Study on ultraviolet absorption characteristics of SF6 decomposition components

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Abstract. Establish the UV spectrum database of the SF6 characteristic decomposition components: Based on the previous research and simulation analysis, obtain the UV spectrum of the SF6 characteristic decomposition components, and establish the corresponding database. Through the analysis of a large number of actual test data, the ultraviolet spectrum database of SO2, CS2 and H2S is obtained and established to realize the quantitative analysis of SO2, CS2 and H2S. The detection accuracy of H2S and the SO2 reaches 10^-6 level, and that of the CS2 reaches 10^-9 level, realizing the low concentration quantitative detection of SF6 characteristic components. The detection of SO2, CS2 and H2S in gas insulated equipment can effectively predict and diagnose the occurrence of partial discharge fault, partial overheating fault and solid insulation fault in gas insulated equipment. As the symbol gas, the generation of H2S directly indicates the occurrence of more serious partial overheating or partial discharge fault, while SO2 is the characteristic component gas. The occurrence of CS2 indicates that there may be a local fault involving solid insulating medium in the equipment. The detection of three gases can provide important conditions for on-line monitoring of gas insulated equipment.

1. Introduction

Detection of the partial discharge signal or partial overheating fault signal caused by equipment insulation fault is the main way for scholars at home and abroad to study the status monitoring of electrical equipment insulation fault. In terms of partial discharge, the common detection methods are: pulse current method, ultrasonic detection method, UHF method and component analysis method [1-3]. Pulse current method is a partial discharge detection method recommended by IEC60270 standard[4,5]. Its greatest advantage is that it can realize the quantitative discharge quantity. However, due to the influence of complex electromagnetic interference on site, the signal-to-noise ratio measured by this method is very low, which is difficult or even unable to meet the requirements of the field monitoring. Ultrasonic testing can effectively avoid electrical interference and initially realize the location of discharge source, but this method is difficult to realize the recognition of partial discharge mode and has poor ability to resist environmental noise interference, which is mainly used for auxiliary measurement[6-8]. UHF method is to judge the internal discharge of electrical equipment by the UHF signal excited by partial discharge received by the built-in or the external antenna sensor. It has high signal-to-noise ratio and can carry out pattern recognition. However, due to the randomness of insulation defects and the reflection of electromagnetic signal, this method is difficult to realize quantitative measurement of discharge.

The traditional partial discharge detection methods are easy to be interfered by electromagnetic and noise in equipment operation site environment, or can not realize the accurate quantitative
measurement of the discharge capacity. The diagnosis of internal fault caused by insulation is relatively vague, and there are certain limitations in practical application. Moreover, the overheat fault is different from the discharge fault, which can not be detected by the electrical, magnetic and acoustic signals excited in the process of fault detection, so there is no good on-line detection method. SF6 decomposition component analysis method is applicable to different fault types, such as partial discharge(PD) fault and the partial over thermal(POT) fault, and is not affected by electromagnetic interference. At present, the SF6 decomposition component analysis method has become a research hot-spot in the field of insulation fault detection of SF6 gas insulated electrical equipment[9-11]. Pure SF6 gas is an extremely stable inert gas, which will not decompose and react with other insulating materials or impurities during normal operation of the equipment. However, under discharge fault and overheating fault, SF6 will be decomposed into a series of low fluoride under the excitation of the energy generated by the fault. Some low fluoride will further react irreversibly with impurities such as micro water and micro oxygen in electrical equipment as well as insulation materials to generate stable products such as SO2F2, SOF2, SO2, CS2 and H2S, SO2, SOF4, H2F, CO and CS2[12,13]. By detecting the components generated by SF6 decomposition, the insulation fault can be judged. At the same time, the research also shows that there are certain differences in SF6 gas decomposition component information (type, concentration, generation rule and component proportion) detected under the different insulation fault types and severity. The diagnosis of internal insulation state of SF6 gas insulated electrical equipment can be further realized by detecting SF6 decomposition component information[14]. The SF6 decomposition component analysis method can not only reflect the sudden fault, but also identify and judge the different types and severity of the fault, and is not disturbed by electromagnetic and noise in the field, so it has high research value and application prospect. The efficient and accurate detection technology of trace gas is the key to the field application of SF6 decomposition component analysis method. In this paper, the ultraviolet spectrum trace gas detection technology is applied to the field of SF6 decomposition component detection, which not only enriches the detection methods of SF6 decomposition gas characteristic components, but also lays the foundation for the online monitoring of SF6 gas insulated electrical equipment fault decomposition characteristic components.

2. Theoretical derivation of UV-DOAS technology

Rayleigh scattering is a kind of the scattering phenomenon caused by the tiny impurity which is smaller than the wavelength of incident light (no more than 1/10~1/5λ) in the absorbing medium. When the impurity is encountered, the light will scatter in all directions, which will cause the attenuation of the incident light in the process of light path. The scattering coefficient of Rayleigh scattering is inversely proportional to the fourth power of incident light wavelength λ.

\[
\alpha_R \propto \frac{1}{\lambda^4}
\]  

(1)

A part of the incident light is scattered by the particulate impurities in the absorbing medium, part of the incident light is absorbed by the absorbing medium, and the rest is transmitted through the absorbing medium, so:

\[
I_o(\lambda) = I_R(\lambda) + I_m(\lambda) + I_e(\lambda)
\]  

(2)

Where IR(λ) is Rayleigh scattering light intensity and Im(λ) is Mie scattering light intensity. Then the Rayleigh scattering intensity can be expressed as follows:

\[
I_R(\lambda) = I_o \cdot e^{-\varepsilon_R(\lambda)L}
\]  

(3)

The intensity of Mie scattering light can be expressed as follows:

\[
I_m(\lambda) = I_o \cdot e^{-\varepsilon_m(\lambda)L}
\]  

(4)

Therefore, beer Lambert's law can be amended as follows:
Finally, considering the interference factors in the measurement of optical path, the beer Lambert law is modified to:

\[ I_i(\lambda) = I_0(\lambda) \cdot e^{-\left[ \sum c_i \cdot \sigma_i(\lambda) + \varepsilon_i(\lambda) + \varepsilon_m(\lambda) \right]L} \]  

(5)

Since \( E(\lambda) \) and \( \beta(\lambda) \) are random variables, it is difficult to calculate the volume concentration of the absorbing medium only according to the formula (6). If two monochromatic lights with similar wavelengths of \( \lambda_1 \) and \( \lambda_2 \) pass through the absorbing medium at the same time, the following results are obtained:

\[ I_i(\lambda_1) = I_0(\lambda_1) \cdot e^{-\left[ \sum c_i \cdot \sigma_i(\lambda_1) + \varepsilon_i(\lambda_1) + \varepsilon_m(\lambda_1) \right]L + \beta(\lambda_1)} \cdot E(\lambda_1) \]  

(6)

\[ I_i(\lambda_2) = I_0(\lambda_2) \cdot e^{-\left[ \sum c_i \cdot \sigma_i(\lambda_2) + \varepsilon_i(\lambda_2) + \varepsilon_m(\lambda_2) \right]L + \beta(\lambda_2)} \cdot E(\lambda_2) \]  

(7)

Since the wavelength difference between the two is very close, it can be approximately considered that \( \varepsilon_R(\lambda_1) \approx R(\lambda_2), \varepsilon_m(\lambda_1) \approx m(\lambda_2), \beta(\lambda_1) \approx \beta(\lambda_2) \). Moreover, if the optical system is adjusted properly, \( I_0(\lambda_2) \cdot E(\lambda_2) \approx I_0(\lambda_1) \cdot E(\lambda_1) \) can be basically satisfied. Therefore, the formula (9) can be simplified as follows:

\[ \sum c_i \cdot (\sigma_i(\lambda_2) - \sigma_i(\lambda_1)) \cdot L = \ln \frac{I_i(\lambda_2)}{I_i(\lambda_1)} \cdot E(\lambda_2) \cdot I_0(\lambda_2) \cdot E(\lambda_1) \cdot I_0(\lambda_1) \]

(8)

According to the measured original absorbance spectrum \( A(\lambda) \) and the slowly varying absorption spectrum \( S(\lambda) \), the differential absorption spectrum \( F(\lambda) \) of the gas to be measured can be obtained:

\[ \sum c_i \cdot \sigma'_i(\lambda) \cdot L = F(\lambda) \]  

(11)

3. Overall structure of detection platform

The hardware structure of the designed gas detection platform is shown in Figure 1. Through the purchased ultraviolet light source, the ultraviolet light with spectrum range of 190–400nm is stably output, and two optical fibers with stable and efficient transmission ability in this band range are purchased to transmit the ultraviolet light to the self-designed gas absorption cell. After many times of reflection in the gas absorption cell, the ultraviolet light absorbed by the gas to be measured is emitted from the light outlet of the gas absorption cell, and then passed through the light. The spectrum is subdivided into different bands by grating and slit, and then transmitted to the CCD(charge coupled device) detector, and the transmitted light intensity of different wavebands is measured. The transmitted light intensity data is imported into the analysis software of the computer through USB data cable, and the absorption spectrum of the gas to be measured in the gas absorption cell is finally obtained.
Figure 1. Gas detection platform.

The selected high sensitivity optical fiber spectrometer has good dynamic response in ultraviolet band, which can quickly and accurately reflect the change of optical signal. The built-in thermo-electric cooler can effectively reduce the dark noise of the detector itself, and has excellent signal-to-noise ratio. By changing the size of the slit, the optical resolution can be adjusted to 0.035nm. A high sensitivity optical fiber spectrometer is selected for spectrum acquisition equipment project, which has good dynamic response in ultraviolet band, and can quickly and accurately reflect the change of optical signal. The built-in thermo-electric cooler can effectively reduce the dark noise of CCD detector, and has excellent signal-to-noise ratio.

By using the way of single reflection, the gas absorption optical path length can be increased as much as possible while reducing the overall size of the gas pool. The optical path length is 0.8m. In order to reduce the loss of ultraviolet light in the reflection process, the inner side of concave mirror in the pool is coated with high reflectivity aluminum film, and the surface is treated with corrosion resistance, which can be used for the measurement of different kinds of gases. The combination of SMA905 fiber connector and collimating mirror group is designed at the light inlet of absorption cell, which not only facilitates the access and fixation of ultraviolet fiber, but also improves the collimation of incident light. The light outlet adopts the design of SMA905 fiber connector and focusing lens, which can increase the light intensity of the emitted light and reduce the loss of ultraviolet light in the optical path.

4. Ultraviolet absorption characteristics of SF6 decomposition components
The ultraviolet visible absorption spectra of the SO2, H2S and CS2, which are the characteristic decomposition components of SF6, were tested. The UV absorption spectra of three gases at different concentrations of the standard gas were recorded by spectrometer. Compared with the background spectrum of N2, the more intuitive gas absorption spectrogram could be obtained which is shown in Figure 2.
Figure 2. Transmission and absorption spectra of three gases.

The above picture shows the typical spectral images of the three gases. It is not difficult to see that there are obvious absorption spectra of the three gases, and they are concentrated in the UV band of 200nm–320nm, which meets detection requirements of this study. In order to more intuitively display and study the properties of the ultraviolet absorption spectra of the three gases and the position of the absorption peaks, the ultraviolet absorption spectra of the three gases at different concentrations were decomposed and detected.

5. SO$_2$, CS$_2$, H$_2$S UV absorption spectrogram

It can be seen from Figure 3 that the absorption peaks of SO$_2$ are mainly concentrated in 190–220nm and 285–310nm. Different concentrations of the SO$_2$ have obvious differences in the absorption bands. Using wavelet function to process the above absorption spectra, we can extract the absorption spectra containing only fast changing parts, as shown in Figure 4, and the bands of 190–220nm and 285–310nm are intercepted.

Figure 3. Ultraviolet absorption spectra of SO$_2$ with different concentrations.

It can be seen from Figure 4 that after removing the slow changing part, SO$_2$ gas has obvious absorption peaks in the two UV absorption bands with change of concentration, and the height of the absorption peak is positively correlated with the gas concentration.
It can be clearly seen from the above figure that the ultraviolet absorption band of CS2 is mainly concentrated in 190~210nm band, and there are obvious differences in the ultraviolet absorption band of the different concentrations of CS2 gas. Similarly, wavelet function is used to process the above ultraviolet spectrum, and the absorption spectrum containing only fast changing part can be obtained, as shown in Figure 5, and wavelength band of 190–210nm is intercepted.

Similar to SO2 gas, it can be seen from Figure 6 that the absorption peak of CS2 with the change of gas concentration in 190–210nm band has a positive correlation with the gas concentration. It can be seen from the above figure that the UV absorption band of H2S is concentrated in the 190–230 nm band. By processing the above ultraviolet spectrum with wavelet function, the absorption spectrum
containing fast changing part can be obtained. As shown in Figure 7, the wavelength band of 190–210 nm is intercepted.

![Absorption spectra of different concentrations of H2S](image)

Figure 7. UV absorption spectra of different concentrations of H2S.

6. Quantitative detection method of decomposed components

The transmission intensity spectra of SO2 with different concentrations were measured from low to high. Before the sample gas of the target concentration is introduced, the gas absorption cell is vacuumed first, and then the standard sample gas of target concentration is introduced to flush the gas absorption cell twice. After the standard sample gas with atmospheric pressure is introduced for the third time, the valves at both ends of the gas absorption cell are closed. The spectrum data at this time is called the sample gas spectrum. The absorption spectra of SO2 gas are as follows:

![Differential absorption spectrogram of SO2](image)

Figure 8. Differential absorption spectrogram of SO2.

It can be seen from Figure 8 that the extracted differential spectral signal is relatively smooth, and the noise signal is better removed. After extraction, the intensity of the spectral signal is magnified several times compared with original spectral signal, and the spectrum changes intuitively with the change of concentration. According to the differential spectrum and information, we can establish the linear relationship between the spectral signal and the concentration through Fourier transform. The results is shown in Figure 9.
Figure 9. Relationship between differential absorption spectrum of SO2 and characteristic value in frequency domain.

Results as shown in Figure 9, there is the highly linear relationship between the characteristic value of FFT and SO2 concentration, and the goodness of fit is as high as 0.9999. The inversion expression of 190–230nm concentration is as follows:

\[ y = 0.8845x + 0.0103 \]  

(1)

Where \( y \) is the FFT characteristic value of the filtered ultraviolet differential absorption spectrum of SO2; \( x \) is the SO2 concentration, unit: μL/L; Inversion expression of 190–230nm concentration is as follows:

\[ y = 0.3241x - 0.043 \]  

(2)

Table 1. Inversion results of SO2 measured data (190 ~ 230nm).

| Gas distribution concentration (ppm) | Inversion concentration(ppm) | Absolute difference average value(ppm) |
|-------------------------------------|------------------------------|---------------------------------------|
|                                     | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |                                     |
| 1                                   | 0.99 | 0.94 | 0.94 | 0.96 | 0.94 | 0.93 | 0.93 | 0.93 | 0.91 | 0.06                                 |
| 2                                   | 2.11 | 2.08 | 2.09 | 2.07 | 2.09 | 2.01 | 2.01 | 2.00 | 1.98 | 0.05                                 |
| 5                                   | 5.19 | 5.10 | 5.06 | 5.08 | 5.07 | 5.09 | 5.08 | 5.07 | 5.07 | 0.07                                 |
| 10                                  | 10.0 | 10.1 | 10.0 | 10.3 | 10.0 | 10.0 | 10.1 | 10.1 | 10.0 | 0.12                                 |
| 20                                  | 20.2 | 20.1 | 20.1 | 20.1 | 20.0 | 20.0 | 20.0 | 19.9 | 19.9 | 0.09                                 |

In order to verify the correctness and applicability of the concentration inversion expression, the inversion results are shown in Table 1. The information in the table shows that the fluctuation of concentration inversion results under each concentration is very small, and the average value of absolute difference is within the acceptable range. Therefore, the concentration inversion expression obtained in this paper has good inversion effect. With the system noise analysis method of signal-to-noise ratio of 1, the FFT eigenvalues of the 30 groups of background spectra were calculated, and the system noise NRMS was determined. Finally, the UV spectrum trace gas detection platform was established in this paper. The detection limits of the trace SO2 in 190nm~ 230nm and 280 ~ 320nm bands were 0.108 μL / L and 0.444 μL / L, respectively.

7. Field test application

10 SO2, CS2 and H2S gases with different concentrations (10ppm, 20ppm, 40ppm, 60ppm, 80ppm, 100ppm, 200ppm, 300ppm, 400ppm and 500ppm) with SF6 as background were prepared by multi group distribution gas system, and then connected to the series sensor module of SF6 decomposition products nondestructive testing device. After the indication value was stable, observe
the indication of each gas window in the human-computer exchange interface of the instrument, 10 groups of data were recorded, and the test results are shown in table 7-5.

Table 2. SO2, CS2 and H2S gas cross interference test results

|        | 1# | 2# | 3# | 4# | 5# | 6# |
|--------|----|----|----|----|----|----|
| SO2    | 0  | 10.2 | 0  | 0  | 0  | 0  |
| 10ppm  |    |     |    |    |    |    |
| 20ppm  |    | 20.3 | 0  | 0  | 0  | 0  |
| 40ppm  |    | 39.6 | 0  | 0  | 0  | 0  |
| 60ppm  |    | 60.5 | 0  | 0  | 0  | 0  |
| 80ppm  |    | 80.3 | 0  | 0  | 0  | 0  |
| 100ppm |    | 100.29 | 0  | 0  | 0  | 0  |
| 200ppm |    | 199.2 | 0  | 0  | 0  | 0  |
| 300ppm |    | 300.97 | 0  | 0  | 0  | 0  |
| 400ppm |    | 400.89 | 0  | 0  | 0  | 0  |
| 500ppm |    | 501.9 | 0  | 0  | 0  | 0  |

According to the above test results, SO2, CS2 and H2S sensor module only responds to SO2, CS2 and H2S gas, while other sensor modules have no response to the gas. The micro water concentration is self-contained in SO2, CS2 and H2S gas, and its indication is displayed in micro water sensor module, while other sensor modules have no response to SO2, CS2 and H2S gas. In conclusion, SO2, CS2 and H2S gas has no cross interference with other sensor modules. According to the measurement range of the target sensor, the gas with the concentration of about 60% of the full scale is introduced. After the sensor indication value is stable, the instrument indication value is Ci. Repeat the measurement for 6 times, and the repeatability is expressed by the relative standard deviation (RSD) of a single measurement, as shown in equation (12).

$$RSD = \frac{1}{c} \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (c_i - c)^2} * 100\%$$  (12)

The weaker the polarity, the better the stability, the smaller the relative standard deviation and the better repeatability. The stronger the electronegativity and the stronger the polarity of the negative ions, which is the difference of the adsorption induced force, and the stronger the polarity, the weaker the stability and the larger the relative standard deviation.

Figure 10. SO2, CS2 and H2S gas cross interference test the response of each sensor module.
Figure 10 shows that the on-line monitoring device of SO2, CS2, and H2S gas in high-pressure equipment based on infrared spectrum absorption technology developed in this project has more stable performance, higher sensitivity, more complete detection gas types, and is suitable for on-site decomposition product measurement.

8. Conclusion
In this paper, the on-line monitoring equipment of SO2, CS2, and H2S is developed. The results show that the sensor module of SO2, CS2, and H2S gas on-line monitoring device of high-pressure equipment has no cross interference of gases, and the gas to be detected has good repeatability. After calibration, the field test data show that the relative error is less than 3%, showing good consistency, repeatability and accuracy, which is suitable for the nondestructive testing of SF6 decomposition products in complex environment of high voltage switchgear.

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