A New Method to Improve the Precision of SO₂ Measurement in Atmosphere

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Abstract: The thesis discusses the status quo and existent problems of SO₂ measurement, explores sensor mechanism of measurement precision of SO₂, and deduces the mathematical measurement model of SO₂ according to Lambert-Beer Law. Aiming at the nonlinearity problem existing in the mathematical model, it employs Taylor’s series expansion to resolve the problem. In addition, it designs the gas room of double optical paths to measure SO₂ by infrared, which utilizes four detectors to eliminate the impact of CO₂ and disturbed noise by receiving signals. Finally, through the analysis of the experimental data, it proves that this method has such features as easy implementation, high precision, strong anti-jamming capability, and real-time and on-line measurement of SO₂ required in the industry field.

1. Introduction

SO₂, CO₂ and NOₓ, the main pollution components in the boiler gas, are brought with the rapid development of modern industry. They do tremendous harm to existent ecological environment people depend on. Thereinto, the emission of SO₂ is one of the most important factors to cause environment pollution, so countries all over the world strengthen the research and development of measuring SO₂. In order to protect environment in China, we must enhance the detection of the pollution gas, discharged by coal coking, oil processing, smelting and so on, and reinforce effective control of environment pollution. According to inadequate statistics, China invested over 40 billion RMB in the project of detection and treatment of SO₂ during the period of “Tenth-Five Year Plan”.

There are a number of methods to measure the concentration of SO₂, which fall into two types at present. One is termed as off-line analysis, such as electrical conductivity method, iodometric method, constant-potential electrolysis, chemiluminescence-based method, etc. Electrical conductivity method refers to the method of measuring concentration by using electrical conductivity, corresponding to that of measured matter, when the solution temperature is constant. It requires ascertaining electrical conductivity periodically, so it is only applied to the analysis in chemical laboratory. Iodometric method is to put amyllum indicator into the standard solution of iodine, and calculate the concentration of SO₂ according to reaction of resultant sulfurous acid and iodine in the process, but it is prone to the artificial errors. These methods feature slow measurement of SO₂, complex structure, and limited application only in laboratory, so it is difficult to meet the requirement of on-line measurement.
The other type is on-line measurement. Take ultraviolet fluorescence for example, this method adopts band-pass filter (intervene filter, film-plate reflect filter) to gain excited spectrum, and the concentration of SO$_2$ is measured by surveying the decreasing intensity of ultraviolet fluorescence. It has less reliability, lower precision, and weaker anti-jamming capability. Most of the on-line methods necessitate complex experiment equipment and high expenses. Obviously, they are not suitable for our country. Therefore it has practical significance to seek out a new and scientific method of SO$_2$ measurement to satisfy the real time, on-line, and precise requirement.

2. Measurement of SO$_2$ by Infrared Absorption

2.1. Principle of Infrared Detection

Every gas has its special absorption spectrum. When shined by infrared, gas molecules absorb some infrared energy and change it into other energy. Molecular vibration frequency is related to its characteristic, and radiation will be absorbed at the wavelength of corresponding frequency. So the characteristic is utilized to measure the absorption of infrared by the measured matter.

SO$_2$ has two infrared special absorption spectrums. One is 3.98μm, and the other is 7.35μm. So SO$_2$ has two obvious special absorption peaks. If the light scattering is not considered, SO$_2$ molecules shined by infrared will absorb the radiant energy of infrared spectrum at 3.98μm and 7.35μm, and transform the radiant energy into the vibratory and rotational energy.

As gas detector, made according to the principle of infrared absorption, has higher stability and precision, longer service life, lower price, more mature technology and products etc [6], it is feasible to develop SO$_2$ sensor, based on the principle of infrared special spectrum absorption, which may satisfy on-line and real-time measurement of SO$_2$ in industry field.

2.2. The Establishment of Mathematical Model

The absorption of SO$_2$ by infrared centralizes in the wave band between the wavelength of 3.98μm and that of 7.35μm, while that of CO$_2$ falls between 2.78μm and 4.28μm, so CO$_2$ overlaps at the spectrum of 3.98μm with SO$_2$. Infrared energy absorbed by gas has relation to gas concentration, and infrared spectrum energy will reduce after SO$_2$, CO$_2$ absorb infrared, so the concentration of SO$_2$ can be measured based on variation degree of infrared energy.

When invariable infrared spectrum pass smoke gas containing SO$_2$, the intensity of infrared spectrum will weaken for SO$_2$ absorb infrared spectrum at the wavelength of 3.98μm. The relationship between the decreasing intensity and SO$_2$ concentration is exponential, and obeys Lambert-Beer Law [7] on condition that it is single absorption. So SO$_2$ concentration can be measured. The infrared intensity absorbed by SO$_2$ can be described as Equation (1):

$$I_1 = I_0 - I_2 = I_0 - I_0 \exp(-αdc) = I_0[1 - \exp(-αdc)]$$

(1)

Thereinto, $I_1$: absorption light intensity, mW; $I_0$: infrared incidence light intensity, mW; $I_2$: light intensity after infrared perforate gas room, mW; $α$: absorption coefficient of SO$_2$ to infrared, m$^{-1}$; $l$: optical path; $c$: volume fraction of SO$_2$.

Equation (2) can be reached by Taylor’s series expansion at zero of Equation (1).

$$I_1 = I_0[1 - \exp(-αdc)] = I_0[αdc - \frac{(αdc)^2}{2!} - \frac{(αdc)^3}{3!} - ... - \frac{(αdc)^n}{n!} - ...].$$

(2)

Considering $αdc \rightarrow 0$, then other items in $[.]$ is infinitesimal of higher order of the first item, Equation (2) can also be described as Equation (3).

$$I_1 ≈ I_0αdc$$

(3)

This is the detection mechanism of infrared to measure SO$_2$. The relationship between the intensity of infrared spectrum absorption and the volume mark of SO$_2$ is direct ratio on condition that input infrared intensity is invariable. So the nonlinearity of Lambert-Beer Law has linearization. This is the SO$_2$ mathematical model of double optical paths to measure the volume mark.
3. Design of measurement gas room

The optical of SO₂ concentration measurement by double optical paths infrared spectrum is represented as Figure 1.

![Figure 1. the optic model of single lamp-houses and four detectors.](image)

1. infrared LED 2. detector 1(R₁) 3. detector 2(R₂) 4. filter with center wavelength is 3.98μm, half width is 0.2μm 5. filter with center wavelength is 4.28μm, half width is 0.2μm 6. gas entry 7. gas exit 8. detector 3(R₃) 9. detector 4(R₄)

Firstly the mixture gases of SO₂ and CO₂ are put into the measurement gas room, the infrared light source on the left of which gives off infrared radiation. Detector 1 receives some directly reflected infrared radiation at 3.98μm of SO₂ sensitive center absorption wavelength, and Detector 2 receives some directly reflected infrared radiation at 4.28μm of CO₂ center sensitive absorption wavelength.

Detector 3 and 4 receive other infrared through measurement gas room. Detector 3 receives infrared radiation at 3.98μm of SO₂ sensitive center absorption wavelength, including wavelength of CO₂. Detector 4 receives infrared radiation at 4.28μm of CO₂ sensitive center absorption wavelength, so the output of Detector 4 reflects the concentration of CO₂.

If the intensity of infrared light source is \( I \), the sensitivity of Detector 1, 2, 3, 4 is \( S₁, S₂, S₃, S₄ \) respectively, the transmission ratio of gas room is \( t₀ \), the infection coefficient of CO₂ to SO₂ is \( t_c \).

When the infrared light source is working, Detector 1, 2, 3, 4 receive radiation signals, and the equations are as follows.

\[
R₁ = IS₁ \tag{4}
\]
\[
R₂ = IS₂ \tag{5}
\]
\[
R₃ = IS₃t₀t_c \tag{6}
\]
\[
R₄ = IS₄t₀ \tag{7}
\]

Equation (8) is drawn based on Equation (4) ~ (7)

\[
\frac{R₁R₄}{R₂R₃} = \frac{IS₁ \times IS₄t₀}{IS₂ \times IS₃t₀t_c} = \frac{S₁S₄}{S₂S₃} \times \frac{1}{t_c} \tag{8}
\]

According to Equation (8), through mathematical manipulation, output signals, generated from this gas room, eliminate the effects, brought by intensity variation of infrared light source, temperature fluctuation, and so on. Output signals are mainly related to the absorption of infrared spectrum by CO₂ at the wavelength of 3.98μm.

4. Design of Hardware System

The detectors of infrared SO₂ transform the mixture gas concentration of CO₂ and SO₂ into the corresponding voltage signals, and then output voltage signals of sensor match the concentration of SO₂. After magnified by amplification circuit through voltage, the signals are delivered into Analog-Digital conversion circuit. Then they are delivered into singlechip for data acquisition, analysis, computation and treatment. Finally the value of concentration is worked out and displayed, and hardware system makes corresponding diagnosis and conducts exception handling.
5. Design of Software System

Software measurement system is designed according to the principle of infrared absorption, the structure of measurement gas room and hardware system.

5.1. System initialization.
Firstly, power on self test is conducted in this apparatus system, including LCD test, memory test and channels test. System judges whether the status of LCD, AT89C52, 8279 and ICL7109 are normal or not. When the system checks memory, it stores some data in one group of memory address, and retrieve the data in the address. If the retrieval data and the value in memory are not equal, the system is abnormal and gives an alarm. Finally, the system checks the SO2 channels of A/D convertor.

5.2. Data pretreatment.
Data collecting errors will increase when analog signal of input channel are superposed by some non-object parameters, such as environment temperature, noise, pressure, electrical source fluctuation, and so on. When object analog signals are weak in input channel in particular, this phenomenon is more serious. In order to eliminate the error of collecting data, arithmetic average is used to solve this problem. So the digital filter may screen output control errors caused by disturbing input signals.

5.3. Data collecting and processing module.
The output signals of detectors contain infrared spectrum absorption by CO2, so it is necessary for output voltage signals to compensate data. Output voltage signals of detectors are matched with concentrations of SO2 and CO2 to eliminate nonlinearity effects of measurement precision by CO2, then curves are linearized. Finally the mathematical model of SO2 sensor is more precisely.

5.4. Displaying and communicating module.
Data are displayed in real time according to SO2 concentration. At the same time, the main measurement and control computer communicates with the data. So the measured data are delivered into the main computer to analyze and dispose synthetically.

6. Experiment Research

The gas in boiler pipe, collected by sampling probe, is treated by heating, drying, filtering. After congealed, the sampling gas is put into entry and analysis system. When the mixed gas of SO2 and CO2 is shined by infrared gas detector, the intrinsic vibration and whirling of molecules will change, and molecules absorb special wavelength of infrared spectrum. The light intensity received by detectors will reduce if gas concentration increases, so gas concentrations are gained by measuring the intensity of infrared spectrum.

After light source works for 10 minutes, light intensity will become stable, when the system absorbs the mixed sampling gases of SO2 and CO2 through the treatment of dust abatement, desulfurization, dehumidification. The output working voltage signals of Detector 1, 2, 3, 4 are got when CO2 concentration is 10ppm, and SO2 concentration is 5ppm. Then another group of data are obtained when SO2 concentration increases, and this process repeats a few times. The data are shown in Table 1. Then the mixed gases are put into gas room as SO2 concentration is 20ppm, and CO2 concentration is 5ppm, and a group of data is got. When CO2 concentration increases, another group of data is got. This process repeats a few times, so the data are shown in Table 2.

Data are input into the SO2 adjustment system according to the tables, and then SO2 voltage signals, rectified by double optical paths, are calculated, as shown in Table 2.

Though the ten groups data calculation, the SO2 precision in single optical path is 3.40, while it is 1.65 in double optical paths, it is more accurate than single optical path. This indicate that double optical paths has more accurate, stronger anti-jamming ability, and so on.
| SO₂ sampling concentration (ppm) | voltage signal of Detector (1mV) | voltage signal of Detector (mV) | voltage signal of Detector (mV) | voltage signal of Detector (mV) |
|-------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0                             | 1.7                             | 1.6                             | 1.4                             | 1.4                             |
| 5                             | 11.5                            | 11.2                            | 20.7                            | 15.6                            |
| 10                            | 11.7                            | 11.4                            | 38.9                            | 27.7                            |
| 15                            | 11.6                            | 11.5                            | 57.6                            | 39.2                            |
| 20                            | 12.2                            | 11.9                            | 79.5                            | 49.5                            |
| 25                            | 12.3                            | 12.1                            | 98.7                            | 59.2                            |
| 30                            | 12.2                            | 12.3                            | 116.5                           | 67.5                            |
| 35                            | 12.3                            | 11.8                            | 135.7                           | 75.1                            |
| 40                            | 12.2                            | 12.1                            | 154.3                           | 82.4                            |
| 45                            | 12.3                            | 11.9                            | 172.2                           | 88.6                            |

| CO₂ sampling concentration (ppm) | voltage signal of Detector (mV) | voltage signal of Detector (mV) | voltage signal of Detector (mV) | voltage signal of Detector (mV) | SO₂ Voltage after adjustment of double optical paths (mV) |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0                               | 1.7                             | 1.5                             | 1.4                             | 1.3                             | 1.5                             |
| 5                               | 11.5                            | 11.3                            | 75.8                            | 8.7                             | 18.3                            |
| 10                              | 11.8                            | 11.5                            | 80.5                            | 15.8                            | 36.2                            |
| 15                              | 11.6                            | 11.7                            | 85.3                            | 22.9                            | 54.1                            |
| 20                              | 11.9                            | 11.9                            | 89.6                            | 29.8                            | 74.7                            |
| 25                              | 12.5                            | 12.3                            | 93.9                            | 36.5                            | 91.8                            |
| 30                              | 12.7                            | 12.6                            | 98.5                            | 43.1                            | 108.9                           |
| 35                              | 12.5                            | 11.9                            | 102.9                           | 50.8                            | 127.5                           |
| 40                              | 12.4                            | 12.3                            | 107.2                           | 56.8                            | 145.3                           |
| 45                              | 12.5                            | 12.3                            | 111.6                           | 61.9                            | 163.7                           |

7. Conclusion
It can be deduced from the experiment data that measurement error, caused by CO₂, can be eliminated by SO₂ detection of the double optical paths infrared. Single light source and four detectors can measure the concentrations of SO₂ and CO₂, and effectively rectify SO₂ voltage signals. So from the measured data, we can see that this method has high measurement precision, simple design, powerful anti-jamming capability, and good promotional value, thus satisfying the on-line measurement of SO₂ required in industry fields.

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