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# Evaluation of sulfur trioxide detection with online isopropanol absorption method

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## ABSTRACT

Measurement of the SO<sub>3</sub> concentration in flue gas is important to estimate the acid dew point and to control corrosion of downstream equipment. SO<sub>3</sub> measurement is a difficult question since SO<sub>3</sub> is a highly reactive gas, and its concentration is generally two orders of magnitude lower than the SO<sub>2</sub> concentration. The SO<sub>3</sub> concentration can be measured online by the isopropanol absorption method; however, the reliability of the test results is relatively low. This work aims to find the error sources and to evaluate the extent of influence of each factor on the measurement results. The test results from a SO<sub>3</sub> analyzer showed that the measuring errors are mainly caused by the gas–liquid flow ratio, SO<sub>2</sub> oxidation, and the side reactions of SO<sub>3</sub>. The error in the gas sampling rate is generally less than 13%. The isopropanol solution flow rate decreases 3% to 30% due to the volatilization of isopropanol, and accordingly, this will increase the apparent SO<sub>3</sub> concentration. The amount of SO<sub>2</sub> oxidation is linearly related to the SO<sub>2</sub> concentration. The side reactions of SO<sub>3</sub> reduce the selectivity of SO<sub>4</sub><sup>2-</sup> to nearly 73%. As sampling temperature increases from 180 to 300°C, the selectivity of SO<sub>4</sub><sup>2-</sup> decreases from 73% to 50%. The presence of H<sub>2</sub>O in the sample gas helps to reduce the measurement error by inhibiting the volatilization of the isopropanol and weakening side reactions. A formula was established to modify the displayed value, and the measurement error was reduced from 25%–54% to less than 15%.

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## Introduction

In the combustion process of fossil fuels, a small fraction of sulfur is converted to sulfur trioxide (SO<sub>3</sub>) (Bongartz and Ghoniem, 2015; Bongartz et al., 2015; Choudhury and Padak, 2016; Cordtz et al., 2013; Fleig et al., 2013; Wang et al., 2015). Flue gas SO<sub>3</sub> has undesirable effects on power plant operation due to plume opacity and corrosion problems (Fernando, 2003; Srivastava et al., 2004; Vainio et al., 2016). As the flue gas temperature drops in the air pre-heater, SO<sub>3</sub> starts to react with water vapor to form gaseous H<sub>2</sub>SO<sub>4</sub> at a rapid rate. As flue gas

with 10 vol.% H<sub>2</sub>O is cooled down from 400 to 200°C, approximately 8.7% and 99.3% of the SO<sub>3</sub> is respectively converted into gaseous H<sub>2</sub>SO<sub>4</sub> on the assumption of approximate equilibrium (Hardman et al., 1998). The high boiling point of H<sub>2</sub>SO<sub>4</sub> generates a high acid dew point for the gas phase. With 10 vol.% water vapor, the H<sub>2</sub>SO<sub>4</sub> concentrations range from 1 to 50 ppmv, and the dew point varies from 116 to 154°C (Banchero and Verhoff, 1975). In this work, the term “SO<sub>3</sub>” includes gaseous SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. It is desirable to precisely measure the SO<sub>3</sub> concentration in the flue gas to limit equipment corrosion, heat loss, and acidic gas discharge. SO<sub>3</sub> measurement is difficult due to its

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high reactivity, and can be hindered by: (1) comparatively low concentrations of SO<sub>3</sub> under typical conditions (Spellicy and Pisano, 2006; Blythe and Dombrowski, 2004), (2) interference from a high SO<sub>2</sub> concentration (Jaworowski and Mack, 1979), (3) losses of SO<sub>3</sub> by surface reactions or filter cake filtration (Belo et al., 2014; Cao et al., 2010; Galloway et al., 2015; Zhuang et al., 2011), and (4) SO<sub>3</sub> condensation (Guo et al., 2017).

The SO<sub>3</sub> measurement methods mainly include the controlled condensation method (CCM) and the isopropanol (IPA) absorption bottle method (Maddalone et al., 1979; Yang and Zheng, 2016). The CCM is the most-used technique, and is based on the condensation of H<sub>2</sub>SO<sub>4</sub> above the water dew point and subsequent sulfate analysis. Maddalone et al. (1979) found that 95% of the injected H<sub>2</sub>SO<sub>4</sub> could be recovered from a synthetic flue gas using the CCM with a coefficient of variance of ±6.7%. This method cannot be used to continuously measure SO<sub>3</sub> concentrations in flue gas online. The IPA absorption bottle method is based on the absorption of SO<sub>3</sub> in an 80 vol% IPA solution diluted in water and sulfate analysis afterward. The main problem is interference by SO<sub>2</sub>. The oxidation of a few parts per million of SO<sub>2</sub> dissolved in the IPA solution will result in a significant amount in proportion to the SO<sub>3</sub> concentration (Fleig et al., 2012). The dissolved SO<sub>2</sub> can be partially removed by bubbling air through the isopropanol solution.

The Pentol SO<sub>3</sub> analyzer (Pentol GmbH, Germany) based on the IPA method is a modified version of the Severn Science Analyzer designed by Jackson et al., and can be used to continuously measure SO<sub>3</sub> in flue gas online (Jackson et al., 1970, 1981). Typical values for the oxidation of SO<sub>2</sub> yield the equivalent of only 0.1 ppmv SO<sub>3</sub> for each 1000 ppmv SO<sub>2</sub> (Jackson et al., 1970). However, different researchers have obtained conflicting conclusions about the measurement errors. The results tested by Cooper at an Orimulsion-fired power plant showed that the SO<sub>3</sub> concentrations obtained with the Severn Science analyzer were 25 times higher than those obtained with the CCM (Cooper, 1995). An almost SO<sub>3</sub>-free mixed gas containing air and 1000 ppmv SO<sub>2</sub> was tested by Fleig, and the results showed that less than 1 ppmv SO<sub>3</sub> was detected with the CCM, while a value of almost 10 ppmv SO<sub>3</sub> was obtained with the Pentol SO<sub>3</sub> analyzer (Fleig et al., 2012). A possible explanation is the oxidation of dissolved SO<sub>2</sub>. It is worth noting that, initially, a gas stripping tube was used to remove dissolved SO<sub>2</sub> (Jackson et al., 1970). However, the gas stripping tube was removed from the current Pentol SO<sub>3</sub> analyzer. Koebel and Elsener (1997) obtained relatively lower SO<sub>3</sub> concentrations with the IPA drop method, for which the sampling process is similar to that of the Pentol SO<sub>3</sub> analyzer, and the explanation was that SO<sub>3</sub> may react with isopropanol, forming the monoester or diester of sulfuric acid. The gas sampling rate is controlled by a mass flow controller (MFC)

calibrated for nitrogen (N<sub>2</sub>). Fleig et al. (2012) found that the actual gas sampling rate was lower due to the high CO<sub>2</sub> concentration under oxy-fuel fired conditions. An MFC correction factor for the flue-gas was calculated, and the reading of the Pentol SO<sub>3</sub> analyzer was divided by this correction factor (Fleig et al., 2012). In addition, volatilization loss of the IPA solution would lead to a positive deviation in measurement results (Barton and Mcadie, 1972).

In summary, the measurement errors of the SO<sub>3</sub> concentration mainly come from the measuring error of the gas sampling rate, IPA solution volatilization, the side reactions of SO<sub>3</sub> with isopropanol, and SO<sub>2</sub> oxidation. The aim of this work is to discover and evaluate the extent of influence of each factor on the measuring results, and then to reduce measuring errors by adjusting the process according to the influence factors. For the factors that cannot be controlled, correction coefficients are proposed to revise the measuring result.

## 1. Measurement principle and experiment platform

Both the sampling process and the analysis method for SO<sub>3</sub> are different between the Pentol SO<sub>3</sub> analyzer and the traditional IPA absorption bottle method. For the IPA absorption bottle method, flue gas is bubbled through an IPA absorption bottle which is placed in an ice water bath, wherein the SO<sub>3</sub> is absorbed. The SO<sub>3</sub> is stored in the IPA solution in the form of SO<sub>4</sub><sup>2-</sup>, which is measured by titration with barium perchlorate using thorin as an indicator.

Compared with the IPA absorption bottle method, the advantage of the Pentol SO<sub>3</sub> analyzer is that it can achieve continuous online SO<sub>3</sub> measurement. The specific measurement principle is as follows. A simplified process diagram of the Pentol SO<sub>3</sub> analyzer is shown in Fig. 1. The flue gas continuously flows through a heated sampling probe and filter, and then contacts the IPA solution. Subsequently, the SO<sub>3</sub> in the flue gas is absorbed into the IPA solution as sulfate ions. As the solution passes through a bed of barium chloranilate, where reaction (1) occurs, and acidic chloranilate ions are formed. The acidic chloranilate ions absorb light preferentially at 535 nm as they pass through the optical cell continually, and then a series of voltages (*U*, mV) are output by the photometer. By maintaining a constant gas-liquid flow ratio (*m*), there is a near-exponential relationship between the SO<sub>3</sub> concentration (*C*<sub>SO<sub>3</sub></sub>, ppmv) and “*U*”, as shown in Eq. (2).



$$\log U = a \times m \times C_{\text{SO}_3} + b \quad (2)$$

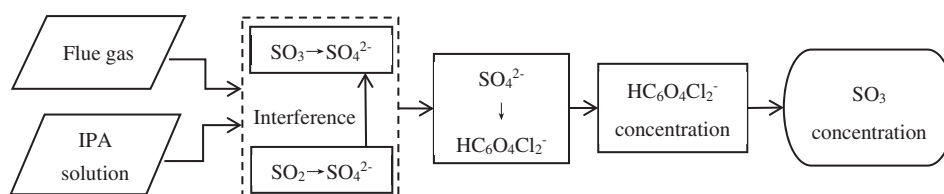


Fig. 1 – Simplified process diagram of the Pentol SO<sub>3</sub> analyzer. IPA: isopropanol.

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