SO₃ Sampling and Detection Analysis Method in Coal-Fired Power Plant

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Abstract. In December 2015, the executive meeting of the State Council decided to fully implement ultra-low emission and energy-saving transformation of coal-fired units by 2020, and to complete the transformation in the eastern and central regions in advance to 2017 and 2018. With the implementation of ultra-low emission transformation technology all over the country, the emissions of smoke, SO₂ and NOₓ have been effectively controlled, and the number of heavy haze days in cities has been reduced, but no targeted control measures have been taken for the emissions of unconventional pollutants such as SO₃. In fact, the harm of SO₃ is far greater than that of SO₂, which will not only cause corrosion of subsequent equipment, form ammonium bisulfate, and cause equipment blockage. If it is discharged into the atmosphere, it will react with water vapor and alkaline substances in the air, thus aggravating the generation of haze. Therefore, it is necessary to measure the SO₃ in the flue gas of power plant accurately. But because of the special nature of SO₃, its detection technology is a difficulty in this field, it is very necessary to carry out the research of high accuracy SO₃ detection technology. In this paper, the most widely used control condensation method and isopropanol absorption method in SO₃ sampling, as well as the titration method in SO₃ detection are introduced in detail. Other methods of SO₃ sampling and detection are briefly introduced.

1. Introduction
In December 2015, the Ministry of Environmental Protection, the National Development and Reform Commission and the Energy Administration jointly issued the work plan for the comprehensive implementation of ultra-low emission and energy saving transformation of coal-fired power plants (HF [2015] No. 164), which promoted the "ultra-low emission and energy saving transformation of coal-fired power plants" to a national special action. That is to say, by 2020, all coal-fired power plants in China that have the conditions for transformation will strive to achieve ultra-low emission (i.e. at the benchmark oxygen content Under the condition of 6%, the emission concentration of soot, SO₂ and NOₓ shall not be higher than 10, 35 and 50mg / m³ respectively). Nowadays, the SCR method for nitrogen oxide treatment is widely used because of its efficient and mature denitration technology, but when this method is used, SO₃ will be generated at the same time, which will cause harm to the environment, so the pollution of SO₃ caused by SCR denitration technology has gradually attracted people's attention. SO₃ is very easy to combine with the water in the flue gas to form H₂SO₄ droplets. The sulfuric acid aerosol is also the precursor of fine particles (PM2.5), thus aggravating the pollution of haze and acid deposition. SO₃ will also increase the dew point of the flue gas, corrode the flue gas and equipment, react with the running ammonia escape to generate liquid ammonium hydrogen sulfate.
to block the power plant equipment, thus increasing the power consumption of the induced draft fan and the investment in equipment. The accurate measurement of SO$_3$ in the flue gas of power plant is an important prerequisite for the treatment of SO$_3$. However, due to the special nature of SO$_3$, its detection technology is a difficulty in this field, it is very necessary to carry out the research of high accuracy detection technology of SO$_3$.

2. Main Methods of SO$_3$ Sampling

There are many researches on SO$_3$ sampling methods at home and abroad, such as the controlled condensation method proposed by Cheney and homalya, which is currently considered as the most accurate sampling method to measure the low concentration of SO$_3$ / H$_2$SO$_4$ in power plants [1], which is also adopted by Chinese standard DLT 998-2016 and German standard VDI 2462 Part 2. In addition, the spiral tube method is widely used in Japan. Other methods include isopropanol absorption method, NaOH method, cotton plug method, salt absorption method, etc.

2.1. Controlled Condensation Method

There are two preconditions for the application of Controlled Condensation Method: ① the H$_2$SO$_4$ in flue gas is completely in the state of steam; ② the majority of H$_2$SO$_4$ in flue gas is in the state of concentration [2]. Install the sampling device as shown in Figure 1, the sampling part is mainly composed of three parts: sampling probe, porous glass fiber filter and spiral collecting tube. The purpose of the filter is to collect the dust particles and collect the condensed SO$_3$ / H$_2$SO$_4$ acid mist droplets on the washed particles after sampling for analysis. The sampler shall be heated to 250 °C (including the filter and the inlet for the SO$_3$ collector), so as to ensure that SO$_3$ / H$_2$SO$_4$ in the flue gas exists in the form of gas, and the acid steam in the flue gas enters the spiral condensation collection pipe. The temperature control of the circulation thermostat should be set above 80 °C. At present, the thermostat used in power plant sampling is water bath heating. Some researches put forward the heating mode of tracing band. The tracing band is controlled by relay to achieve accurate temperature control, which overcomes the inconvenience of traditional water bath heating in field operation and reduces the error [3].

Before sampling, read the gas volume meter and record, then turn on the sampling pump, and the rate of sample gas extraction is between 4L / min and 10L / min. If SO$_3$ is expected to be less than 5mg / m$^3$, a higher flow rate (6L / min to 10L / min) or an extension of the sampling period from the usual
30 minutes to 2H should be set. When the concentration is higher than 50mg / m³, the sampling period can be shortened. Under these conditions, SO₃ will condense on the surface of the collector, and the condensate in the pipe wall can be observed by naked eyes. After sampling, close the sampling pump, read the data of pressure, temperature and gas volume flowmeter, accurately record the sampling time and volume (converted to standard atmospheric state and dry basis), wash the spiral collecting pipe and the connect pipes between the equipment with 50ml deionized water for three times continuously, and finally use deionized water to fix the volume in a 250ml conical flask.

2.2. isopropanol absorption method

The isopropanol solution with 80% volume fraction is used as the absorption solution and placed in the ice bath to absorb the H₂SO₄ vapor in the flue gas. Then the thorium barium titration method is used to detect the SO₃ concentration. The minimum detection limit can reach 0.05mg/m³. This sampling method is shown in Figure 2. In order to prevent the condensation of sulfuric acid steam, the sampling pipeline needs to be insulated above 160 ~ 200℃, so the pipeline material is best to use quartz or GG-14 glass and other high temperature resistant glass materials. The sampling bottle is composed of four parts. The first absorption bottle is piped into 100ml of 80% isopropanol aqueous solution, the second and third absorption bottles are added into 100ml and 50ml of hydrogen peroxide solution, and the last absorption bottle is put into desiccant to prevent damage to the air extraction equipment behind. During sampling, the absorption bottle needs to be put into ice water, and the sampling flow is set at 1 L / min, the sampling time is about 20 minutes, and the sampling volume is recorded (it needs to be converted to standard state and dry basis). Take the absorption solution back to the laboratory after sampling, record the volume of the sampling solution, wash the connecting tube with about 50ml of deionized water for three times, and fix the volume in the conical flask.

The basic principle of the method is: in the environment of ice bath, SO₃ / H₂SO₄ vapor can be well dissolved in isopropanol solution, and the isopropanol solution can inhibit the dissolution of SO₂. After sampling, the concentration of SO₄²⁻ can be determined by titration with Ba²⁺ standard solution containing thorium reagent. The function of hydrogen peroxide is to absorb SO₂. By using the oxidizability of H₂O₂, all SO₂ can be oxidized to SO₄²⁻, which can be determined by the same method. If only SO₃ is collected in the field sampling, the hydrogen peroxide device can be removed. It is recommended that the absorption bottle here be replaced with 80% isopropanol absorption solution, and add 2-3 drops of thorium reagent and 0.1-0.2ml of barium perchlorate standard solution. When the liquid color of the absorption bottle changes, stop pumping immediately. This method can fully collect
sulfur trioxides and effectively prevent the escape of sulfur trioxides\cite{7}. There are also some studies that combine the condensation method and absorption method. Compared with the use of single method, SO$_3$ is trapped to a greater extent\cite{8}.

2.3. spiral tube method
The sampling principle of spiral tube method is to use vacuum pump to pump the flue gas from the smoking duct, and the centrifugal force will be generated when the flue gas flows through the spiral tube, so the SO$_3$ in the form of fog will condense on the inner wall of the spiral tube, and the collected samples will be taken back to the laboratory for analysis. This method is widely used in Japan. The principle of collection of the spiral tube method is similar to that of the control condensation method\cite{1}.

Based on JIS-Z-8808-1995, some researchers added spiral tube to measure SO$_3$, and compared this method with EPA 202 method. The conclusion is that the former is more accurate than the latter in measuring SO$_3$ at the inlet and outlet of WESP\cite{9}.

3. Main Methods of SO$_3$ Detection
For the SO$_4^{2-}$ solution sampled from the power plant, the commonly used detection methods are the titration method and other methods such as ion chromatography of the standard HJ544-2016, spectrophotometry and iodimetry, etc.

3.1. Titration Methods
1) Experimental drugs and preparation
   a) Color reagent (0.2% thorium reagent): 0.2000g thorium reagent is dissolved in 100ml deionized water.
   b) Absorption solution (80% isopropanol solution): mix 800ml isopropanol with 200ml deionized water and shake well.
   c) BaCl$_2$ stock solution (0.0125mol/l BaCl$_2$ solution): 0.3053g BaCl$_2$ is dissolved in 100ml 80% isopropanol solution.
   d) Titration solution (0.00125mol/l BaCl$_2$ solution): take 10ml of BaCl$_2$ stock solution, put it into a 100ml volumetric flask, add 80% isopropanol solution to the volume, and shake it up.

2) Experimental Procedure
   Take three absorption bottles, add 100ml, 50ml and 50ml of 80% isopropanol solution respectively; drop two drops, one drop and one drop of 0.2% thorium reagent in turn, and shake them well. At this time, the solution should be pink. Use isopropanol absorption method for sampling. After sampling, transfer the absorption solution of the three absorption bottles to the conical bottle, wash the absorption bottles and connecting pipes with 80% isopropanol solution, and then pour them into the conical bottle together. The absorption solution is divided into two parts and titrated separately. Put a proper amount of titration solution into a 2ml micro buret, record the liquid level reading $V_1$, $V_1'$ before titration, control the titration speed with the left hand, shake the conical bottle with the right hand, the solution will change from yellow to pink and reach the titration end point, at this time, stop the titration immediately, accurately read the liquid level reading, and record it as $V_2$, $V_2'$.

3) Result calculation
   Dosage of BaCl$_2$ titration solution (ml): $V_0 = (V_2-V_1) + (V_2'-V_1')$
   If the sampling volume is $V$ liter, the SO$_3$ concentration expression is $100V_0/V$, and the unit is mg/m$^3$.

   The isopropanol solution absorbed SO$_3$ was titrated after being placed for different times. The results showed that the placing time was within 4h, which had no effect on the determination results of SO$_3$. However, if the placing time was too long (such as 15h), the determination results increased\cite{10}.

   After the SO$_3$ is collected from 80% isopropanol solution, the content of SO$_4^{2-}$ ion in the sample can be measured indirectly by the above titration method. Besides, arsenazo - III can be used as indicator, barium acetate can be used as titration solution\cite{11}, the color before titration is rose red, and
the end-point color of titration is violet blue. Both methods can detect the content of SO$_3$ in the flue gas quickly and reliably, which have been successfully applied in many sets of denitrification performance tests. Some literatures have introduced that starch is used as indicator and iodine is used to titrate samples$^{[12]}$. The operation is more complicated, so we will not give a detailed introduction here.

3.2. Spectrometric method

The earliest optical measurement method is infrared spectroscopy, also known as "infrared spectrophotometry", which is a kind of molecular absorption spectrum. Due to the complex composition of the flue gas in the power plant, the infrared spectrum is complex and difficult to analyze, and the SO$_2$ content in the flue gas is far higher than SO$_3$, and the spectrum overlap is large, so the accuracy is relatively low$^{[14]}$.

At present, there are many methods to measure with special light source, the most effective ones are quantum cascade laser method (QCL) and Fourier infrared spectroscopy (FTIR). FTIR is a spectral analysis instrument which uses infrared spectrum to analyze impurity concentration through Fourier transform. Quantum cascade laser method has many applications in the field of chemical sensing and detection. It is a method that uses quantum cascade (QC) laser as a tunable narrow-band light source and measures SO$_2$ based on super sensitive infrared absorption. This method can detect SO$_2$, SO$_3$ by analyzing the spectrum$^{[16]}$.

Ion chromatography is a kind of chromatography method which uses ion exchange resin with low exchange capacity as a fixed relative ionic substance to separate and use conductivity detector to continuously detect the conductivity change of effluent. This method is convenient to detect, suitable for the determination of H$_2$SO$_4$ in air or power plant flue gas, and has high sensitivity and accuracy, but high equipment cost. Experimental data showed that$^{[17]}$, compared with barium chloride turbidimetric spectrophotometry, there was no significant difference between the two methods (P > 0.05).

3.3. Spectrophotometry

The standard method of SO$_3$ detection is given by the Environmental Protection Agency of the United States in the <method for the determination of SO$_3$ and SO$_2$ emissions from fixed sources>. The SO$_3$ in flue gas is collected by isopropanol solution with volume fraction of 80%. A few drops of thorium reagent are added as color indicator, and a certain concentration of barium perchlorate solution is used to titrate the sample to detect the SO$_3$ content. However, the disadvantages of this method are as follows: first, the consumption of absorption solution used in sampling is large; second, when thorium reagent is used as color indicator, because the color is very light and close, the end point of titration is not easy to judge (from the beginning of the pale yellow to the end point of titration in the light red). According to the method of ISO detection of SO$_2$,$^{[18]}$ some researchers put forward a spectrophotometric method to determine the concentration of SO$_4^{2-}$. After the SO$_3$ was collected with 80% isopropanol solution as the absorption solution, the excess barium perchlorate was used to react with SO$_4^{2-}$ in the absorption solution. The remaining Ba$^{2+}$ ions and thorium reagent were combined to form thorium barium complex. The wavelength of the spectrophotometer was fixed at 530 nm to measure the absorbance of the solution. The SO$_3$ concentration was calculated according to SO$_4^{2-}$ standard curve. Compared with the previous titration method, this new method uses less isopropanol absorption solution, has better precision and accuracy, and can reduce human measurement error during operation, so it has more application and promotion prospects$^{[19]}$. In addition, some researchers have also designed a flow injection spectrophotometer based on Lambert Beer law and the principle of spectrophotometer, which can meet the needs of online measurement of SO$_3$ concentration in laboratory conditions, but the application of this method in actual conditions needs further research$^{[20]}$.

3.4. Other methods

The principle of other methods for SO$_3$ detection, such as iodimetry, is as follows. Due to the very
hydrophilic nature of SO$_3$ / H$_2$SO$_4$, when KIO$_3$ and KI solution are dropped into the sample after sampling, dilute sulfuric acid will react with it, and solid I$_2$ will be generated in the solution. Add several drops of starch with a certain mass fraction into the solution as the color indicator, titrate with a certain concentration of sodium thiosulfate (Na$_2$S$_2$O$_3$) as the standard solution, then the amount of I$_2$ generated can be obtained, and then indirectly calculate the concentration of sulfuric acid sample.

Corrosion probe method measures the concentration of sulfuric acid vapor according to a linear relationship among the corrosion degree of the probe, corrosion time and temperature of flue gas. This method is to make a special probe so that it can easily absorb sulfur trioxide and sulfuric acid steam. After sampling, wash the probe and determine the concentration of the washing solution to indirectly calculate the acid steam concentration [2]. The disadvantage of this method is that it cannot get the concentration data of sulfuric acid steam continuously, and there will be operational errors in the data.

4. Conclusion
The accurate measurement of SO$_3$ in the flue gas of power plant is an important prerequisite for the treatment of SO$_3$. However, due to the special nature of SO$_3$, its detection technology is a difficulty in this field. In order to accurately determine SO$_3$ / H$_2$SO$_4$ in the flue gas in the actual situation on site, it is necessary to combine a variety of sampling technologies and analysis methods to obtain better analysis results.

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