

Original Research

Validation and Accuracy Study of SO₃ Detection Using the Controlled Condensation Method

Ding Yang¹, Fang Zheng², Xinglian Ye^{1,2*}, Jun Guo², Zongshu Zou¹, Xizhong An¹

¹College of Metallurgy, Northeastern University, Shenyang, China

²State Environmental Protection Engineering and Technology Center for Power Industrial Dust Control, Longyan, China

Received: 9 July 2018

Accepted: 15 December 2018

Abstract

The SO₃ in coal-fired flue gas is easy to condense, reduce the smoke emission transparency and cause corrosion on the surface of the equipment. With the urgency of accurate measurement and effective treatment of SO₃, this article focuses on the development of the controlled condensation method (CCM) for SO₃ testing. An SO₃ test accuracy verification device is set up for evaluating the test accuracy of CCM, and the influence of factors on the accuracy of CCM is performed, such as sampling a gun's heating temperature, sampling flow rate, high SO₂ concentration and difference of SO₃ concentration during the test procedure. The CCM can effectively avoid the interference of SO₂ on capture efficiency. With the increase of heating temperature and flow rate, the capture efficiency first increases and then decreases. Reasonable control of the tracing temperature and sampling flow rate helps to improve the accuracy of CCM. In a certain range of SO₃ concentration, the capture efficiency has a linear relationship with SO₃ concentration. The finding of the current study shows that this is feasible and provides significant references as to how to improve SO₃ detection accuracy.

Keywords: controlled condensation method, SO₃ sampling system, influence factors, accuracy

Introduction

Recently, sulfur trioxide (SO₃) has captured more and more attention for its health risks and environmental harm [1-3]. The emitted SO₃ has become an important source of acid rain and condensable fine particulate emissions, thus causing damage to forests and buildings. Due to very active chemical nature of SO₃ in coal-fired flue gas, it is easy to combine with water vapor to form acid mist, which increases the dew point of flue gas [4].

When the wall plate temperature of the equipment is lower than the acid dew point, the acid mist condenses on the surface of the equipment and causes corrosion [5-7]. The research of Moretti et al. and Cao et al. [8, 9] clearly reported that when the flue gas is discharged from the stack and the level of SO₃ reaches 5 ppm, this will result in the blue feather phenomenon. Dunn et al. and Srivastava et al. [10, 11] investigated that the SO₃ easily adheres to a boiler and selective catalytic reduction (SCR) system after moisture absorption would generate ammonium bisulfate, which is difficult to remove. If the ammonium bisulfate sticks on the surface of the catalyst, it will cause clogging in the catalyst duct. According to the research of Ueda et al. and Huang et

*e-mail: xinglianye1228@126.com

al. [12, 13], SO_3 reacting with escaping ammonia will increase the chances of blockage in the equipment, then worsens the problems of SO_3 that were neither prominent nor serious in power plants at first. Pan and Deeming et al. [14, 15] found that when the concentration of SO_3 in flue gas is above 10 ppm under high humidity, blue feathers tend to appear at the outlet of the chimney, resulting in decreased transparency of smoke exhaust. Therefore, the control of SO_3 emissions is urgent, and accurate measurement of SO_3 concentration in flue gas is of great significance.

In order to solve the above problem, many SO_3 test methods in flue gas mainly include the Fourier transform infrared analysis test method [16], isopropanol absorption method [17], dew point meter [18], salt method [19], differential optical absorption spectroscopy (DOAS) [20], controlled condensation method (CCM) [21] and so on. Fourier transform infrared method is mainly based on the Zeeman effect correction background and atomic absorption spectroscopy principle. However, since SO_3 , SO_2 and H_2O in the flue gas are close in infrared band, the test process is easily affected, and test accuracy and stability cannot meet the testing requirements of low-concentration SO_3 [16]. The isopropanol absorption method uses 80% isopropanol to suppress the interference of SO_2 in the flue gas [22], but the isopropanol is highly volatile at the high flue gas temperature during the sampling process. The sample gas exchanges with the isopropanol absorption fluid will result in increased absorption liquid temperature, isopropanol evaporation, and SO_3 entrainment, and then introduce errors into the testing result. In addition, the contact time between SO_3 and absorption liquid is short and SO_3 cannot be fully absorbed, which leads to test results lower than the actual value [22]. In the process of testing, the volume fraction of water in the absorption liquid increases and part of the SO_2 is dissolved in the absorption liquid, which makes the test result higher than the real value. The higher the SO_2 concentration, the larger the error tends to be. Experiments and research results show that the isopropanol absorption method cannot be applied to accurately test SO_3 in the flue gas [23]. Among these test methods, CCM turns out to be one of the best methods for accurate measurement of SO_3 because of its high reliability and adaptability, free from SO_2 and PM interference, low detection limit and precise operation requirement [24]. Maddalone et al. [25] evaluated the CCM method, and acceptable results can be obtained. CCM mainly uses the principle of physical adsorption. After the flue gas temperature decreases, SO_3 condenses into acid mist, which is then collected by centrifugal force [26]. The applied range of the CCM is relatively wide. But at present there is less research on the test accuracy of the CCM, so it is urgent to compare the key influential factors of this method, which can provide reference for the accurate test of SO_3 and guidance for the application of new treatment technology of SO_3 .

In this paper an SO_3 calibration device was set up to ensure that the SO_3 sample gas can be accurately, consistently and continuously generated. The factors influencing the test accuracy of the CCM during the test sampling, including the heating temperature, the sampling flow rate, the high concentration of SO_2 and the difference of SO_3 concentration were analyzed to demonstrate the accuracy of the control condensation method.

Methods

The Principle for Detecting SO_3 of CCM

The sampling system of CCM consists of three main components, namely sampling gun with heating and filtering unit, condenser tube and water bath unit, and flue gas sampling device [26], as shown in Fig. 1. According to GB/T 21508-2008 [27], EPA 8A [28, 29], JIS K 0103-2005 [30] and the related literature [4, 9], the CCM mainly utilizes particle centrifugal motion principle in this research.

The main principle of CCM is that the flue gas containing SO_3 passes through the sampling gun with heat tracing and the quartz filter under the action of a certain flow rate. The purpose of doing this is to make SO_3 exist in a gaseous state, and remove most of the dust particles in the flue gas at the same time. After that, the flue gas enters the condenser tube in the water bath. The temperature of the condenser tube is controlled between 60-85°C, which means that the temperature of the water bath unit is also 60-85°C. The temperature of the flue gas from the sampling gun is lowered, and the SO_3 in the flue gas is condensed into acid mist particles at the inlet or the front end of the condenser tube. Due to the combined effect of inertia and viscous force, the acid mist is centrifuged in the condenser tube and adsorbed on the inner wall of the condenser tube. The condenser tube is cleaned with deionized water or 80% isopropanol, and the sampling volume of the flue gas is recorded. Then the concentration of SO_4^{2-} in the cleaning solution and the absorption bottle was tested, and finally the concentration of SO_3 in the flue gas was calculated. The liquid absorption bottle and the dry bottle after the condenser tube are respectively used to absorb harmful substances and moisture in the flue gas. These will protect the sampling pump and prevent pollution of the environment, with normal temperature [31] of about 2-35°C.

During the experiment, SO_2 or NO_2 , CO_2 , etc. in flue gas, are not easy to condense and collect on the inner wall of the condenser tube, so the content of SO_2 or NO_2 , CO_2 , etc. in the cleaning solution is small, so the effect on the outcome is limited. And if using deionized water for cleaning, the subsequent laboratory analysis will use barium chromate spectrophotometry for testing, and the first step of the method is to add

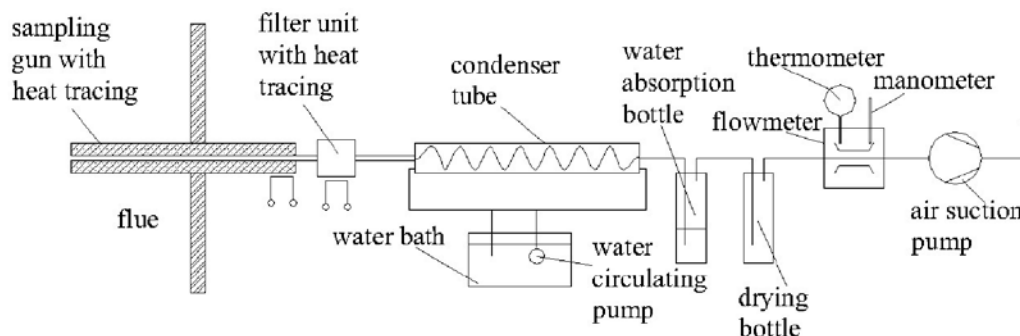


Fig. 1. SO₃ sampling system.

a certain amount of hydrochloric acid to remove the impact of SO₂; if using 80% isopropanol for cleaning, then thorium reagent titration or thorium reagent spectrophotometry would be used for testing. In this method, 80% isopropanol can inhibit the dissolution of SO₂ in the cleaning solution. The main principle of laboratory analysis is that SO₄²⁻ reacts with an excess of barium ions, and the remaining barium ions react with the thorium reagent to form thorium-barium complexes. Thorium-barium complexes are then determined according to the color depth of the thorium-barium complexes. The accuracy of the two laboratory analytical methods is not easily affected by several common gases found in the flue gas.

Calibration Device

Structure of the Calibration Device

As shown in Fig. 2, the calibration device of the SO₃ testing system mainly consists of SO₂ standard gas, mass flowmeter, SO₃ generator, steam generator, sampling gun, spiral condenser tube, water bath, drying bottle and flue gas sampler. The basic principle of the system is that the O₂ coming from the air mixes with SO₂ standard gas and enters into the SO₃ generator. Then the gas containing a concentration of SO₂ passes through the high-alumina catalyst to convert to SO₃

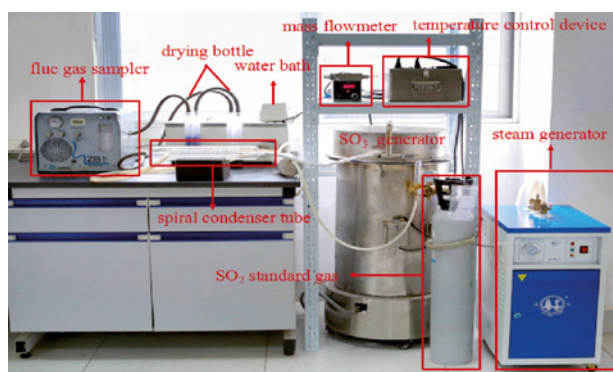


Fig. 2. Calibration device of SO₃ sampling system.

gas. The concentration of SO₂ at the inlet and outlet of the SO₃ generating device is measured by NGA2000 to calculate the SO₃ theoretical value. Then compared with the SO₃ value trapped in the condenser tube, and the capture efficiency is finally calculated.

The SO₂ standard gas is obtained through procurement, the concentration of SO₂ was configured before purchasing according to requirements. The catalyst used in the experiment is a catalyst for sulfuric acid production from wylton, with the main component vanadium oxide. There are two kinds of catalysts used: catalyst PH75 fitting for high temperature and PH78 fitting for low temperature. The experiment is carried out after loading 10g PH78 and 10g PH75. Although the catalyst used is selective, mainly to catalyze the SO₂ to SO₃, it does not exclude the possibility that the main component N₂ in the air is catalyzed to generate NO_x, and the concentration of CO changes. So the NO_x and CO concentration were measured in the inlet and outlet of the generator by NGA2000. The supplementary data are shown in Table 1, and results revealed that the concentration of NO_x and CO in the inlet and outlet of the generator was almost unchanged (around 0 ppm), which indicates that the transitions between CO, N₂ and NO₂ would cancel out.

For the calibration systems, the catalytic efficiency of SO₂ converting to SO₃ gas is a fixed value (about 75%). The concentration of SO₃ was affected by the flow rate of SO₂ standard gas and the SO₂ standard gas concentration. So, the concentration of SO₃ generator can meet the requirements by adjusting the flow rate of the SO₂ standard gas and the SO₂ standard gas concentration. For example, if the SO₃ concentration of 30 ppm is needed, when the sampling flow rate and the SO₂ standard gas concentration should be 7 L/min and 300 ppm, respectively, the flow rate of SO₂ standard is 0.7L/min. The SO₂ standard gas can be obtained according to requirements and analyzed by NGA2000. The flow rate of SO₂ standard gas is controlled by a mass flow meter, accurate to within 0.01 L/min. Furthermore, in order to ensure that the concentration of SO₃ is correct, the SO₂ concentration at the inlet and outlet of the SO₃ generator in each test will both be tested by NGA2000.

Table 1. Concentrations of NO_x and CO at inlet and outlet of the generator.

| Measuring points | Inlet of the generator | Outlet of the generator |
|--|------------------------|-------------------------|
| The concentration of NO _x ppm | 0.1 | 0.1 |
| The concentration of CO ppm | 0 | 0 |

Sulfur Balance Determination of the Calibration Equipment

When testing the sulfur balance in the inlet and outlet of the SO₃ generator, the sampling gun heating temperature was 220°C. In order to ensure the reliability of the calibration device, the flowmeters used for the measurement were separately compared and calibrated (the specific data is shown in Table 2). NGA2000 zero was adjusted and calibrated to ensure that it accurately tests the SO₂ concentration in inlet and outlet of the device. The analysis method of SO₄²⁻ concentration in the cleaning liquid was tested and the appropriate laboratory analysis method was selected to ensure the accuracy of the amount of SO₃ trapped in the condenser tube. After the above steps were taken, in order to ensure that all the SO₂ which is missing from the generator is converted into SO₃, instead of being adsorbed on the catalyst or other things in the generator, the sulfur balance of the inlet and outlet of the generator was conducted by adjusting the concentration of SO₂ at the inlet of the generator at about 50ppm, verified by NGA2000, and using sodium hydroxide to absorb the sulfide at the outlet of the generator including SO₂ and

SO₃, at the same time the heating temperature of the sampling gun is 220°C, the flow rate is about 5 L/min (Table 3).

Results and Discussion

Model Validation

In this process, CCM were conducted to test SO₃. The parameters that can be controlled include the sampling gun's heating temperature, gas flow rate and the concentration of SO₃. The sampling flow rate is 4.13 m/s, the sampling gun's heating temperature is 220°C and the concentration of SO₃ is about 30 ppm. The simulated conditions are illustrated in Fig. 3. In order to improve the test accuracy and ensure that the method can be more adaptable, this experiment was applied to measure the influence of the sampling gun's heating temperature, sampling flow rate, SO₃ concentration change and high SO₂ concentration on capture efficiency of SO₃ by CCM.

Effect of Sampling Gun's Heating Temperature on Capture Efficiency

To prevent the SO₃ acid mist from condensing within the sampling gun, corroding the sampling tube [32], and under-estimation of the test result, it is necessary to guarantee the SO₃ existing in gaseous form before the condenser tube. Namely, the heating temperature of the sampling gun must be higher than the acid dew point [33]. However, the related standards

Table 2. Calibration data for flowmeters.

| Standard flowmeter L/min | | 0.50 | 1.00 | 2.00 | 3.00 | 5.00 | 7.00 |
|--------------------------|-------------|------|------|------|------|------|------|
| Mass flow meter L/min | Flow L/min | 0.50 | 0 | 2.01 | 2.98 | 4.96 | 6.94 |
| | Deviation % | 0.0 | 0.0 | 0.5 | 0.7 | 0.8 | 0.9 |
| Sampler flow L/min | Flow L/min | --- | 1.01 | 2.02 | 3.02 | 5.04 | 7.03 |
| | Deviation % | --- | 1.0 | 1.0 | 0.7 | 0.8 | 0.4 |

Note: The maximum flow deviation is 1.0%. the flowmeter using in the test can meet the requirements.

Table 3. Sulfur balance test.

| SO ₂ gas concentration ppm | Gas sampling volume DNL | Import sulfur mass theoretical value mg | Export sulfur capture value mg | Recovery % |
|---------------------------------------|-------------------------|---|--------------------------------|------------|
| 50.0 | 200.3 | 3.58 | 3.56 | 99.5 |
| 49.8 | 200.5 | 3.57 | 3.52 | 98.7 |
| 49.6 | 201.6 | 3.57 | 3.59 | 100.6 |
| 50.2 | 200.8 | 3.60 | 3.65 | 101.4 |
| 50.0 | 198.5 | 3.54 | 3.48 | 98.2 |
| 50.3 | 199.7 | 3.59 | 3.56 | 99.3 |

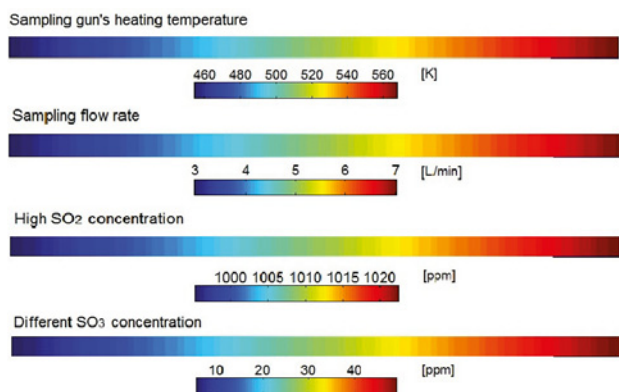


Fig. 3. Simulated conditions.

require different heating temperature, for example GB/T21508-2008 and EPA method 8A require the heating temperature above 260°C [27, 29], while DL/T 998-2016 requires a temperature above 150°C. And the standard recommendations on the heating temperature are limited in detail. On the basis of the SO₃ calibration system, the SO₃ capture efficiency was systematically tested at heating temperatures of 180°C, 220°C and 300°C respectively.

Table 4 shows the capture efficiency of the condenser tube with different sampling heating temperatures. The experimental results show that when the heating temperature was 180°C, the average capture efficiency of SO₃ was only 46.65%, meaning that the capture rate was very low. When the heating temperature was 220°C, the average efficiency of the condenser tube was 67.24%,

and the capture effect was significantly improved. When the tracing temperature was 300°C, the capture average efficiency of the condenser tube was 49.25%. The results come out that if the tracing temperature is too low, SO₃ easily reacts with ammonia, sodium oxide and other alkaline substances, or condenses in the sampling pipeline, which resulting in the loss of SO₃ and reduced collection efficiency. On the other hand, when the temperature is too high, the flue gas through the condenser tube cannot be quickly cooled, causing SO₃ to be unable to form acid mist in time and be carried out of the condenser with the flue gas, thereby reducing the collection efficiency of the condenser. Thus, the control of heating temperature is the key factor to test SO₃ accuracy, and from the point of the results the sampling gun of the heating temperature with 220°C is suggested.

Effect of Sampling Flow Rate on Capture Efficiency

The specific parameters of the condenser used in this test are shown in Table 5. The test sampling flow rates were 2.95 m/s, 4.13 m/s, 5.31 m/s and 7.08 m/s, respectively. Table 6 shows the collection efficiency of the condenser at different sample flow rates. Experimental results show that the capture efficiency increases first and then decreases, and the highest capture efficiency can be obtained when the sampling flow rate is about 4.13 m/s. The main reason probably is when the sampling velocity is relatively small, the centrifugal force generated by the condenser tube is not strong enough to drive the acid mist adhering to the

Table 4. Capture efficiency of condenser tube with different heating temperatures.

| Sampling gun's heating temperature °C | Theoretical value of SO ₃ mg | SO ₃ amount captured in condenser tube mg | Capture efficiency % | Relative deviation % |
|---------------------------------------|---|--|----------------------|----------------------|
| 180 | 32.75 | 15.31 | 46.75 | 0.21 |
| | 33.06 | 15.61 | 47.21 | 1.20 |
| | 33.11 | 15.23 | 45.99 | -1.41 |
| 220 | 32.42 | 21.68 | 66.87 | 0.62 |
| | 33.15 | 22.72 | 68.54 | 1.93 |
| | 32.17 | 21.64 | 67.27 | 0.04 |
| 300 | 33.66 | 22.31 | 66.28 | -1.43 |
| | 32.4 | 15.98 | 49.32 | 0.14 |
| | 33.26 | 16.02 | 48.17 | -2.21 |
| | 32.92 | 16.55 | 50.27 | 2.07 |

Note: The sampling flow rate is 4.13 m/s and the concentration of SO₃ is about 30 ppm.

Table 5. Condenser tube size parameters.

| Inner diameter mm | Screw pitch mm | Circle diameter mm | Number of turns |
|-------------------|----------------|--------------------|-----------------|
| 6 | 11 | 35 | 28 |

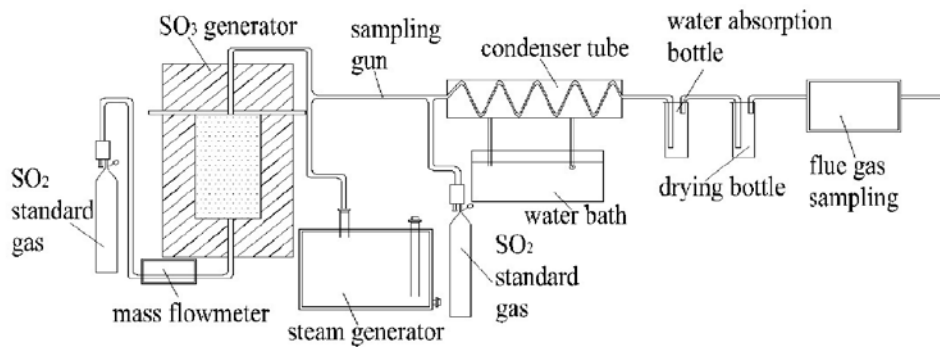


Fig. 4. Devices of the effect test with high SO₂ concentration.

inner wall, causing the SO₃ to be carried out by gas; as the flow rate increases, the centrifugal force generated becomes larger, benefiting the acid mist attached to the inner wall of the condenser tube, then the collection efficiency improves. However, if the flow rate is further increased, it means the time of acid mist particles in the condenser tube is shorter, and the acid mist is more susceptible to secondary impact and crushing, and then the probability of being carried becomes larger. Thus,

according to the analysis of the test results, the sampling flow rate with 4.13 m/s is a good choice.

Effect of High SO₂ Concentration on Capture Efficiency

In order to study the effect of high SO₂ concentration on capture efficiency of SO₃ by CCM, the high concentration of SO₂ gas was injected before

Table 6. Capture efficiency of condenser tube with different sampling flows.

| Sampling flow rate m/s | Theoretical value of SO mg | SO ₃ amount captured in condenser pipe mg | Capture efficiency % | Relative deviation % |
|---------------------------|-------------------------------|---|-------------------------|-------------------------|
| 2.95 | 35.47 | 13.75 | 38.77 | -4.65 |
| | 31.98 | 13.4 | 41.90 | 3.07 |
| | 32.45 | 13.4 | 41.29 | 1.58 |
| 4.13 | 32.42 | 21.68 | 66.87 | 0.09 |
| | 32.17 | 21.64 | 67.27 | 0.69 |
| | 33.66 | 22.31 | 66.28 | -0.79 |
| 5.31 | 32.93 | 17 | 51.62 | -2.97 |
| | 33.42 | 17.68 | 52.90 | -0.57 |
| | 35.22 | 19.4 | 55.08 | 3.53 |
| 7.08 | 33.39 | 14.65 | 43.88 | 1.18 |
| | 34.9 | 15.4 | 44.13 | 1.76 |
| | 40.87 | 17.2 | 42.08 | -2.95 |

Note: The sampling gun's heating temperature is 220°C and the concentration of SO₃ is about 30 ppm.

Table 7. Data of effect test at high SO₂ concentrations.

| The SO ₂ concentration at reactor outlet ppm | Theoretical value of SO ₃ mg | Test value of SO ₃ mg | Capture efficiency % | Relative deviation % |
|--|--|-------------------------------------|-------------------------|-------------------------|
| 995 | 31.34 | 20.78 | 66.31 | -2.04 |
| 995 | 32.17 | 21.98 | 68.32 | 0.95 |
| 1023 | 32.65 | 22.34 | 68.42 | 1.09 |

Note: The sampling gun's heating temperature is 220°C, the sampling flow is 4.13 m/s, the concentration of SO₃ is about 30 ppm.

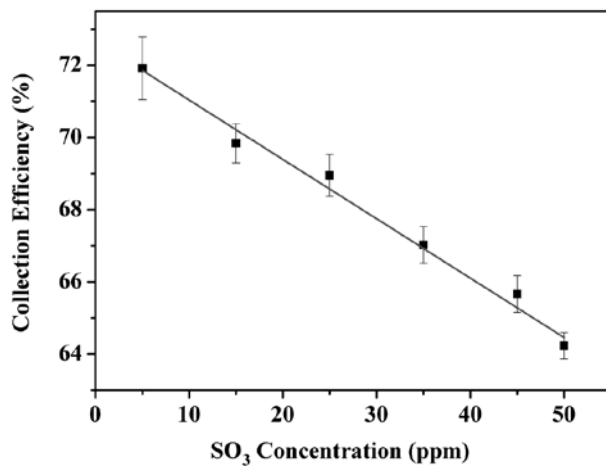


Fig. 5. Capture efficiency of condenser tube at different SO₃ concentrations.

the condenser tube. The schematic diagram of the experimental apparatus is shown in Fig. 4. The SO₂ can be slightly soluble in water and then oxidize to sulfuric acid after being sulfurous acid. If the concentration of SO₃ is low, the relative error of the test increases and the accuracy is affected. Therefore, the higher the SO₂ concentration, the more likely it is to influence SO₃ test

accuracy. The SO₂ in the flue gas of coal-fired power plants is below 1000 ppm. Thus, the SO₂ concentration for this experiment is controlled at about 1000 ppm.

Table 7 shows the results of effect test in high SO₂ concentrations. As can be seen from the comparison of Table 6, there is no obvious change in the capture efficiency of SO₃ when a certain amount of SO₂ passes through before the condensing tube. This phenomenon illustrates that a high concentration of SO₂ for the SO₃ test does not produce significant interference. To further research, since the temperature of the condenser tube is lower than the acid dew point, SO₃ in the flue gas begins to condense to form acid mist. However, the temperature of the condenser tube is much higher than the dew point of SO₂, so SO₂ cannot condense and attach to the inner wall, so SO₂ has no effect on the collection efficiency of the SO₃. Therefore, the CCM is suitable for the test of high SO₂ concentration section in coal-fired power plants, even if the SO₂ concentration is as high as 1000 ppm.

Effect of Different SO₃ Concentrations on Capture Efficiency

To further research the SO₃ emissions from coal-fired power plants, the range of 5 ppm - 50 ppm

Table 8. Capture efficiency of condenser tube with different SO₃ concentrations.

| The SO ₃ concentration ppm | Theoretical value of SO ₃ mg | SO ₃ value captured in condenser tube mg | Capture efficiency % | Relative deviation % | Average collection efficiency % |
|---------------------------------------|---|---|----------------------|----------------------|---------------------------------|
| 5 | 23.25 | 16.89 | 72.65 | 1.02 | 71.91 |
| | 23.47 | 16.93 | 72.13 | 0.31 | |
| | 25.62 | 18.18 | 70.96 | -1.33 | |
| 15 | 27.65 | 19.46 | 70.38 | 0.77 | 69.84 |
| | 28.30 | 19.77 | 69.86 | 0.02 | |
| | 28.17 | 19.52 | 69.29 | -0.79 | |
| 25 | 29.11 | 20.16 | 69.25 | 0.44 | 68.95 |
| | 29.54 | 20.17 | 68.28 | -0.98 | |
| | 30.32 | 21.02 | 69.33 | 0.54 | |
| 35 | 31.70 | 21.31 | 67.22 | 0.30 | 67.02 |
| | 32.12 | 21.65 | 67.40 | 0.57 | |
| | 33.40 | 22.19 | 66.44 | -0.87 | |
| 45 | 34.36 | 22.67 | 65.98 | 0.49 | 65.66 |
| | 33.87 | 22.04 | 65.07 | -0.89 | |
| | 33.28 | 21.94 | 65.93 | 0.41 | |
| 50 | 35.26 | 22.63 | 64.18 | -0.07 | 64.23 |
| | 36.44 | 23.28 | 63.89 | -0.53 | |
| | 34.59 | 22.35 | 64.61 | 0.60 | |

Note: The sampling gun's heating temperature is 220°C and the sampling flow is 4.13 m/s.

Table 9. Comparison test between CCM and isopropanol absorption methods.

| Test condition | The time from sampling to analysis is 24h | | The time from sampling to analysis is 24h | |
|---|---|---|---|---|
| | Recovery of CCM % | Recovery of isopropanol absorption method % | Recovery of CCM % | Recovery of isopropanol absorption method % |
| 10 ppm SO ₃ | 70.51 | 63.75 | 70.39 | 68.02 |
| 10 ppm SO ₃ + 1000 ppm SO ₂ | 70.32 | 85.34 | 70.17 | 92.55 |
| 20 ppm SO ₃ | 69.23 | 65.62 | 69.46 | 66.78 |
| 20 ppm SO ₃ + 1000 ppm SO ₂ | 69.83 | 83.58 | 69.32 | 113.60 |

Note: 10 ppm SO₃ means the concentration of SO₃ is 10 ppm at the outlet of the generator, 10 ppm SO₃ + 1000 ppm SO₂ means the concentration of SO₃ is 10 ppm, and extras adds SO₃ with 1000 ppm concentration.

of SO₃ concentration was set by adjusting the SO₃ concentration generated by the calibration device in this study. The effects of capture efficiency with different SO₃ concentrations were studied in this test.

The experimental results of the collection efficiency with different SO₃ concentrations are shown in Table 8, and the relationship between the collection efficiency and SO₃ concentration is shown in Fig. 5. Test results show that with the increase of SO₃ concentration, the capture efficiency of the condenser tube is reduced. In a certain concentration range, the capture efficiency shows a linear relationship with the SO₃ concentration. As shown in Fig. 5, the SO₃ concentration and capture efficiency are regressed by the formula $y = -0.1644x + 72.678$, and correlation index is $R^2 = 0.9826$, the reliability is greater than 99%. Investigating the reason of test, when the SO₃ concentration is changing, the formation of the SO₃ acid mist particle size is different, and the different concentrations of acid mist have different requirements for the attachment area of the inner wall. When the area of the condenser tube wall is constant, the SO₃ condensing area decreases, varying with the increase of SO₃ concentration, which results in a lower SO₃ capture efficiency. From the result, the SO₃ test data can be corrected by the formula between SO₃ concentration and capture efficiency, then the test result can close to the true SO₃ concentration.

Comparison Test between EPA Method 8 and CCM

At present, the widely used SO₃ test methods include CCM and isopropanol absorption. According to the above test, the best heating temperature of the sampling gun is 220°C and the suitable sampling flow rate of CCM is 4.13 m/s; referring to relevant literature [28, 29], the sampling velocity of the isopropanol absorption method was set to 1L/min, then the SO₂ concentration at the inlet of the generator was adjusted to make the concentration of SO₃ at the outlet with 10 ppm and 20 ppm respectively, and after that the test was conducted. The comparison test results are shown in Table 9.

Table 9 shows that the recovery rate of CCM and the isopropanol absorption method is reduced with the increasing of the SO₃ concentration. But facing the high concentration of SO₂, the isopropanol absorption method is obviously vulnerable, while the CCM is not affected. Meanwhile, when the time from sampling to laboratory analysis is different, the recoveries of two methods differ significantly, and the isopropanol absorption method is significantly disturbed. With the extension of the time from sampling to analysis, the recovery of isopropanol absorption method increases, even exceeding 100%, while the recovery of CCM is not obviously changed. The main reason for the instability of the results is that although 80% isopropanol can inhibit the solubility of part SO₂, there is still some interference of SO₂, especially with the high concentration of SO₂ and the extension of the time from sampling to analysis. The amount of SO₂ oxidized increases, bringing about serious interference. Comparing the two methods, although the recovery of CCM is only about 70%, it is affected by SO₂ and the interval between sampling and analysis lesser, and the recovery rate is stable. Correcting the test data according to the above regression equation, the result can be relatively accurate and reliable.

Conclusions

This paper analyzes the advantages and disadvantages of Fourier transform infrared spectroscopy, isopropanol absorption method and CCM to test SO₃ concentration in flue gas. Then the CCM is adopted to test the SO₃ concentration, an SO₃ test accuracy verification device is set up to carry out comparative experiments that influence the test accuracy of CCM. The factors considered include the sampling gun's heating temperature, sampling flow rate, high SO₂ concentration and SO₃ concentration difference. The results show that the heat tracing temperature has an important influence on the condensation and acid fog formation of SO₃ in the sampling line, which affects the capture efficiency of the condenser tube. Reasonable control of the tracing temperature helps to improve the accuracy of CCM. Acid mist particles

adhered and broken in the serpentine tube were related to the flow rate in the tube, which affected the capture efficiency of the condenser tube. The specific trend was to increase first and then decrease with the increase of the flow rate, which means the reasonable sampling flow rate plays an important role to the accurate testing of SO₃. The capture efficiency increases with the increase of flow rate and then decreases with the increase of flow rate. Appropriate sampling flow rate plays an important role in the measurement accuracy of SO₃. The high concentration of SO₂ has little effect on capture efficiency, and the CCM can effectively avoid the interference of SO₂ on capture efficiency, suitable for the SO₃ testing of a coal-fired power plant. With the increase of SO₃ concentration, the collection efficiency of the condenser tube is reduced. In a certain range of SO₃ concentration, the collection efficiency showed a linear relationship with SO₃ concentration. The conclusion of the experiment has important reference significance for how to improve the accuracy of SO₃ detection.

Acknowledgements

This work was financially sponsored by the National Key Research Plan (2016YFC0203703).

Conflict of Interest

The authors declare no conflict of interest.

References

- XIANG B., SHEN W., ZHANG M., YANG H., LU J. Effects of different factors on sulfur trioxide formations in a coal-fired circulating fluidized bed boiler. *Chemical Engineering Science*, **172**, 262, **2017**.
- BRACHERT L., KOCHENBURGER T., SCHABER K. Facing the sulfuric acid aerosol problem in flue gas cleaning: pilot plant experiments and simulation. *Aerosol Science and Technology*, **47** (10), 1083, **2013**.
- PAN D., YANG L., WU H., HUANG R. Removal characteristics of sulfuric acid aerosols from coal-fired power plants. *Journal of the Air & Waste Management Association*, **67** (3), 352, **2017**.
- FLEIG D. SO₃ formation under oxyfuel combustion condition. *Industrial & Engineering Chemistry Research*, **50** (50), 8505, **2011**.
- WANG H.L. Formation and control of SO₃ from coal-fired power plants. *Electric Power Environmental Protection*, **30** (5), 17, **2014** [In Chinese].
- WANG B. Measurement and analysis on sulphur trioxide in coal-fired power plant flue gas. *Northeast Electric Power Technology*, **38** (1), 47, **2017** [In Chinese].
- XIANG B. Experimental and modeling studies on sulfur trioxide of flue gas in a coal-fired boiler. *Energy & Fuels*, **2017**.
- MORETTI A., TRISCORI R., RITZENTHALER D. A system approach to SO₃ mitigation. *Babcock and Wilcox Company and American Electric Power*, **2006**.
- CAO Y., ZHOU H., JIANG W., CHEN C.W., PAN W.P. Studies of the fate of sulfur trioxide in coal-fired utility boilers based on modified selected condensation methods. *Environmental Science & Technology*, **44**, 3429, **2010**.
- DUNN J.P., KOPPULA P. R., STENGER H.G., WACHS I.E. Oxidation of sulfur dioxide to sulfur trioxide over supported vanadia catalysts. *Applied Catalysis B Environmental*, **19**, 103, **1998**.
- SVACHULA J., ALEMANY L.J., FERLAZZO N., FORZATTI P., TRONCONI E., BREGANI F. Oxidation of SO₂ to SO₃ over honeycomb denoxing catalysts. *Industrial & Engineering Chemistry Research*, **32**, 826, **1993**.
- HUANG R.T., YU R., WU H., PAN D.P., ZHANG Y.P., YANG L.J. Investigation on the removal of SO₃ in ammonia-based WFGD system. *Chemical Engineering Journal*, **289**, 537, **2016**.
- UEDA Y., NAGAYASU H., HAMAGUCHI R., MIYAKE K., MATSUURA K., NAGATA C. SO₃ removal system for flue gas in plants firing high sulfur residual fuels. *Mitsubishi Heavy Industries Technical Review*, **49** (4), 6, **2012**.
- PAN D.P. Removal effect of wet flue gas desulfurization system on flue particle and SO₃ acid mist from coal-fired power plants. *Proceedings of the CSEE*, **36** (16), 4356, **2016** [In Chinese].
- DEEMING A.S. Rediscovering the chemistry of sulfur dioxide: New developments in Synthesis and Catalysis. *Synthesis*, **46** (20), 27, **2014**.
- WU J. Coal-fired flue-gas mercury control technologies. *Energy & Environment Research in China*, **77**, **2015**.
- VDI 2462-2-2011 Measurement of gaseous emissions-Determination of sulphur trioxide in water vapour containing exhaust gas-Condensation method. *German Association for Science and Technology*, **2011**.
- XIANG B., ZHANG M., YANG H., LU J. Prediction of acid dew point in flue gas of boilers burning fossil fuels. *Energy & Fuels*, **30** (4), 3365, **2016**.
- VAINIO E., FLEIG D., ANDERS B., KLAS A., FILIP J., MIKKO H. Experimental evaluation and field application of a salt method for SO₃ measurement in flue gases. *Energy & Fuels*, **27** (5), 2767, **2013**.
- TOKURA A., TADANAGA O., NISHIMIYA T., MUTA K., KAMIYAMA N., YONEMURA M., FUJII S., TSUMURA Y., ABE M., TAKENOUCHE H., KENMOTSU K., SAKAI Y. Investigation of SO₃ absorption line for in situ gas detection inside combustion plants using a 4- μ m-band laser source. *Applied optics*, **55** (25), 6887, **2016**.
- SPÖRL R., WALKER J., BELO L., SHAH K., STANGER R., MAIER J., WALL T., SCHEFFKNECHT G. SO₃ Emissions and removal by ash in coal-fired oxy-fuel Combustion. *Energy Fuels*, **28**, 5296, **2014**.
- YANG D., ZHENG F. Detection technique of SO₃ content in coal-fired flue gas and accuracy analysis. *Clean Coal Technology and Sustainable Development*, 563, **2016**.
- XIANG B.X., SHEN W.F., ZHANG M., YANG H.R., LU J.F. Effects of different factors on sulfur trioxide formations in a coal-fired circulating fluidized bed boiler. *Chemical Engineering Science*, **172**, 262, **2017**.
- SPÖRL R., WALKER J., BELO L., SHAH K., STANGER R., MAIER J., WALL T., SCHEFFKNECHT G. SO₃ emissions and removal by ash in coal-fired oxy-fuel combustion. *Energy Fuels*, **28**, 5296, **2014**.

25. MADDALONE R.F., NEWTON S.F., RHUDY R.G., STATNICK R.M. Laboratory and field evaluation of the controlled condensation system for SO₃ measurements in flue-gas streams. *Journal of the Air Pollution Control Association*, **29**, 626, **1979**.
26. WU H., PAN D.P., ZHANG R., YANG L.J., PENG Z.M., YANG B. Abatement of Fine Particle Emissions from a Coal-Fired Power Plant Based on the Condensation of SO₃ and Water Vapor. *Energy Fuels*, **31** (3), 3219, **2017**.
27. GB/T 21508-2008 Performance test method for coal-fired flue gas desulphurization equipment. Beijing: Standards Press of China, **2008** [In Chinese].
28. EPA-8 Determination of sulfuric acid vapor or mist and sulfur dioxide emissions from Kraft recovery furnaces. USA, **1996**.
29. EPA-8 Determination of sulfuric acid mist and sulfur dioxide emission from stationary source. USA, **1996**.
30. JIS K 0103-2005 Method for determination of sulfur oxides in flue gas precipitation-titration method. Association, Japanese Standards, **2005**.
31. AHNA J.Y., OKERLUND R., FRY A., EDDINGS E.G. Sulfur trioxide formation during oxy-coal combustion. *International Journal of Greenhouse Gas Control*, **5**, 127, **2011**.
32. LIU H.X. Study on SO₃ generation, control and testing technology for coal-fired power plants. *Electric Power*. **48** (9), 151, **2015** [In Chinese].
33. WHITTINGHAM G. The influence of carbon smokes on the dew-point and sulphur trioxide content of flame gases. *Journal of Applied Chemistry*, **1** (9), 382, **2007**.