A Method of Trace Gases Detection Based on Non-resonance Photoacoustic Spectroscopy

Zhizhen Zhu\textsuperscript{1,2}, Jiaxiang Liu\textsuperscript{1} and Yonghua Fang\textsuperscript{1,*}

\textsuperscript{1}Key Laboratory of Environmental Optics and Technology, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, 230031, Anhui, China
\textsuperscript{2}University of Science and Technology of China, Hefei, 230026, Anhui, China
\textsuperscript{*}Corresponding author email: yhfang@aiofm.ac.cn; Email: 734961000@qq.com

Abstract. It is significantly important for public health protection and environmental monitoring to complete accurate measurement of concentration information of hazardous gases and greenhouse gases. Based on the thermal effect of gas infrared absorption and the acoustic theory of photoacoustic (PA) cell, non-resonant photoacoustic spectroscopy (PAS) is an effective method to monitor gases. The basic principle of PAS is introduced, and the instrumental structure is addressed. The experiment is taken with ammonia as example and water vapor as interference. The responding coefficient of ammonia is calculated, and the output concentration is corrected with water vapor filter by correction method.

1. Introduction

In recent years, due to the needs for environmental pollution monitoring, greenhouse source and sink distribution research, chemical gas leakage monitoring, the need for high-performance gas detection system is more and more urgent [1][2].

With its outstanding advantages of high sensitivity, large dynamic range and real-time measurement of various gas components, gas photoacoustic spectroscopy technology is gradually applied to gas monitoring in air environment quality, medical treatment, fermentation process, operation status of power facilities and other aspects [2][3].

Resonance photoacoustic spectroscopy based on a laser source has achieved a very high detection resolution and sensitivity [4] due to its narrow line width and high spectral power. Currently, the detection of some gases has approached the limitation sensitivity of the photoacoustic spectroscopy ($10^{-13}$). However, the limitation of tunable laser wavelength coverage and the high cost of lasers limit the wide application of this technology. For most applications, the detection sensitivity of $10^{-6}$ magnitude has actually met the requirements [5][6]. Therefore, the technology of non-resonance photoacoustic spectroscopy with thermal infrared radiation light source has attracted people's attention again because of its advantages, such as simultaneous detection of multiple gases, reliable performance, smaller volume and low cost. In recent years, the development of low-noise, high-sensitivity microphone and weak signal electronic detection technology, the improvement of low-noise photoacoustic cell making technology, and the application of computer control and data processing technology make it possible to greatly improve the sensitivity of non-resonance photoacoustic spectrum detection based on infrared thermal radiation source [4][7].

In this paper, a method for detecting trace gases based on non-resonance photoacoustic spectroscopy is introduced. With ammonia as the measured gas, a correction method for water vapor signal is proposed. The detection coefficient of ammonia is calibrated experimentally and the detection limitation is evaluated.
2. Principle of Photoacoustic Detection
When the incoming light is modulated at a certain frequency (tens to thousands of Hertz), the pressure is modulated at the same frequency to form an acoustic wave that can be detected by a microphone mounted on a photoacoustic cell and converted into an electrical signal. The generation and detection of photoacoustic signals is a process of energy conversion from light, heat, sound to electrical signal. The detection principle is shown in Figure 1.

For a circular photoacoustic cell operating in a low-frequency non-resonance state, when the exciting light source is incident along the central axis of the cavity, the mode of annular and axial variation will not be triggered in the cavity, but only the high-order excitation mode of radial changes will be generated. When the modulation frequency $\omega$ is lower than the normal frequency of the lowest mode of the photoacoustic cell, the cavity of the photoacoustic cell works in the non-resonant planar wave mode. If the power of the beam is $W (\text{w/cm}^2)$, the mode amplitude of the acoustic signal can be expressed by Equation (1):

$$A_0(\omega) = \frac{i\alpha(\gamma - 1)W}{\omega\pi b^2(1 + i/\omega\tau_0)}$$  (1)

Here, $\alpha$ is the gas absorption coefficient; $b$ is the radius of the cylindrical photoacoustic cell; $\gamma$ is ratio of constant pressure heat capacity to constant volume heat capacity of the gas; and $\tau_0$ is the damping time of the acoustic signal.

For the photoacoustic spectroscopy device using electret microphone as piezoelectric sensor, the output voltage of the device responds to the pressure signal uniformly in the operating frequency range, and the output voltage signal of the device can be obtained [3]:

$$U = S_{\text{min}} C_{\text{g}} \sigma NW$$  (2)

Where $S_{\text{min}}$ is the sensitivity of microphone (mV/Pa); $C_{\text{g}} = \frac{i(\gamma - 1)}{\omega\pi e^2[1+(i/\omega\tau_0)]}$ is called photoacoustic cell constant (Pa·cm/w); $\sigma$ is the cross section of gas absorption (cm$^2$); $N$ is the number of gas molecules per unit volume (molec/cm$^3$).

It is shown in Equation (2) that the photoacoustic signal has a linear relationship with the gas concentration when other parameters are known. The measured gas concentration can be calculated directly by calibrating the linear coefficients of the photoacoustic signal and concentration of the measured gas.

3. Structure of Device
The non-resonant photoacoustic spectroscopy device is shown in Figure 2. After the broadband radiation generated by the infrared source is focused by the parabolic reflector, the frequency modulation is carried out by the stroboscopic effect generated by the modulation disk rotating at a constant rate, and then the pulse light needs to transmit a series of filters. The incident light pulse repeatedly excites the corresponding gas molecules in the photoacoustic cell at the modulation frequency, the absorption energy of the gas in the sealed photoacoustic cell is finally converted into molecular kinetic energy, which causes the local pressure change of the gas, thus generating periodic mechanical pressure fluctuation in the photoacoustic cell. The micro pressure fluctuation can be
detected by placing a microphone on both sides of the photoacoustic cell. The strength of the acoustic signal corresponds to the composition and content of the trace gas molecules measured in the photoacoustic cell. Therefore, the content of the gas components to be measured can be obtained by detecting the acoustic signal with a microphone and converting it into an electrical signal.

The filter is the key part of the device. In practical application, it is necessary to select the filter according to the radiation characteristics of the light source and the standard absorption cross section of the gas. The filter should not only ensure the strong absorption of the measured gas, but also avoid the cross interference with other interference gases as much as possible.

The measured gas is ammonia, and the carrier gas is air. Considering that water vapor (H₂O) in the air is the main interference gas, it is necessary to try to avoid the cross interference when selecting the filter according to the absorption coefficient spectrum of water vapor. The absorption spectra of water vapor and ammonia are shown in Figure 3.

After determining the ammonia filter, H₂O filter is selected to correct the ammonia signal. The filter parameters are as in Table 1.
Table 1. Selected filter parameters

| Gases | CWL(μm) | HPB(nm) | TP(%) |
|-------|---------|---------|-------|
| H₂O   | 4.7     | 150     | 70    |
| NH₃   | 2.248   | 180     | 70    |

Table 1 shows the selected filter parameters, where CWL represents the center wavelength, HPB represents the bandwidth, and TP represents the filter transmittance.

4. Experimental Results

4.1 Calibration for Ammonia

It can be seen from Equation (2) that, when the values of other parameters are constant, there is a linear relationship between the photoacoustic signal amplitude and concentration of gas. Then, by preparing several groups of standard gases with known concentrations to be measured, the corresponding photoacoustic signals are measured, and the calibration equation between the photoacoustic signal amplitude and concentration is obtained by least square regression. At room temperature, the standard ammonia gases with different concentrations (air as carrier gas) are charged into the photoacoustic cell for one minute. The cavity volume of the photoacoustic cell is about 12.7ml, and the mass flow controller is used to fill the photoacoustic cell at a flow rate of 50ccm/min (ml/min). The gas in the cell can be completely renewed in one minute. By measuring standard gases with different concentrations of ammonia, the linear relationship between photoacoustic signal and concentration is obtained as in Equation (3).

\[ u = 3.88959 \times 10^{-5} c + 0.08876 \]  

(3)

Where \( u \) is the voltage value of photoacoustic signal (V), \( c \) is the ammonia volume fraction (μL/L).

Relationship between ammonia photoacoustic signal and concentration is as in Figure 4.

![Figure 4. Relationship between photoacoustic signal and concentration of ammonia](image)

4.2 Correction of Water Vapor Interference

Ammonia is very soluble in water, and one volume of water can dissolve 700 volumes of ammonia. In the detection of ammonia with air as carrier gas, the influence of water vapor on ammonia concentration has to be considered. The moisture content in the air often changes, and the water vapor has spectral characteristics in almost all infrared bands, so it needs to be corrected. In this paper, water vapor filter is selected to calibrate ammonia. The calibration process is divided into two steps: firstly, calculate the detection coefficient of water vapor filter to get the volume fraction of water vapor; secondly, calculate the mixing coefficient of ammonia and water vapor to get the water vapor concentration.
correction formula.

4.2.1 Calibration of Water Vapor Detection Coefficient

Because the water vapor content in the air is unknown, the air carrier gas signals with different humidity are measured twice. In order to facilitate the comparison, the ambient temperature is controlled at 25°C, and the air humidity of the two experiments is recorded with a hygrometer. The photoacoustic signals corresponding to the water vapor filter of air carrier gas measured twice are as follows:

\[
\begin{cases}
    u_1 = h x_{air1} + n \\
    u_2 = h x_{air2} + n
\end{cases}
\]  

(4)

Where \( u \) is the voltage signal (V) output by the water vapor filter; \( x_{air} \) is the volume fraction of water vapor in the air (μL/L); \( h \) is the response coefficient; \( n \) is the bias coefficient, that is, the voltage signal in dry air.

Convert Equation (4) to ratio form as in Equation (5).

\[
\frac{u_1 - n}{u_2 - n} = \frac{x_{air1}}{x_{air2}}
\]

(5)

At the same temperature, the water vapor concentration in the air is directly proportional to the humidity, so Equation (5) can be expressed as the humidity ratio relationship. The voltage signal value (air as carrier gas) and humidity measured twice are shown in Table 2.

Table 2. The voltage signal value (air as carrier gas) and humidity measured twice

| No. | Photoacoustic signal (V) | Humidity |
|-----|--------------------------|----------|
| 1   | 0.07389                  | 31%      |
| 2   | 0.07464                  | 36%      |

By substituting the voltage and humidity measured twice into Equation (5), the background photoacoustic signal of dry air as carrier gas is obtained as 0.06805, and the unit is V.

At room temperature of 25°C, the regression coefficient of four different concentrations of water vapor (air as carrier gas) is calculated by the least square method. The four measured values and the fitting curve are shown in Figure 5. Combined with the dry air background photoacoustic signal obtained earlier, the relationship between water vapor photoacoustic signal and concentration is as follow:

\[
u = 2.65247 \times 10^{-5} c_{H_2O} + 0.06805
\]

(6)

Where \( u \) is the voltage value of photoacoustic signal (V), \( c_{H_2O} \) is the water vapor concentration (μL/L).
4.2.2 Correction of ammonia detection coefficient

Water vapor has absorption band in almost all infrared bands. The photoacoustic signal of ammonia filter is a mixture of ammonia and water vapor. The influence of water vapor on ammonia signal should be deducted. Under the environment of 25°C and 31% humidity, the mixture of water vapor and ammonia with different concentrations is respectively configured for 5 times of average measurement, and the experimental data record is shown in Table3.

Table 3. Photoacoustic signal and corresponding concentrations of ammonia and water vapor

| No. | 1    | 2    | 3    | 4    | 5     |
|-----|------|------|------|------|-------|
| Photoacoustic signal (V) | 0.08956 | 0.091234 | 0.092718 | 0.094603 | 0.095887 |
| Concentrations of ammonia (μL/L) | 0 | 40.21418 | 80.42836 | 120.6425 | 160.8567 |
| Concentrations of water vapor (μL/L) | 0 | 113.9402 | 227.8803 | 341.8205 | 455.7607 |

Using the least square regression, relationship between the photoacoustic signals with ammonia filter and the concentration of ammonia and water vapor are as in Equation (7):

\[
u = 6.86417 \times 10^{-6} c_{NH_3} + 1.13056 \times 10^{-5} c_{H_2O} + 0.08976
\]  

(7)

In the Equation (7), \(c_{NH_3}\) represents ammonia concentration (μL/L); \(c_{H_2O}\) represents water vapor concentration (μL/L).

Substituting Equation (6) into Equation (7), the relationship between ammonia photoacoustic signal and concentration after water vapor correction is obtained as in Equation (8).

\[
u = 3.66439 \times 10^{-5} c_{NH_3} + 0.42623 u_{H_2O} + 0.06076
\]  

(8)

In order to compare the results before and after correction, the known concentration of ammonia (42.277μL/L) and the unknown concentration of water vapor are configured here. The volume fraction before and after correction is calculated by Equation (3) and Equation (8), respectively (see Table 4). It
can be seen that the water vapor correction improves the accuracy of quantitative detection.

### Table 4. Comparison of volume fraction before and after water vapor correction

| Volume fraction(μL/L) | Concentration configured | Concentration before correction | Concentration after correction |
|-----------------------|--------------------------|---------------------------------|-------------------------------|
| 42.277                |                          | 46.236                          | 42.209                        |
| Relative errors       |                          | -                               | 9.36%                         | 0.16%                         |

5. Conclusion
In this paper, a method of trace gas detection based on non-resonance photoacoustic spectroscopy is introduced in detail. In the experiment, ammonia was used as the measured gas, the air as carrier gas. Water vapor filter was used to correct the concentration of ammonia, which improved the accuracy of quantitative detection. Non-resonance photoacoustic spectroscopy can detect ammonia in μL/L level, and measure other gases only by changing or adding specific filters. It will have a wide range of application prospects in gas monitoring for atmospheric environment quality, medical treatment, fermentation process, operation status of electric power facilities, etc.

6. References
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