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The Interference of CH_4 in SO_2 Monitoring by NDIR Method and Countermeasures

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Abstract: The NDIR method was not applicable for the determination of SO_2 from coke oven stacks of coking industry, on account of the CH_4 interference problem. This article analyzed the interference of CH_4 in SO_2 monitoring by NDIR method. We used a gas distributing device to prepare the mixed gas including CH_4 and SO_2 based on the real exhaust conditions. The study has compared the results of gas samples with different mixing ratios and has found that the CH_4 caused the SO_2 readings to rise. The higher the concentration of the CH_4 in the mixed gas, the more deviation in the SO_2 measurement is. Meanwhile, there was an obvious linear correlation between the CH_4 concentration and the deviation--about 16 μmol/mol CH_4 could contribute to 1 μmol/mol SO_2 deviation. In this article, we have tested two methods to remove the CH_4 interference deviation: gas filter and auxiliary sensor. The optical filter method could remove more than 85% of deviation while the auxiliary-sensor method could remove all the deviation caused by CH_4, with indication error under ±1 μmol/mol. The test results showed that the NDIR method with suitable countermeasures can be used for the coking industry and other applications which have CH_4 interference problem.

Keywords: Methane, Sulfur Dioxide, Non-Dispersive Infrared (NDIR), Interference, Gas Filter, Auxiliary Sensor

1. Introduction

Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The Non-dispersive infrared (NDIR) technology for gas measurement targets the wavelength absorption in the infrared spectrum and is applied widely as a means to identify and quantify particular gases. NDIR is used to monitor the air pollutants emitted from various sources e.g., NO_X, SO_2, CO, CO_2, etc. The analyzers adopting this technology are usually simple in structure, low in cost, high in measurement accuracy and stability, and can be very convenient for human-machine interaction, making them ideal monitoring equipment for continuous emission monitoring systems for stationary sources [1, 2].

However, the absorption peaks of different components in the mid-infrared absorption band selected by NDIR may overlap, resulting in some absorption interference between different gas components, such as H_2O and NO, H_2O and SO_2, CH_4 and SO_2, etc. [3, 4]. Liu Tonghao found that for the coking exhaust gas containing high concentrations of CH_4, the results of NDIR determination of SO_2 were significantly higher, and CH_4 introduced a positive interference of about 5% to the determination of SO_2 [5]. Wang Qiang of the China Environmental Monitoring Station [6] tested three portable NDIR flue gas analyzers commonly available in the market, the test result they had good comparability and applicability in pollution sources CEMS comparison monitoring and supervisory detection. Zhang Feilong tested three models of NDIR SO_2 analyzers in the market, and the test results of 200 mg/m^3 SO_2 ranged from 202.1 to 368.0 mg/m^3 at CH_4

concentration of 1000 mg/m^3 [7]. Qiao Zhiwei tested four principles of SO_2 analyzer, and the results confirmed that CH_4 has positive interference with SO_2 analyzer based on NDIR and OFCEAS method [8].

In order to eliminate the interference of CH_4 in the flue gas to the SO_2 determination by NDIR analysis, this study tested a mixture gas with CH_4 and SO_2 at different concentrations to obtain the interference contribution of CH_4, established a linear regression equation, and used two different methods to improve the NDIR sensor to eliminate CH_4 interference for environmental monitoring work.

2. NDIR Method in Gas Monitoring

2.1. Statement of the Problem

The measurement principle of NDIR is based on the Lambert-Beer law: when light passes through the sample gas, the gas molecules selectively absorb light at specific wavelengths and the concentrations of the sample gas can be calculated from the attenuation of the light flux [9, 10]. The wavelengths of the characteristic absorption peaks on the infrared spectra of different gas components vary due to the different absorption frequencies of different chemical bonds and functional groups. The absorption spectra of SO_2 and CH_4 in the near-infrared region are shown in Figure 1. The infrared absorption bands of SO_2 are 4 μm and 7.2~10 μm [11]; CH_4 molecules have four intrinsic vibrations, resulting in four fundamental frequencies accordingly, all of which are in the mid-infrared band. The wave numbers of the four fundamental wavenumbers are ν_1 =2913.0 cm^{-1}, ν_2 =1533.3 cm^{-1}, ν_3 =3018.9 cm^{-1}, and ν_4 =1305.9 cm^{-1}. Each intrinsic vibration corresponds to a spectral absorption band and their wavelengths are 3.43, 6.53, 3.31, and 7.66 μm [12].

The maximum absorption peak of SO_2 is around 7.35 μm, while the maximum absorption peak of CH_4 is 7.66 μm. Therefore, the maximum absorption peak of CH_4 interferes the detection of SO_2. Hence, when NDIR is applied for SO_2 measurement, measures should be taken to eliminate the interference, if CH_4 is present in the sample gas.

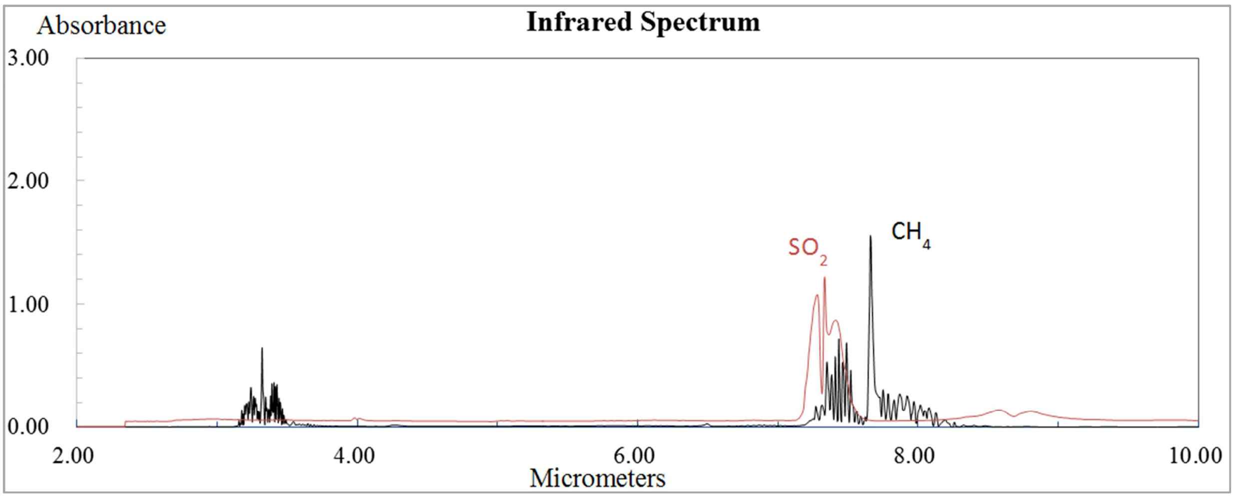

Figure 1. *The absorption peak of SO_2 and CH_4 in IR spectrogram.*

2.2. Solutions to Eliminate Interference

There are two countermeasures to eliminate the CH_4 interference, one is the using of filters that convert the infrared light emitted from the light source to narrow band spectrum in a specific wavelength range to eliminate some of the CH_4 interference [13-15].

Solid filters, which can be sprayed with different refractive index film materials according to different applications [16], are commonly used to filter out the waveband that generates interference and transmit narrow-band light in the specified wavelength range. This can eliminate the CH_4 interference in the 7~8 μm waveband, for example, the absorption peak at 3.43 μm; however, the interference in the narrow band cannot be totally removed, for example, the absorption peak at 7.66 μm.

Horiba's NIDR products use two methods to remove the CH_4 interference, gas filter and auxiliary sensor, the online analyzer can suite any application meets the user's testing requirements.

2.2.1. Gas Optical Filter

To reduce the interference of CH_4, one of the commonly adopted measures is to use an optical filter. According to different uses, the filter can be sprayed with different refractive index film materials [16], so that the waveband of interference will be filtered out, leaving only the specified wavelength range of narrow-band light.

The wavelength selected for SO_2 analyzer usually falls between 7 to 8 μm, and the infrared light emitted from the light source can selectively pass through the narrow band of 7~8 μm by configuring a suitable optical filter, which can eliminate the CH_4 interference in the band of 7~8 μm, such as the absorption peak around 3.3 μm; however, the interference in the narrow band of light still cannot be removed, such as the absorption peak at 7.66 μm.

Figure 2. *HORIBA's gas filter.*

HORIBA uses a gas optical filter sealed with high-concentration CH_4 gas as shown in Figure 2. The pre-treated and purified flue gas enters the sample gas chamber through the inlet by a heat tracing pipeline; the air enters the reference gas chamber through a different pipeline. Since the gas optical filter is sealed with CH_4, the signals of both reference gas and sample gas contain the absorbance of CH_4.

By subtracting the reference signal from the signal of sample gas using special algorithm, the interference of CH_4 around 3.3 μm can be removed, this process is the gas filter correlation. The gas optical filter only eliminates CH_4 interference around 3.3 μm and has no effect on the other spectra. It can effectively improve the quality of CH_4 absorption spectral signal, and at the same time improve the signal-to-noise ratio of spectral signal. The NDIR with gas optical filter has applied to real-time, online measurements and achieves the desired results.

2.2.2. Auxiliary Sensor

Another method is to use two NDIR sensors, with the primary sensor measuring SO_2 and the auxiliary sensor measuring CH_4, then deduct the interference signal from the SO_2 signal, finally calculated the SO_2 measuring result without CH_4 interference.

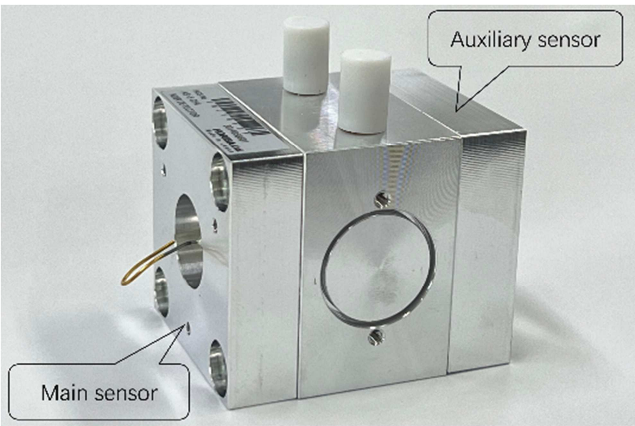

Figure 3. *HORIBA's SO_2 sensor.*

This method can remove almost all the CH_4 interference, the instrument is suitable for the application which requires high accuracy, especially the ultra-low emission sites. But the structure of NDIR sensor with additional auxiliary sensor is more complicated, and the instrument's price is higher than the instrument using the gas optical filter. So, this needs a balance for the accuracy requirement and the budget.

3. Research Methodology

3.1. Main Instruments

In the testing, we used three types NDIR method online analyzers. The instruments used in the testing are as following:

1. Model PG-350 portable flue gas analyzer (Japan, HORIBA, with no interference removal countermeasure)
2. Model PG-350F portable flue gas analyzer (Japan, HORIBA, use gas filter remove CH_4 interference)
3. ENDA-600ZG (Japan, HORIBA, use auxiliary sensor remove CH_4 interference)
4. Gas distribution device (China General Research Institute of Metrology)
5. All the gas cylinders used for the testing were purchased from standard gas company

3.2. Laboratory Test Method

For the laboratory testing, we used a gas distribution device to prepare the mixed sample gas including CH_4 and SO_2, the background gas is N_2. In order to acquire stable, accurate data, all the 3 analyzers were turned on and fully warmed up, calibrated before measurement, the zero point of the instrument was calibrated with high purity N_2, and the span calibration was with SO_2 standard gas.

After calibration, different concentrations of CH_4 were introduced into PG-350 and PG-350F respectively, and then the SO_2 reads displayed on the instrument were recorded. Then the gas mixture of CH_4 and SO_2 of different concentrations was introduced and the SO_2 test values were recorded.

3.3. Field Test Method

The field test was conducted at a cock oven field. The SO_2 in the exhaust gas of stationary sources was measured by using three analyzers PG-350, PG-350F and ENDA-640ZG, the testing procedure was in accordance with the regulation HJ 629-2011 "The Non-dispersive Infrared Absorption Method for the Determination of Sulfur Dioxide in the Exhaust Gas of Stationary Sources".

The momentary values were saved by minutes, and the average data is calculated by summing the momentary values acquired every 1 second for 15minitues, and then dividing the cumulative total by the data counts. All the 3 analyzers were under the same working condition, and the testing was carried out three times consecutively, taking the average value as the measurement result [17].

4. Results and Discussion

4.1. Effect of CH_4 on SO_2 Interference

In order to confirm the interference of CH_4 on SO_2

detection, an experiment was designed to further verification. The experiment was conducted using a NDIR analyzer PG-350 without the CH_4 remove countermeasures, the sample gas is fed directly into the NDIR sensor through the gas path. Because moisture also has an effect on the SO_2 test results, the gas cylinder and gas distribution system are used for gas distribution in order to eliminate other interfering factors. Different concentrations of CH_4 gas were introduced, the background gas was pure nitrogen, with 0 μmol/mol of SO_2.

The result was showed in Figure 4, CH_4 has a positive interference to SO_2 with a clear linear fit [11], about 16 μmol/mol CH_4 generates 1 μmol/mol of SO_2 indication interference, and the linear regression equation obtained by linearly regressing the CH_4 concentration on the obtained SO_2 readings is Y=0.0584X+6.6147, with a linear coefficient of 0.9987.

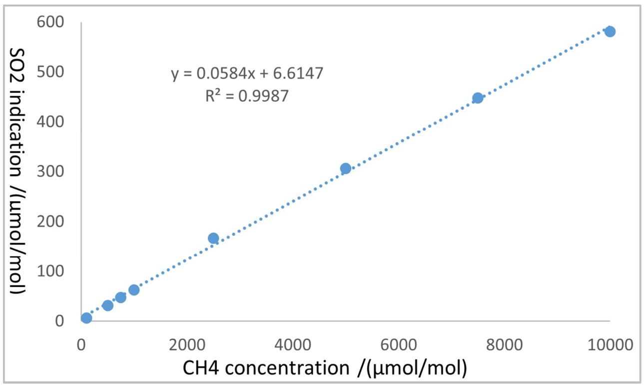

Figure 4. *The effect of different concentrations of CH_4 on the SO_2.*

4.2. Effect of CH_4 on SO_2 at Different Concentrations of SO_2

In order to verify the effect of CH_4 in the gas mixture with different concentration SO_2, a gas mixture with different concentrations of SO_2 at 0, 35 and 100 μmol/mol and CH_4 gas at 0, 100, 500, 1000, 5000, 7500 and 10000 μmol/mol was configured for testing, and the test results are shown in Figure 5.

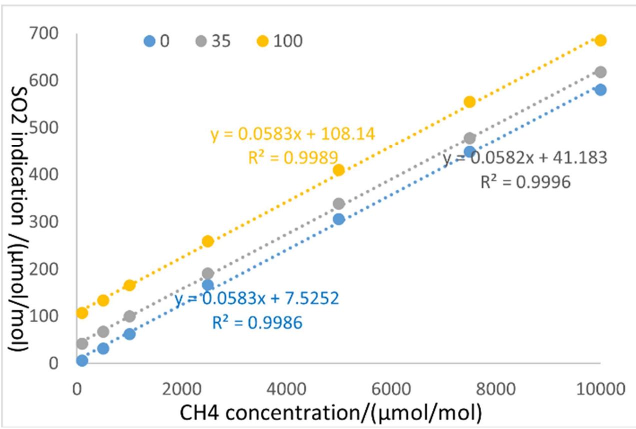

Figure 5. *The effect of different concentrations of CH_4 on the SO_2.*

It can be seen that the test results of three different concentrations of SO_2 are linearly increasing with the increase of CH_4 concentration, and the three curves are close to parallel with slopes of 0.0583, 0.0582, and 0.0583, which are basically the same. It can be concluded that the interference contribution value of CH_4 to SO_2 is related to the concentration of CH_4 and not much related to the concentration change of SO_2, and the same measures can be taken to eliminate the CH_4 interference in different SO_2 concentration values.

4.3. Eliminate Interference by PG-350F and ENDA-640ZG

Table 1 shows the results of laboratory tests of 10 μmol/mol SO_2 gas mixed with different concentrations of CH_4 gas, using PG-350 (with no countermeasure) and PG-350F (gas filter).

The correct efficiency of the gas optical filter is shown as below:

$$\eta = 1 - \frac{B-10}{A-10} \tag{1}$$

Where A— Indication from PG-350;

B— Indication from PG-350F.

From the data, it can be seen that the test results of PG-350F are significantly lower than those of PG-350 without interference removal device, but the gas filter cannot remove all the CH_4 interference, the correct efficiency is more than 85%, and for different concentration CH_4 gas, the interference efficiency is higher for lower concentrations CH_4 gas.

Table 1. *The correct efficiency of gas optical filter for CH_4 interference.*

CH_4 (μmol/mol)	PG-350 (μmol/mol)	PG-350F (μmol/mol)	*η*/%	*R*/%
100	16.1	10.4	93.4%	0.04%
500	42.5	13.9	88.0%	0.39%
1000	74.7	17.9	87.8%	0.79%
2500	168.4	30.8	86.9%	2.08%
5000	314.9	49.8	86.9%	3.98%
7500	452.4	67.4	87.0%	5.74%
10000	585.6	87.3	86.6%	7.73%

Since the gas filter cannot eliminate all the CH_4 interference, the interference for NDIR analyzer with gas optical filter is calculated by the following equation:

$$R = \frac{B-10}{1000} \tag{2}$$

Where B— Indication from PG-350F.

1000— PG-350F full span

The technical specifications for SO_2 portable monitoring instrument [18] require when introduced with 50 mg/m^3 CH_4, the interference error should be less than ± 5%, the gas optical filter can totally meet this requirement. Besides, for the NDIR instrument equipped with gas optical filter which full range is 1000 μmol/mol, the instrument can used for the flue gas emission field where CH_4 concentrations are around 5000 μmol/mol, it can keep the CH_4 interference under 4%, fully meet the regulation requirement. And, equipped with gas optical filter, the instrument is relatively simple to modify and portable, so this method can be used for emergency and portable monitoring where the accuracy requirement is not particularly high.

Figure 6 shows the test results of PG-350 (with no countermeasure), PG-350F (gas filter) and ENDA-640ZG (auxiliary sensor) in the coke oven flue gas emission site. The SO_2 concentration in testing flue gas is about 35 µmol/mol. The CH_4 concentrations were adjusted by changing the working conditions of the flue gas treatment equipment. Figure 5 shows that the SO_2 test results from three different analyzers, and the results ranking is PG-350 > PG-350F > ENDA-640ZG. The reading of ENDA-640ZG is stable near 35 µmol/mol, and the fluctuation is less than 1 µmol/mol, and the slope of its test curve is -0.00008, which can be approximated as a horizontal straight line. The auxiliary sensor method is obviously better than the gas filter interference elimination method, which can eliminate all CH_4 interference and produce accurate SO_2 test results. Therefore, it is recommended to use the auxiliary sensor elimination method for online monitoring of stationary sources with high testing requirements [19], especially for coke oven flue gas with high CH_4 concentration, and ultra-low emission sites.

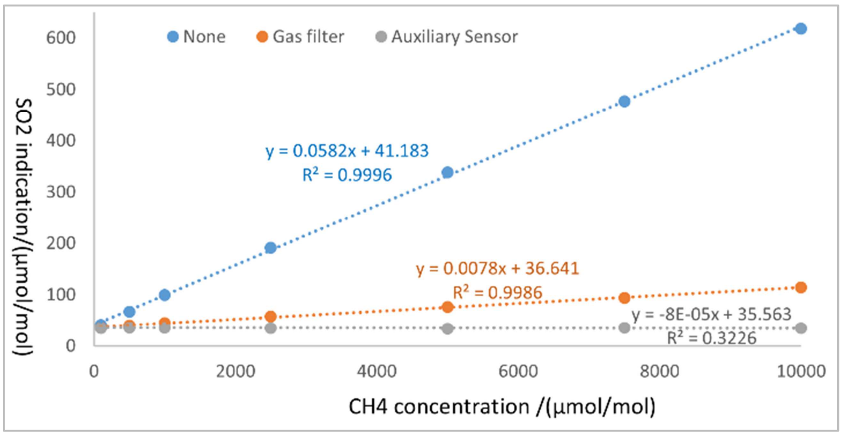

Figure 6. *The effect of different CH_4 concentrations on the 35µmol/mol SO_2.*

5. Conclusion

In this paper, we studied the interference problem of CH_4 during the NDIR measurement of SO_2, and the tests showed that there was a stronger linear relationship between the CH_4 concentration and the interference of SO_2, and the cause of the interference mainly came from the increase of CH_4 concentration, the change of SO_2 concentration was not associated with the interference of SO_2. The method of using gas filter to eliminate the absorption waveband of CH_4 can remove more than 85% of the CH_4 interference, and using the auxiliary sensor to measure CH_4, and then correcting by the mathematical model can remove almost all the CH_4 interference.

In the actual monitoring, the portable optical method monitoring instrument are required that CH_4 interference should be within ±5%. For the flue gas with CH_4 concentrations under 5000 µmol/mol, the gas filter method can be used to remove the CH_4 interference, which takes both the accuracy of the data and the portability of the analytical instrument into account. For ultra-low emission sites or sites with high CH_4 concentration such as coke oven exhausts, CH_4 interference is more distinct. Hence, the recommended countermeasure is using auxiliary sensors, to obtain accurate and long-term stable test results.

The NDIR method was not applicable for the determination of SO_2 from coke oven stacks of coking industry, on account of the humidity and CH_4 interference questions. Now with the development of technology, there were different methods to remove the CH_4 interference. This study has tested two different countermeasures to eliminate the CH_4 interference and has good test result based on the laboratory and field testing. The countermeasures not only meet the requirements of regulation, but also easy for marketization. This will expand the NDIR's application in coking industry and other applications with CH_4 interference question, such as projects of changing coal into coal gas.

In the actual onsite application, it is recommended to select the appropriate way to eliminate CH_4 interference according to different flue gas conditions and testing requirements, in order to obtain the expected monitoring data and provide a reliable data source for environmental protection work.

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References

[1] Fan Chuanming, Li Jiehong. Contrastive analysis of on-site determination methods of SO_2 from stationary sources [J]. Environment and Development, 2019, (3): 145-148.

[2] Ren Yaodong. Discussion on Standard Methods for Monitoring Sulfur Dioxide in Stationary Pollution Sources [J]. Shandong Chemical Industry, 2020, 49 (13): 85-86.

[3] Feng Yongchao, Hu Yong. Effect of humidity and CO on the fast analysis of SO_2 by three different methods [J]. Environmental Science & Technology, 2016, 39 (S1): 203-206.

[4] Chen Xiaoning, Liu Jianguo, Si Fuqi, et., al. Application of Gas Filter Correlation Technique in IR Monitoring System of Methane [J]. Opto-Electronic Engineering. 2008, 35 (4): 49-52.

[5] Liu Tonghao, Zhang Shoubin, Jing Hong, et., al. Study on the Interference of Methane to the Determination of Sulfur Dioxide in Stationary Pollutant Exhaust Gas by Non-dispersive Infrared Absorption Method [J]. Environmental Monitoring in China. 2020, 36 (6): 143-149.

[6] Wang Qiang, Zhong Qi, Zhou Gang, et., al. The Comparison of Performance and Application for Portable Type Sulfur Dioxide Flue Gas Analyzer by Non-Dispersive Infrared Method. Environmental Monitoring in China, 2014, 30 (3): 149-153.

[7] Zhang Feilong, Li Yang, Qiao Nan. Influence of CH_4 Gas on Non-Dispersive Infrared Absorption Method for the Determination of SO_2 in Waste Gas [J]. Shanxi Metallurgy, 2021, 44 (2): 31-33.

[8] Qiao Zhiwei, Wang Anqi, Zhang Zhenxin, et., al. Study on the Performance of Low Concentration Sulfur Dioxide Analyzers Based on Different Principles [J]. Environmental Monitoring and Forewarning, 2017, 9 (6): 29-32.

[9] Wei Fusheng, et al. Air And Waste gas monitor analysis method [M].4 version. Beijing: China Environmental Science Press, 2003: 428-429.

[10] Teng Enjiang, et al. Operations management of Flue gas and dust Continuous Emission Monitoring System [M]. Beijing Chemical Industry Press, 2008: 15-23.

[11] ROTHMAN L S, GORDON I E, BABIKOV Y, et., al. The HITRAN 2012 Molecular Spectroscopic Database. QUANT J, RADIAT t. Transf. 2012, 96, 139-204.

[12] Zhang Yu, Wang Yiding, Li Li, et al. The Principle and Technical Analysis of Methane Detection Using Infrared Absorption Spectroscopy [J]. Spectroscopy and Spectral Analysis, 2008, 28 (11): 2515-2519.

[13] Hu Tibao, Luo Zhongchang. Anti-interference Measure of SO_2 Infrared Gas Analyzer [J]. Analytical Instrumentation, 2018 (5): 124-129.

[14] Sun Youwen, Liu Wenqing, Wang Shimei, et al. Research on the Method of Interference Correction for Nondispersive Infrared Multi-Component Gas Analysis [J]. Spectroscopy and Spectral Analysis, 2011, 31 (10): 2719-2724.

[15] Yuan Shuai, Wang Guangzhen, Fu Dehui, et al. Cross Interference Characteristics of Photoacoustic Spectroscopy Multi-gas Analyzer [J]. Acta Photonica Sinica, 2021, 50 (4): 0430002.

[16] Ren Lijun, Ma Bin, Liu Guohong, et al. Research Progress of Non-dispersive Infrared Sensor for Gas Detection [J]. Journal of Instrumental Analysis, 2020, 39 (7): 922-928.

[17] Ministry of Environmental Protection. Stationary source emission-determination of sulphur dioxide Non-dispersive infrared absorption method: HJ 629-2011 [S]. Beijing: China Environmental Science Press, 2011.

[18] Ministry of Ecological Environment. Specifications and test procedures for portable monitoring instrument for SO_2 and NOX based on ultraviolet absorption method in flue gas emitted from stationary sources: HJ 1045-2019 [S]. Beijing: China Environmental Science Press, 2019.

[19] Ministry of Environmental Protection. Specifications and test procedures for continuous emission monitoring system for SO_2, NOx and particulate matter in flue gas emitted from stationary sources: HJ 76-2017 [S]. Beijing: China Environmental Science Press, 2017.