective absorption of infrared light, that is, different gas components have specific infrared absorption spectra, so the composition of the gas can be determined based on the wavelength information of the infrared light source used to excite the photoacoustic effect of the gas; on the other hand, since the intensity of the acoustic wave is related to the volume fraction of the absorbed gas component, the quantitative relationship between the intensity of the acoustic wave and the volume fraction can be used to determine the volume fraction of the gas component.

Based on the above principles, the photoacoustic spectrometer shown in Fig.1 is designed, which mainly includes distributed feedback semiconductor lasers, laser controllers, choppers, photoacoustic cells, phase-locked amplifiers, and computers. The distributed feedback semiconductor laser of NEL company used in this device has an emission line width of 2MHz, which can be ignored relative to the absorption line width of the gas (generally in GHz). Therefore, this laser is an ideal monochromatic light source for laser control. The laser controller uses ITC502 from Thorlabs. The photoacoustic cell in this paper is designed as a first-order longitudinal resonant photoacoustic cell. Its longitudinal section is also shown in Fig.1. The central resonant cavity is a cylindrical cavity with a length of 10cm and a diameter of 1cm. The cavities at both ends of the resonant cavity are called buffer chambers. They are used to isolate the noise caused by the light absorption of the window sheet. The length of the buffer room is 5cm and the diameter is 4cm. The photoacoustic cell is made of brass, the inner surface is polished, and both ports are sealed by quartz windows plates with a transmittance greater than 90%. The sound wave produced by the photoacoustic effect is detected by Knowles' microphone EK3024. The microphone EK3024 is placed in the centre of the resonant cavity and its opening is just flush with the tube wall of the resonant cavity, so the best detection effect can be obtained. The sensitivity of EK3024 is 22mV/Pa. The chopper uses Stanford's SR540. Its frequency modulation range is 4~3.7kHz. The square wave signal output by the chopper and the sine wave signal output by the microphone are used as the reference signal and the signal to be measured of the phase-locked amplifier SR830. After cross-correlation detection, the photoacoustic signal is extracted and sent to the computer.

Fig.1 Schematic diagram of photoacoustic spectrometer

Since the type of gas detected by the photoacoustic spectrometer depends on the working wavelength of the laser, this paper chooses the working wavelength of the laser according to the following principles:

I. In order to make the system have a high detection sensitivity, it is appropriate to choose absorption lines with strong absorption in the infrared spectrum of the gas;

II. To avoid cross absorption interference between gases, the absorption lines of the gas to be measured should avoid overlapping with the absorption lines of other faulty characteristic gases and non-faulty characteristic gases;

III. Make the tuning range of the laser cover several adjacent absorption lines, because its characteristic parameters may change with the extension of the working time of the laser, choose
a wavelength range with multiple strong absorption lines can ensure that at least one absorption line is available;

IV. The selected laser operating wavelength is within the commercially available laser wavelength range.

Based on this, this paper chooses 1654nm and 1520nm lasers to detect CH$_4$ and C$_2$H$_2$ respectively. Figure 2 shows the infrared spectra of CH$_4$ and C$_2$H$_2$ near 1654nm and 1520nm.

3. Photoacoustic detection of multi-component gas

3.1. Cross-absorption experiment between gases

In order to test whether the infrared radiation of the two lasers has been cross-absorbed by CH$_4$ and C$_2$H$_2$, the following experiment was performed: a certain volume fraction of CH$_4$ gas was injected into the photoacoustic cell, and repeat the measurement multiple times of the photoacoustic signals under 1520nm and 1654nm lasers respectively, and the result is shown in Fig.3(a). Similarly, after cleaning the photoacoustic cell with N$_2$, fill the cell with a certain volume fraction of C$_2$H$_2$ gas, and repeat the measurement of the photoacoustic signals multiple times under two lasers of 1520nm and 1654nm respectively, and the measurement result is shown in Fig.3 (b).

It can be seen from Fig.3 that the 1654nm laser only causes absorption of CH$_4$, while the 1520nm laser only absorbs C$_2$H$_2$. It can be seen that the use of lasers of these two wavelengths does not cause cross-interference between gases, indicating that the system has good selectivity. In addition, it can be seen from Fig.3 (a) and (b) that the signals measured under the 1520nm and 1654nm lasers are not zero. This is caused by noise, not gas absorption.
3.2. Multi-component gas photoacoustic quantification method

Theoretical research shows that there is the following relationship between photoacoustic signals and gas volume fractions [11]:

\[ S_{PA} = C_{cell} N_{tot} c \sigma P \]  

In the formula, \( S_{PA} \) is the photoacoustic signal, \( C_{cell} \) is the cell constant, \( N_{tot} \) is the total gas molecular density, \( \sigma \) is the absorption cross section of the gas, \( c \) is the gas volume fraction, and \( P \) is the laser power. In ideal situation, using \( m \) laser lines to analyze the \( n \) component gases (\( m \geq n \)), the photoacoustic signals under the \( m \) spectral lines can be obtained. According to formula (1), for the volume fraction of each component of the gas, an equation system (formula (2)) can be established.

\[
\begin{align*}
S_1 &= C_{1i} P_i N_{tot} \sum_{k=1}^{n} \sigma_{ik} c_k \\
&\vdots \\
S_n &= C_{ni} P_i N_{tot} \sum_{k=1}^{n} \sigma_{nk} c_k
\end{align*}
\]

In the formula, \( S_i \) is the photoacoustic signal under the spectral line \( i \); \( P_i \) is the power of the spectral line \( i \); \( N_{tot} \) is the total particle number density; \( \sigma_{ik} \) is the absorption cross section of the gas component \( k \) under the spectral line \( i \), and \( c_k \) is the volume fraction of the gas. If there is no cross-absorption between gases, that is, \( \sigma_{ik} = 0 \) (\( i \neq k \)), then formula (2) can be simplified as:

\[
\begin{align*}
S_1 &= C_{11} P_1 N_{tot} \sigma_{11} c_1 \\
&\vdots \\
S_n &= C_{n1} P_1 N_{tot} \sigma_{n1} c_1 \\
S_1 &= C_{1n} P_n N_{tot} \sigma_{1n} c_n \\
&\vdots \\
S_n &= C_{nn} P_n N_{tot} \sigma_{nn} c_n
\end{align*}
\]

Using the measured photoacoustic signal and using formula (2) or (3) to invert the gas volume fraction, there are some problems. For example, in actual measurement, due to the influence of various noises in the system, the photoacoustic signal measurement results will have deviations; at the same time, no matter the experimental value or the theoretical value of the cell constant, laser power, gas particle number density, and absorption coefficient must be different from the real value, these errors will be added to the analysis results of the gas volume fraction during the inversion calculation. In view of these problems, according to the photoacoustic spectroscopy device with good selectivity, this paper proposes a gas photoacoustic quantitative analysis method based on least squares regression. The idea of this method is: first, obtain a large number of photoacoustic signals of a single gas component of known volume fractions; then, the least-
squares regression method is used to perform a one-dimensional linear regression on the photoacoustic signal and the volume fraction of the gas component to obtain a quantitative relationship between them; according to this relationship, the measured photoacoustic signals of the multi-component mixed gas are used to invert the volume fractions of different components of the gas.

Establishing a quantitative relationship between photoacoustic signals and gas volume fractions has the following two steps:

I. the measurement of photoacoustic signals of known gas volume fractions;
II. the least squares regression fit of the measured photoacoustic signals and their corresponding gas volume fractions.

In the experiment, several CH₄ and C₂H₂ gas samples with different volume fractions based on the mass flow controller between 10 and 10000 μL / L were used. To avoid gas leaks due to poor airtightness of the photoacoustic cell, use the flowing gas method to have the gas flow through the photoacoustic cell slowly, and use gas chromatograph to finalize the gas volume fraction; when measuring the photoacoustic signal, in order to reduce the measurement error caused by system noise interference, conduct multiple measurements to obtain an average reading.

Fig. 4 shows the relationship between the volume fractions of CH₄ and C₂H₂ and their photoacoustic signals. It can be seen that the volume fraction of CH₄ and C₂H₂ maintains a linear relationship with their photoacoustic signals in the range of the volume fraction shown in the figure. The result of linear fitting using the least square regression method is:

\[
\text{CH}_4: \quad y_{\text{CH}_4} = 0.351x_{\text{CH}_4} + 1.257 \\
\text{C}_2\text{H}_2: \quad y_{\text{C}_2\text{H}_2} = 1.305x_{\text{C}_2\text{H}_2} + 1.064
\]

According to the previous analysis, using the relationship between the volume fractions of CH₄ and C₂H₂ established by equations (4) and (5) and their photoacoustic signals, the volume fractions of CH₄ and C₂H₂ in the mixed gas can be retrieved.
3.3. Multi-component gas photoacoustic detection

In order to verify the correctness and accuracy of the above method and the above two formulas, Table 1 shows the comparison of the detection results of mixed gas composed of different volume fractions of CH$_4$ and C$_2$H$_2$ using photoacoustic spectroscopy and gas chromatography. The deviation $e$ represents the percentage of the difference between the photoacoustic spectrum detection value $C_{\text{PAS}}$ and the gas chromatography detection value $C_{\text{GC}}$ in the $C_{\text{GC}}$, namely:

$$e = \left| \frac{C_{\text{PAS}} - C_{\text{GC}}}{C_{\text{GC}}} \right| \times 100\%$$

(6)

It can be seen from Table 1 that the gas chromatography and photoacoustic spectroscopy systems have little difference in the detection results of CH$_4$ and C$_2$H$_2$ in the mixed gas, and the deviation of the detection of CH$_4$ does not exceed 6.6%, while the deviation of the detection of C$_2$H$_2$ is no more than 7.4%. It can be seen from the experimental results that the multi-component gas analysis method based on the DFB semiconductor laser array light source and the gas quantitative analysis method established are effective.

Table 1 Comparison of results determined by gas chromatography and photoacoustic spectrometry

| Test | Gas chromatography | Photoacoustic spectrometry |
|------|-------------------|---------------------------|
|      | CH$_4$(µL/L)      | C$_2$H$_2$(µL/L)          | CH$_4$(µL/L) | Deviation (%) | C$_2$H$_2$(µL/L) | Deviation (%) |
| 1    | 3861.5            | 3216.5                    | 3844.7       | 0.4           | 3238.2           | 0.7           |
| 2    | 1024.6            | 856.2                     | 1015.5       | 0.9           | 887.3            | 3.6           |
| 3    | 834.1             | 543.9                     | 822.9        | 1.3           | 558.2            | 2.6           |
| 4    | 53.4              | 32.7                      | 55.5         | 3.9           | 30.8             | 5.8           |
| 5    | 18.3              | 9.5                       | 19.5         | 6.6           | 10.2             | 7.4           |

4. Conclusion

In this paper, methane and acetylene are taken as examples to study the photoacoustic spectrum detection method of multi-component fault characteristic gas. The photoacoustic spectrum detection device designed based on distributed feedback semiconductor laser has good selectivity to methane and acetylene. The volume detection range is large, which can meet the application requirements of online monitoring of gas in oil. The proposed multi-component gas photoacoustic quantitative analysis method based on least squares regression does not require the cell constant and gas absorption coefficient and laser power and other parameters when inverting the gas volume fraction, so it avoids errors introduced by these parameters. The theoretical analysis and experimental results in this paper provide a meaningful reference for the design of a photoacoustic spectrum detection device for dissolved gases in oil.

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