Thermo Scientific Sulfur Trioxide CEMS Development

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In this manuscript, we shall present a preliminary discussion of our efforts and related results pertaining to three important components that impact the development of the Thermo Scientific SO$_3$ CEMS: SO$_3$ Generation, SO$_3$ Detection and SO$_3$ Sample Handling.

Introduction

The formation of SO$_3$ in a coal-fired power plant has many undesirable consequences on the plant's equipment and emissions, presenting the need for a reliable and accurate monitoring method to help minimize adverse effects. High concentrations of SO$_3$ can cause corrosion, fouling and plugging of plant equipment, forcing replacement of hardware and stricter limitations on load [R.K. Srivastava et al., 2002]. SO$_3$ also reacts with moisture in the stack to form fine droplets of sulfuric acid at the stack exit; these droplets scatter light and cause a visible "blue plume" that leads to an unfavorable perception of the plant's environmental impact.

Methods such as dry sorbent injection can be effective at neutralizing SO$_3$ and other acidic gases, but the lack of a controlled injection process can result in an overuse of sorbents, which can be wasteful and expensive, and could overload the plant equipment. Conversely, using less sorbent will negatively impact the removal of Mercury and reduce the life of plant equipment due to corrosion. Therefore, it becomes increasingly important to continuously monitor SO$_3$ to ensure the right amount of sorbent is being injected to optimize plant operations and costs.

Our goal is to produce a continuous SO$_3$ measurement system that delivers research grade performance in a package that is easy to use and

is designed specifically for the power generation industry.

Comparison of Detection Methods

Various SO$_3$ detection techniques were investigated, both in the laboratory and in the field, to determine the measurement method that yields the best detection limit and optimum selectivity. Lab testing with the FTIR detection method in controlled conditions indicated the possibility of isolating and measuring the SO$_3$ spectra. However, after more than a month of field testing, the FTIR system failed to perform at the same sensitivity as in the lab. In most cases, the detection limit exceeded 12 ppm (parts per million), much worse than then the 1 ppm detection limit for SO$_3$ obtained under lab controlled conditions. The deteriorated performance in the field can be mainly explained by the significant water interference in the spectrum from moisture in the flue gas.

The differential method, which converts both SO$_3$ and H$_2$SO$_4$ into SO$_2$, and uses molecular fluorescence

for detection, was also tested. The baseline SO$_2$ concentration is measured on one channel, and the "total" SO$_2$ (SO$_2$, SO$_3$ and H$_2$SO$_4$) is measured on the second channel. During the field test, significant values (up to 80 ppm) of total H$_2$SO$_4$/ SO$_3$ were observed at high SO$_2$ concentrations in the first half of the monitoring period (downstream of an SCR).

After a process change. which lowered both the SO$_2$ and subsequent SO$_3$ concentration, the SO$_3$ and H$_2$SO$_4$ concentrations dropped to an undetectable level. Based on the peak to peak noise level at low SO$_2$ levels, the best estimated detection limit would be 4 ppm.

The final measurement approach, which has yielded the best results to date, is an SO$_3$ absorption gas analyzer which utilizes a Quantum Cascade (QC) Laser in conjunction with a multi-pass cell.

The high resolution of the QC Laser allows excellent SO$_3$ detection and optimum selectivity (i.e. minimal SO$_2$ and water interference). The spectral resolution of this approach is one

Figure 1: SO₃ Injection Results

Air Heater Inlet
10%Water, 600 F Flue Gas
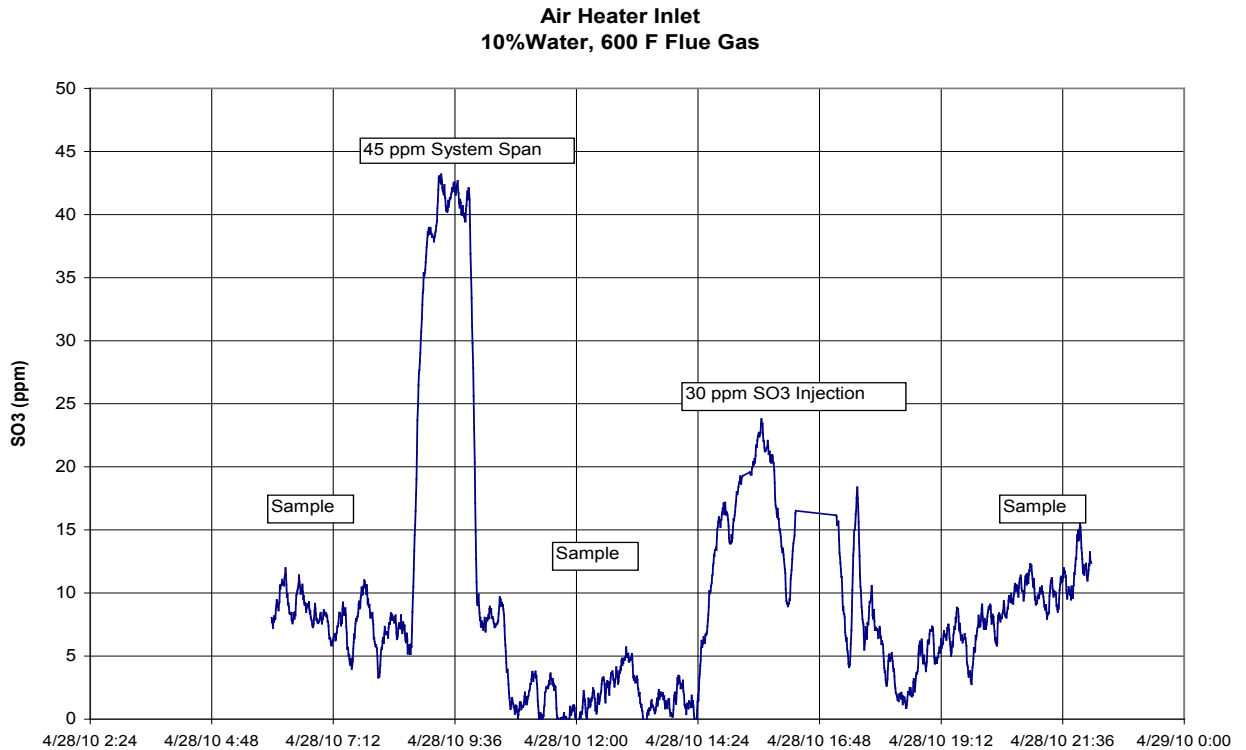
to two orders of magnitude better than the FTIR method. Our target Lower Detection Limit (LDL) for the system is 0.2 ppm. Current lab and field testing puts our detection limit at 1.0 ppm. Modification and improvements to our prototype are underway in order to achieve our target LDL.

SO₃ Generation

The SO₃ generator was used in three separate field campaigns between May 2009 and August 2010. At two of these field tests, we utilized SO₃ injection equipment to introduce a known concentration of SO₃ into the flue gas.

Our system was calibrated using our SO₃ generator which is integrated into our extraction probe. At both locations, the concentration measured by the SO₃ prototype was within 15% of the calculated SO₃ injection (see Figure 1). During these field tests, we focused on the repeatability of the daily calibrations and the response time of upstream SO₃ injection. The next steps include conducting control condensate tests in parallel with our CEMS that are operating in full-scale combustion sources. This will occur both upstream and downstream of

particulate control devices. SO₃ transport/loss issues are minimized or eliminated by having the standard gas generator as close as possible to the sampling point. SO₃ calibration is accomplished by injecting the standard SO₃ from the source generator into the extraction probe (system span). This technique has been developed to generate standard SO₃ concentrations from sub ppm up to hundreds of ppm. The generated SO₃ concentration has been validated by a parallel comparison using an FTIR analyzer to ensure the full conversion of SO₂ into SO₃.

SO₃ Detection

The current prototype of our gas analyzer has been designed to operate at high temperatures and is located within 25 feet of the extraction probe. Application of this device offers a unique approach to detect SO₃ at a system detection limit of 0.15 ppm (2σ) for a one-minute data acquisition rate. We selected a DFB QC laser (from a variety of vendors), which will be operated in a pulse mode, coupled with a low-frequency sweep ramp. The prototype uses a three-stage TE cooled photovoltaic detector.

Figure 2: SO₃ Reference Spectrum (purple), Incoming Spectrum (blue)
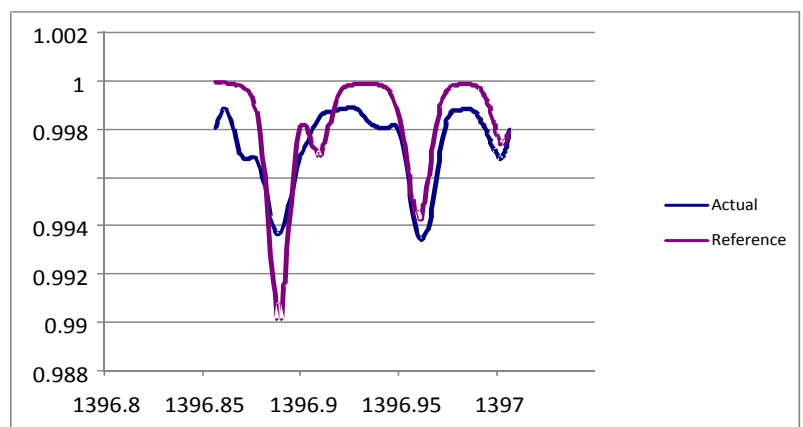
We also integrated a high-temperature optical cell (12.8 m) into the QC Laser analyzer. Figure 2 shows a reference spectrum (calculated) and the incoming spectrum (actual) of a sample for field testing on a full scale, coal fired power plant. The sample pressure is reduced to decrease broadening and resolve fine spectral features. This also facilitates better SO_3 selectivity as any water or SO_2 spectral features are restricted from overlapping with the SO_3 features.

SO_3 Sample Handling

There are a variety of sample handling/measurement configurations for SO_3 such as extraction, cross-duct and in-situ.

At first, it may be apparent that the cross-duct or in-situ measurement methods are better choices because of the reactive nature of SO_3. However, there are significant issues with both approaches. Since many sample locations are upstream of particulate control devices, the ash can foul up the front end of the in-situ device or cause light attenuation issues in cross-duct measurements.

Neither the in-situ nor the cross-duct approach allows us the ability to control the pressure and temperature of the sample.

The duct or stack pressure is close to ambient pressure which causes excessive pressure broadening of the SO_3, SO_2 and water absorption peaks that are in close proximity to each other. This pressure broadening causes interference between SO_3, SO_2 and water. Most sample streams contain SO_2 and water many orders of magnitude higher in concentration than SO_3.
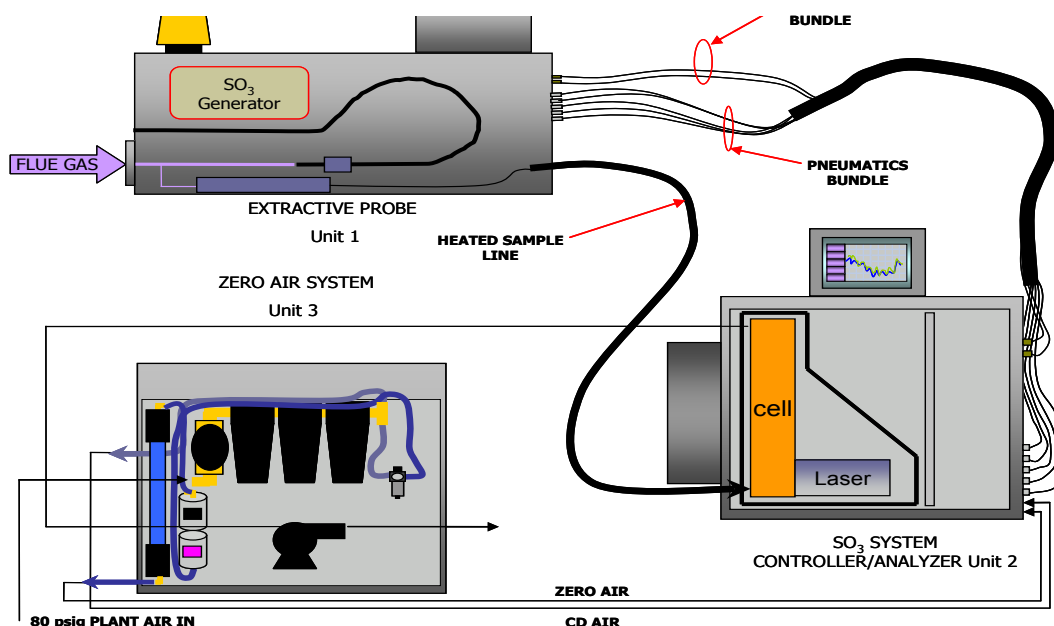
This combination of pressure broadening and interference gases results in a poor SO_3 detection limit. On the other hand, the sample extraction method facilitates control of pressure in order to maximize the sensitivity and selectivity of the SO_3 measurement. There are also known reliability and maintenance issues with the in-situ approach. A system detection limit of at least 0.2 ppm is required to achieve likely industry specifications of 1 to 2 ppm for SO_3 measurement. After evaluating the results and challenges associated with each sampling method, it is believed that our approach of extracting, diluting and controlling the pressure and temperature of the sample will allow us to meet the requirements of the industry.

Summary

Development of the Thermo Scientific SO_3 CEMS will continue through the end of 2010, with prototype designs comprising of an extraction probe, SO_3 calibrator, and a QC Laser Gas analyzer. Field testing of various prototypes has enabled us to identify a suitable detection technology, fine-tune its performance and improve sensitivity. The QC laser system demonstrated highly sensitive SO_3 measurements, with an LDL of 1 ppm. However, system modifications are still needed in order to obtain our target system detection limit of 0.2 ppm. We plan to achieve our goal of developing a reliable and sensitive SO_3 CEMS by evaluating the design on full scale boilers, burning different types of fuel and positioning the system downstream of various control devices.

Figure 3: SO_3 Sampling Handling System

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