Quantitative detection of trace H$_2$S based on ultraviolet differential optical absorption spectroscopy

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Abstract. As an important decomposition component of SF$_6$, H$_2$S can provide an important information for the evaluation of insulation state of SF$_6$ gas insulated equipment. Since H$_2$S has obvious absorption in the ultraviolet (UV) range of 190~230 nm, the UV absorption spectrum detection platform is established to realize its detection. In this paper, SF$_6$ decomposition component detection platform based on UV spectroscopy was built, and the UV absorption spectrum of H$_2$S was obtained. Since the UV absorption spectrum directly obtained by the instrument is susceptible to spectral scattering and high frequency noise, the detection sensitivity is low. Therefore, this paper uses the UV differential algorithm to obtain the UV absorption spectrum of H$_2$S. After experimental tests, the $R^2$ of the fitted line is as high as 0.999. Moreover, the method has good repeatability for detection of H$_2$S, the results show that the absolute error does not exceed 0.2 μL/L. The noise is calculated by randomly collecting 30 sets background spectrum, and the detection limit is 0.590 μL/L when the signal-to-noise ratio is 1. A method for detecting H$_2$S gas concentration based on UV differential absorption spectroscopy is proposed, which is suitable for on-line monitoring of trace H$_2$S in the decomposition components of SF$_6$ gas insulated equipment.

1. Introduction

As an excellent insulating gas, SF$_6$ has strong insulation performance and arc extinguishing performance. Its electric strength is about 2.5 times that of air under the action of uniform electric field, and the arc extinguishing ability is up to 100 times of air [1]. SF$_6$ gas insulated equipment such as GIS and GIL are widely used in the power industry because of their small occupation, safety and reliability, easy maintenance, and low electromagnetic and environmental hazards [2,3].

However, the operating experience shows that SF$_6$ gas insulated equipment has inevitable insulation defects throughout its life cycle from production to installation, such as metal burrs generated during equipment manufacturing, air bubbles remaining during the casting process of insulating parts, loose parts during the transportation, metal particles that have not been cleaned during installation and maintenance, and poor contact during the operation. The existence of these defects will lead to insulation faults such as partial discharge, partial overheating, and insulation cracking [4,5]. When the partial discharge or other faults occurs in the SF$_6$ gas insulation equipment, SF$_6$ may be decomposed in components such as CS$_2$, SO$_2$, H$_2$S, SOF$_2$, and SO$_2$F$_2$ [6]. If these defects are not discovered in time, as the operation time of the electrical equipment increases, the insulation defects will further deteriorate and eventually lead to equipment damage. In order to ensure long-term trouble-free operation of SF$_6$ gas insulated electrical equipment, real-time monitoring of its insulation state is necessary.
**H₂S** is a typical SF₆ decomposition component, and its accurate detection has important engineering significance. The optical detection for gas has the advantages of high sensitivity, fast detection speed, and high reliability. In recent years, the optical detection methods for H₂S mainly include Fourier infrared absorption spectroscopy and photoacoustic spectroscopy [7-10]. Infrared absorption spectroscopy can detect various decomposition components and realize on-line monitoring. However, this method has characteristic peak overlap problems which limits its detection accuracy and detection types of gas [11]. Photoacoustic spectroscopy uses the detection of acoustic characteristics when gas molecules are excited to vibrate, and has a relatively high sensitivity for H₂S detection. But weak acoustic signals or the conversion of acoustic signals are susceptible to ambient temperature, pressure and external noise [12]. The above two methods have some limitations in the online monitoring application of the components.

Ultraviolet (UV) absorption spectroscopy, qualitative and quantitative detection of gas types and concentration by detecting absorption spectrum of the gas in the UV band. The method has been widely used in the field of atmospheric environment detection, and has the characteristics of high detection speed, high sensitivity, low gas consumption, simultaneous detection of multiple gas concentrations. It has been applied to the analysis and detection of SF₆ decomposition components of electrical equipment [13]. H₂S has strong absorption in the 190–230nm band, so it can be detected by UV spectroscopy. However, its absorption spectrum is often susceptible to interference from scattering and high-frequency noise, resulting in low detection sensitivity. Therefore, this study uses the UV differential spectrum and wavelet function to establish an H₂S concentration inversion algorithm to achieve high-precision detection of H₂S.

2. **Mechanism and measurement basis**

The generation of H₂S mainly occurs when there is a small amount of water involved in the decomposition process of superheat decomposition and partial discharge of SF₆. The mechanism is that SF₆ first is heated or breaks after collision, and produces S²⁻. H₂O breaks to produce H⁺. Finally, S²⁻ combined with H⁺ to generate H₂S. The chemical formula of the reaction mechanism is described as follows:

\[ \text{SF}_6 + 2e^- \rightarrow S^{2-} + 6F^- \]  \hspace{1cm} (1)

\[ S^{2-} + 2H^+ \rightarrow H_2S \]  \hspace{1cm} (2)

The UV absorption spectrum of H₂S can be obtained from the MPI-Mainz database. Figure 1 shows the UV absorption spectrum of H₂S provided by the database. As can be seen, the spectrum of H₂S is mainly concentrated in the 180–230 nm, which belongs to the deep UV band.

![Figure 1. H₂S UV absorption spectrum.](image-url)
According to Lambert Beer's Law [14]:

\[ I(\lambda) = I_0(\lambda)e^{-LC(\lambda)} \]  

(3)

Where \( I_0(\lambda) \) is the initial light intensity; \( I(\lambda) \) is the absorption light intensity; \( L \) is the length of the absorption light path; \( C \) is the concentration of the gas to be measured, in units of mol/cm\(^3\); \( \sigma(\lambda) \) is the absorption cross section of the gas, in units of cm\(^2\)/mol. Lambert Beer's law reveals the quantitative relationship between the absorption degrees and the optical path and concentrations.

In the measurement, the non-spectral noise signal such as dark current generated by the photodetector during the spectrum acquisition process and the background noise signal of the absorption spectrum caused by the jitter of the experimental equipment such as fiber need to be deducted, the processed spectrum \( A(\lambda) \) can be expressed as:

\[ A(\lambda) = \ln \left( \frac{I_0(\lambda) - I_N(\lambda)}{I_0(\lambda) - I_T(\lambda)} \right) \]  

(4)

Where: \( I_0(\lambda) \) is the background spectrum; \( I(\lambda) \) is the H\(_2\)S spectrum; and \( I_N(\lambda) \) is the dark spectrum. The above formulas are the theoretical basis for quantitative detection of H\(_2\)S.

3. Experimental platform

The entire detection system consists of four main parts: the UV light source, the gas pool, the spectrometer, and the gas distribution system, as shown in figure 2. The UV light source is a xenon lamp source. The wavelength range of the light source is 190~400 nm. The detection platform uses deep UV fiber to transmit UV light, which can ensure transmission efficiency above 80% in the band above 180 nm. The gas pool is made of stainless steel, and its inner wall is treated with Teflon coating to avoid the adsorption of the detection gas. The UV light is reflected in the gas pool and the path length is 0.8 m. The spectrometer has a detection range of 185~410 nm and contains the UV absorption band of H\(_2\)S. The gas distributor is an intelligent dynamic gas distribution instrument with a maximum dilution ratio of 300:1 and an accuracy of ±1% FS. It can be matched with the required concentration of H\(_2\)S. The exhaust gas generated during the test is passed into the exhaust gas treatment device. The gas contact parts are made of stainless steel and Teflon tube.

The experiment steps are as follows:

After the gas distributor is preheated, the background gas and the standard gas are connected, and 1, 2, 5, 10, and 20 μL/L H\(_2\)S gas are sequentially prepared from low concentration to high concentration.

Passing high-purity N\(_2\) into the gas pool, vacuuming the gas pool by vacuum pump to clean the pool, repeating this work three times, then flushing high-purity N\(_2\) into the gas pool as background gas.

Before the light source is introduced into the gas pool, the spectral data collected by the spectrometer at this time is recorded. This spectrum is called dark spectrum \( I_d \). When the UV light is
preheated to stability, the spectral data of the background gas is measured as $I'_0$.

In order to avoid mutual interference of different concentration, the H$_2$S spectrum should be measured in the order from low to high, that is $I_1$, $I_2$, $I_5$, $I_{10}$ and $I_{20}$ were recorded. 10 sets of spectral data were collected for each concentration. One group was used for qualitative and quantitative analysis of H$_2$S, and the other 9 sets were used as accurate data to verify the inversion formula.

In order to eliminate the possible interference of the instrument at the beginning and the end of the spectrum, 6 data points are discarded at the first and last ends respectively. The absorption spectrum is calculated according to equation (4), and the differential absorption spectrum is further obtained by the algorithm.

4. Results and analysis

4.1. H$_2$S initial spectral data

The UV absorption spectrum and the UV differential absorption spectrum of H$_2$S gas were obtained, as shown in figure 3. Figure 3(a) shows the UV absorption spectrum of different concentrations of H$_2$S. The results show that as the gas concentration increases, the overall absorption increases significantly. H$_2$S has UV absorption in the wavelength band before 250 nm, but the narrow band absorption is only within 210 nm. When the concentration of H$_2$S is 5, 10, or 20 μL/L, UV absorption spectrum shows significant narrow-band absorption. While the 2 μL/L H$_2$S narrow-band absorption is weak. The 1 μL/L H$_2$S has substantially no narrow-band absorption characteristics. Figure 3(b) is the corresponding UV differential absorption spectrum extracted from the UV absorption spectrum of different concentrations of H$_2$S. It can be seen that there is no absorption data in the background spectrum, and each concentration of H$_2$S exhibits a narrow band. As the concentration increases, the narrow band absorption of H$_2$S gradually increases. However, the UV differential absorption spectrum of various concentrations of H$_2$S are obviously affected by high-frequency noise. The lower the concentration, the more severe the effect is.

![Figure 3](image_url)

**Figure 3.** UV absorption spectrum and differential absorption spectrum of H$_2$S. (a) UV absorption spectrum and (b) Differential absorption spectrum.

The inevitable interference in the absorption process due to spectral scattering caused by impurity particles and airflow disturbances and the instability of the instrumentation equipment in the measurement process will lead that the inversion of the concentration by the original spectrum will has a large error. In contrast, UV differential absorption spectroscopy can reflect the concentration of H$_2$S, but it is severely affected by noise, especially in the case of low concentration. Therefore, before performing accurate quantitative analysis, it is necessary to further processed the spectrum.

4.2. Feature extraction and concentration inversion

UV differential absorption spectrum extracted only by removing the "slowly varying" part. In order to
maximize the removal of high frequency and low frequency noise interference, the Meyer wavelet function is used to process the UV differential absorption spectrum of H₂S. The differential absorption spectrum after treatment is shown in figure 4. Figure 4(a) shows the differential absorption spectrum of different concentrations of H₂S after filtering. The spectrum shows obvious characteristics and is hardly disturbed by noise. It can be clearly seen that with the increase of concentration, the absorption is gradually strengthened. Compared with the original absorption spectrum, the UV absorption spectrum values of each concentration are increased by several times, which is very beneficial for the quantitative detection of low concentration H₂S. Subsequently, the FFT transformation of the filtered UV absorption spectrum is further performed, shown in figure 4(b). The FFT spectrum of H₂S at each concentration peaked at the same wavenumber position (0.4345 nm⁻¹), the characteristic information was very concentrated, and the H₂S concentration increased correspondingly with the FFT peak value.

![Figure 4](image-url)  
**Figure 4.** UV absorption spectrum after filtering and FFT spectrum. (a) UV absorption spectrum after filtering and (b) FFT spectrum.

![Figure 5](image-url)  
**Figure 5.** The relationship between the FFT eigenvalues and the concentration.

In summary, the UV differential absorption spectrum after wavelet processing and its FFT peak in the wavenumber domain can be used to achieve qualitative and quantitative analysis of H₂S, and both have shown good potential.

In order to avoid the error that may be caused by the randomness of single-point data, the sum of the FFT values corresponding to the wavenumbers of 9 nm⁻¹, 10 nm⁻¹, and 11 nm⁻¹ is selected as the FFT eigenvalues to characterize the concentration of the trace H₂S. In this study, the FFT eigenvalues at different concentrations were calculated, the H₂S concentration and its corresponding FFT eigenvalues were linearly fitted by least squares method. The fitting results are shown in figure 5. The results show that FFT eigenvalue and H₂S concentration have a high linear relationship, the R² is up to
0.9999, and the inversion expression of H₂S concentration is:

\[ y = 0.4694x + 0.5269 \]  

(5)

Where \( y \) is the FFT eigenvalue; \( x \) is the H₂S concentration, the unit is μL/L.

Therefore, obtaining the UV spectrum of H₂S with unknown concentration, through smoothing and filtering, the FFT eigenvalues can be obtained, then the H₂S concentration can be calculated by equation (5). In order to verify the correctness and applicability of the obtained concentration inversion expression, this paper uses the other nine sets at each concentration to employ the inversion calculation. The inversion results are shown in table 1. The information in the table indicates that the absolute error of the inversion concentrations is less than 0.2 μL/L, and the overall fluctuation is small, which proves the availability of the concentration inversion expression.

### Table 1. The inversion results of the nine sets of measured data at each concentration.

| Initial concentration (μL/L) | Inversion concentration (μL/L) | Absolute error (μL/L) |
|-----------------------------|-----------------------------|----------------------|
| 1                           | 1.27                        | 1.27                 | 1.25 | 1.16 | 1.31 | 0.80 | 0.94 | 1.08 | 1.08 | 0.19 |
| 2                           | 1.91                        | 1.85                 | 1.86 | 1.97 | 1.87 | 1.70 | 2.04 | 1.73 | 1.99 | 0.13 |
| 5                           | 4.85                        | 4.85                 | 5.05 | 5.05 | 5.05 | 4.91 | 4.91 | 4.91 | 4.91 | 0.14 |
| 10                          | 9.75                        | 9.82                 | 9.58 | 9.91 | 9.91 | 9.62 | 9.96 | 9.95 | 9.86 | 0.18 |
| 20                          | 19.84                       | 19.84                | 19.87 | 20.06 | 19.51 | 19.91 | 20.02 | 20.03 | 20.06 | 0.13 |

### 4.3. Detection limit analysis

The experiment extracts the effective information of the spectral signal by subtracting the background spectrum and the dark spectrum, the wavelet function processing, the FFT transform, etc., and minimizes the interference of the noise signal on the gas detection. However, due to the equipment itself, the inevitable interference signal influences the concentration detection. Moreover, in the baseline subtraction and wavelet processing, the effective spectral signal cannot be completely extracted, and noise may be introduced in the extraction process. In addition, the wavelet processing amplifies the noise of the characteristic signal while amplifying the characteristic signal. Therefore, it is necessary to analyze the system noise to determine the detection limit of the detection platform.

Randomly adopting 30 sets of background spectrum, and processing the background spectrum with the same processing method of H₂S detection, calculating the FFT eigenvalues, as shown in figure 6. The eigenvalues are randomly distributed within a certain range, which has the characteristic of the system noise. To meet the statistical law, the noise level is usually characterized by the RMS value of noise, which is recorded as \( N_{\text{RMS}} \), and can be expressed as:

\[ N_{\text{RMS}} = \sqrt{\frac{\sum_{i=1}^{n} N_i}{n}} \]  

(6)
The detection limitation is an important indicator of the gas detection platform. The system noise is the main factor affecting the detection limit. The detection limit can be measured by the signal-to-noise ratio. The gas concentration to be measured corresponding to the $S_{NR}$ of 1 is used as the detection limit [15], shown as follow:

$$c_{\text{min}} = \frac{c}{S_{NR}} \quad (7)$$

Where $c_{\text{min}}$ represents the detection limit of the gas to be tested, $c$ is the known gas concentration, and $S_{NR}$ is the corresponding signal-to-noise ratio of the gas. The lower limit of detection of trace H$_2$S by the UV spectrum trace gas detection platform constructed by equation (7) is 0.590 μL/L. The results are shown in table 2.

### Table 2. Detection limit of H$_2$S.

| Background gas | 1μL/L H$_2$S FFT amplitude | System noise | $S_{NR}$ | Lower limit of detection (μL/L) |
|----------------|---------------------------|--------------|----------|---------------------------------|
| N$_2$          | 2.95                      | 1.74         | 1.69     | 0.590                           |

5. Conclusion
In this paper, an optical detection platform based on UV differential absorption spectroscopy was built. The absorption characteristics of H$_2$S in the UV range of 180–230 nm were used for spectral detection. By the differential algorithm and wavelet processing on the spectrum, the H$_2$S concentrations were obtained.

- Based on the principle of UV differential absorption spectroscopy detection, the detection process avoids the interference caused by scattering and other factors, and ensures the detection accuracy.
- This paper uses the wavelet function to process the spectrum and invert the absorption spectrum into the frequency domain, effectively reducing the interference of high and low frequency noise, enhancing the effective signal and improving the detection accuracy.
- The inversion equation between the FFT eigenvalues and H$_2$S concentrations is obtained. The $R^2$ is 0.9999, and the detection limit is as low as 0.590 μL/L.

Acknowledgments
This work was supported by Science and Technology Project of State Grid Jiangsu Power Co., Ltd. (Grant No. J2018043).

References
[1] Christophorou L G and Olthoff J K 2000 Electron Interactions with SF$_6$ J. Phys. Chem. Ref. Data. 29 267-330
[2] Tang J, Zeng F, Pan J et al 2013 Correlation analysis between formation process of SF$_6$, decomposed components and partial discharge qualities IEEE T. Dielect. El. In. 20 864-75
[3] Wang Z J and Xia H P 2018 Influence of relationship between UHF signals and discharge quantity of partial discharge under varius pressure in gas insulated switchgear Electr. Power Eng. Technol. 37 107-11
[4] Shi J L, Song Y X, Yang J G, Wang C and Xiao L 2017 Analysis and treatment of partial discharge abnormal signal in 252 kV GIS equipment Electr. Power Eng. Technol. 36 127-31
[5] Christophorou L G, Olthoff J K and Van Brunt R J 1997 Sulfurhexa fluoride and the electric power industry IEEE T. Dielect. El. In. 13 20-4
[6] Belmadani B, Casanovas J, Casanovas A M et al 1991 SF6 decomposition under power arcs - physical aspects IEEE T. Dielect. El. In. 26 1163-76
[7] Helman M, Moser H, Dukowiaci A et al 2017 Off-beam quartz-enhanced photoacoustic
spectroscopy-based sensor for hydrogen sulfide trace gas detection using a mode-hop-free external cavity quantum cascade laser *pl. Phys. B* **123**

[8] Sharma R, Mitra C and Tilak V 2016 Diode laser-based trace detection of hydrogen-sulfide at 2646.3 nm and hydrocarbon spectral interference effects *Opt. Eng.* **55** 037106

[9] Spagnolo V, Patimisco P, Pennetta R *et al* 2015 THz Quartz-enhanced photoacoustic sensor for H2S trace gas detection *Opt. Express* **23** 7574

[10] Chen W, Kosterev A A and Tittel F K 2008 H2S trace detection using off-axis integrated cavity output spectroscopy in the near-infrared IEEE Conference on Lasers & Electro-optics (Baltimore, USA).

[11] Ren J 2010 Study on SF6 decomposition products under partial discharge by Fourier transform infrared spectroscopy (Chongqing, China: Chongqing University)

[12] Tang J, Zhu L, Liu F *et al* 2011 Development of SF6 decomposition components detection device using acoustic technology *H. V. E.* **6** 1313-20

[13] Wang X, Li C, Zhao Y *et al* 2015 Online detection methodology of decomposition product SO2 in SF6 electrical equipment based on ultraviolet spectroscopy *H. V. E.* **41** 152-8

[14] Li X 2016 The quantitative detection research of SF6 characteristic decomposition components SO2 and CS2 based on ultraviolet differential optical absorption spectrometry (Chongqing, China: Chongqing University)

[15] Liu H 2015 The quantitative detection research of SF6 characteristic decomposition component H2S based on cantilever enhanced photoacoustic spectrometry (Chongqing, China: Chongqing University)