Demonstrating Compliance with Sub-ppm Acid Mist Limits: Can EPA Method 8 Handle the Challenge?

Extended Abstract No.

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Abstract

EPA Method 8 for measuring SO_2 and H_2SO_4/SO_3 has been used for years in the utility industry, but was designed and validated for use at sulfuric acid plants. However, the method is increasingly being specified in operating permits to measure very low levels of SO_3 at coal fired power plants and other sources. This paper looks into the capabilities of the method in a typical coal-fired boiler gas stream; focused on the method detection limit (MDL) for Method 8 and several areas where biases arise, especially at low levels of SO_3. Areas that are addressed include: experimentally determined MDL, SO_2 oxidation bias, titration error, analyst bias, and filter bias. A discussion is also included on potential procedures to improve the accuracy of the method at low SO_3 concentrations. All results presented in this paper are preliminary at this time and are subject to further analysis.

Introduction

There is increasing interest in the utility industry as well as other industries in measuring low levels (1 ppm or less) of sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4) in flue gas streams. One of the major factors driving this interest is the widespread installation of selective catalytic reduction (SCR) units for the control of nitrogen oxides (NOx). The catalyst used in SCR systems also catalyzes the formation of SO_3. This increased SO_3 has attracted the attention of regulators for a variety of reasons including its contribution to increased opacity problems (blue plume) from some units and changes in operational parameters in electrostatic precipitators.

In the past, SO_3 emissions have been largely ignored by regulators and permit writers. However, for the reasons stated above, SO_3 emission limits are becoming increasingly common in plant operating permits. Emission limits as low as 0.67 ppm have been noted in recent permits. This creates issues for both sources attempting to determine compliance and for vendors establishing or proving equipment guarantee levels.

As emission limits are pushed ever lower, eventually the issue of method detection limit must be raised. In the case of SO_3, there are two commonly used measurement methods -- EPA Reference Method 8 and various versions of ASTM D3326, better known as “Controlled Condensation”. The results reported in this paper focus on EPA Method 8 since this method has been established as the reference and is commonly required for compliance determination in plant operating permits.

Method 8 was originally developed for and validated on measurement of SO_2 and SO_3 from sulfuric acid plants.[1] The method has never been validated on utility boilers. The stack gas from these two types of facilities is quite different. For example, a coal-fired utility boiler contains various sized particulate matter and significant levels of moisture, while sulfuric acid plants have low levels of particulate and very low levels of moisture since SO_3 is hygroscopic. EPA's collaborative study (Hamil et al.) did not address the issue of detection limits for the method.[1] A detection limit of 0.06 mg/m^3 (0.04 x 10^{-7} lb/ft^3) is stated in the method.[6] This is equivalent to 0.012 ppmv at standard temperature and pressure. However, neither a review of available literature nor a discussion with EPA technical staff revealed the source of this detection limit determination.

The idea of the method detection limit is based on the work of Dr. Lloyd Currie of the National Institute of Science and Technology (NIST).[2] Prior to his work, there existed 8 different operational definitions for detection, all of which yielded different results. In 1968 standard definitions used for method detection were published.[2] Within the work three new hypothetical terms, called the critical value, detection limit, and determination limit were defined. With these definitions, Currie hoped to create a system where measurement methods would be standardized to allow direct comparison to any other reference method testing the same substance.

The procedure for determining method detection limit (MDL) was outlined by Glaser in 1981.[3] The MDL is defined graphically as an error distribution. The definition states that 99% of the trials measured at the MDL must be significantly different than the measured blank level.[3] Glaser attests that detection limits have complications due to changing terms and definitions and the lack of a standard defined procedure. These defined significance levels must be defined by a standard in order to be able to compare results between measurement methods.

The procedure outlined by Glaser was improved by those such as Kirchmer, who pointed out the procedure's lack of a blank level analysis and any way to account for the various test biases.[4] The EPA has since addressed some of these issues, but many of them still remained unresolved.

Experimental Setup

Method Detection Limit Methodology

The United States Environmental Protection Agency (USEPA) defines the method detection limit (MDL), as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than blank response and is determined from analysis of a sample in a given matrix containing the analyte.[5]

A key component of the MDL is estimation. Currie's critical value is dependent on the ability to estimate measurement variability on blank samples. Unfortunately, blank variability sometimes cannot be detected by certain measurement processes and in these cases it becomes necessary to estimate measurement variability at the lowest detectable concentration. This is the principle behind the MDL; provide a procedure for estimating a quantity at the lowest detectable concentration that is related to Currie's critical value.

This study was based on the procedures outlined in the EPA's federal regulations (40 CFR 136), which define the quantities that were mentioned previously; a confidence level of 99% with 6 degrees of freedom constitute significant levels according to the EPA.[5] For example, to determine the MDL of a pollutant, a minimum of seven replicate samples with a concentration near the estimated detection limit are analyzed. The standard deviation is multiplied by the t-distribution for 6 degrees of freedom (3.143). The current study also conducted 7 replicates for the blank level and adding the result to the estimated MDL result to compensate for any doubt in the background concentration. This results in a measured level that was calculated with 99% confidence to be above the average blank measurement.

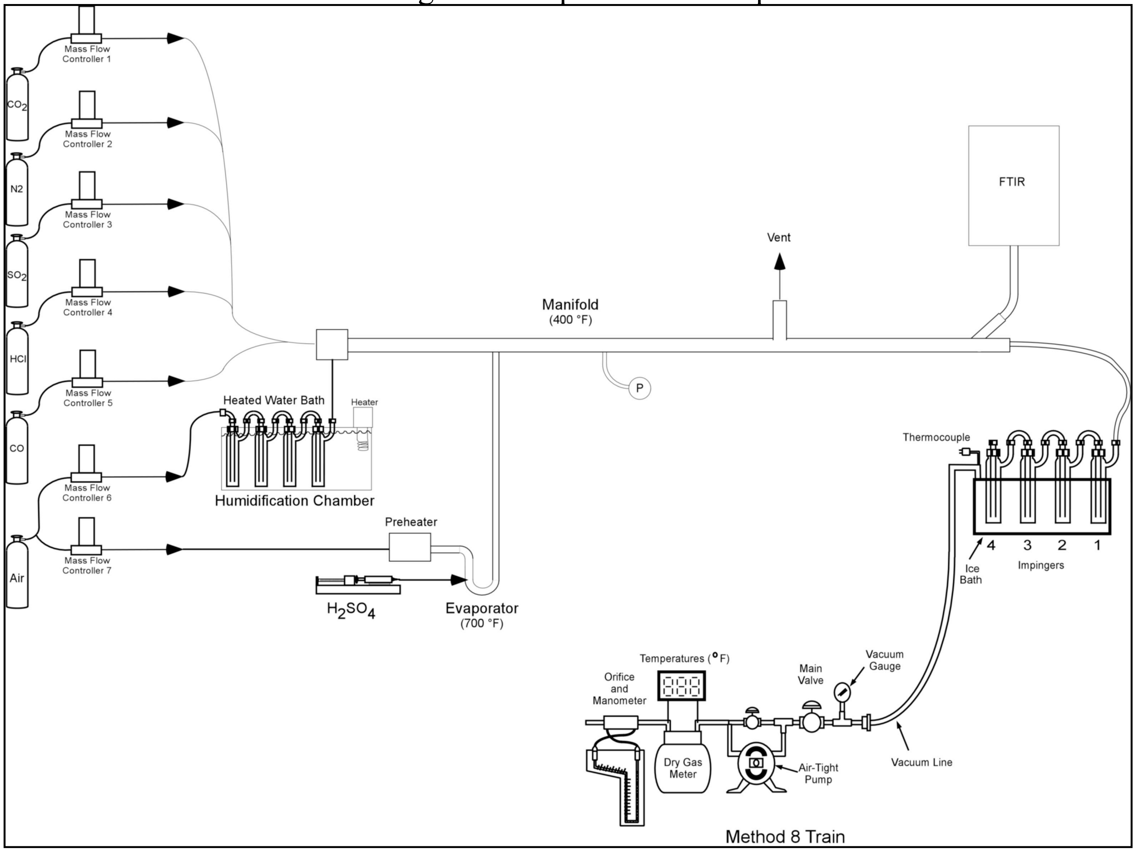
EPA's MDL procedure (40 CFR 136) is focused on outlining the procedures for measuring the MDL in an analytical process and not necessarily for evaluating the process of collecting the sample. For this reason additional precautions were taken during the overall study. These precautions include extra blank runs as mentioned above, fine tuning the SO_3 concentration during the MDL runs, conducting a 2^k factorial analysis for matrix effects, and evaluating the experimental setup and sampling method for a range of accuracy before conducting the final MDL measurements. These additional analyses were conducted to evaluate any bias that was not previously reported.

The experimental setup can be found in Figure 1. The purpose of the setup is to simulate the exhaust gas of a coal-fired boiler by accurately controlling the mass flow rate of all constituents. The setup is comprised of several components: injection ports, Method 8 train, and FTIR spectrometer. The injection ports can further be separated into gas injection and acid injection. Humidification of the gas stream was accomplished via the humidification chamber as seen in the figure. The impingers are located in a heated water bath set to a predetermined temperature. By running a nitrogen or oxygen carrier gas through the water filled impingers the humidity of the sample stream can be controlled. The acid is injected into the system using a calibrated syringe pump and heated evaporator section maintained at 700 ºF. The remaining constituents used in the setup are regulated using an array of mass flow controllers. Table 1 lists the gases used along with the concentration levels.

The analytical systems used for measurement purposes include an EPA Method 8 train and MKS FTIR spectrometer. The FTIR was used in the preliminary stages of the study to evaluate the response to the SO_3/H_2SO_4 signal and compare extractive FTIR analysis to EPA Method 8. The EPA Method 8 train was operated in accordance with 40 CFR part 60 Appendix A.

The EPA method does not have a demonstrated detection limit. While the EPA states that the detection limit of Method 8 for sulfuric acid is 0.06 mg/m^3, this was apparently calculated theoretically.[6] This effectively means that for typical field conditions the limit is unknown. In addition, the last full study conducted on Method 8 was finished in 1974.[1] This further discounts any known detection limit for Method 8. The purpose of this test is to define the true limitations of EPA Method 8 by determing the detection limit under simulated field conditions

Figure 1: Experimental setup



Method 8

Several aspects of the Method 8 train were examined during this experimental study. These include the efficiency at which the solutions absorbed the analytes, the catalytic conversion of the sulfur compounds during sampling, and any biases associated with titration analysis.

USEPA Method 8 is designed to separate and measure sulfuric acid (as sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4)), and sulfur dioxide (SO_2) emissions.[6]

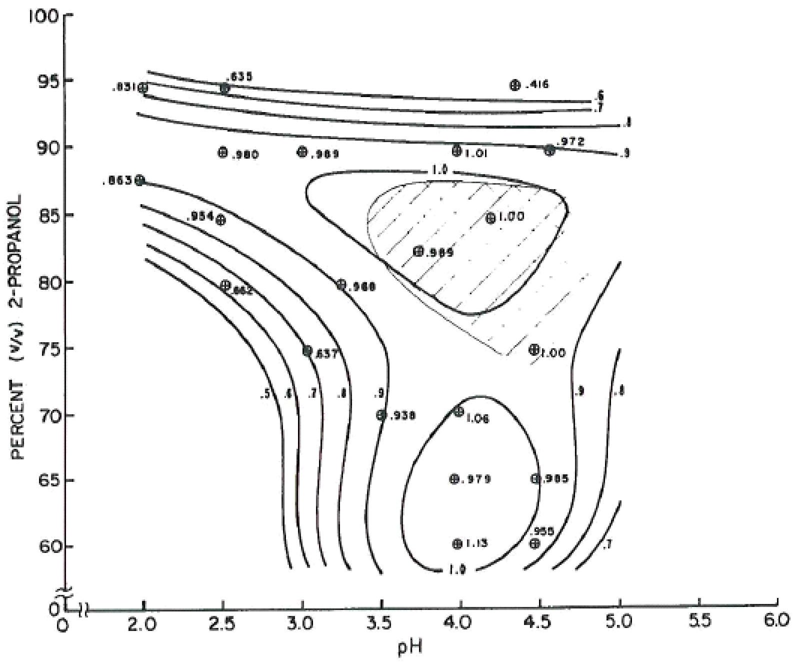
Table 1**:** Concentration values for simulated flue gas used in test matrix

	Low	**High**
H2O	4%	8%
H2SO4/SO3	1 ppm	5 ppm
O2	5%	10%
SO2	10 ppm	100 ppm
CO	Fixed 45 ppm	
CO2	Fixed 10%	
HCL	Fixed 1 ppm	
NOx	Fixed 9 ppm	

The Method 8 sample train begins with a glass probe used to extract samples at an isokinetic rate. Downstream of the probe the sample passes through a series of chilled impingers. The first is an impinger that contains a solution of 80% isopropyl alcohol (IPA) in water and is designed to absorb the sulfuric acid and sulfur trioxide (as sulfuric acid). The sample then passes through a glass fiber filter to capture any entrained acid mist and proceeds into two impingers - connected in series - filled with 3% hydrogen peroxide (H_2O_2). These two impingers are designed to capture the SO_2 in the gas stream. Lastly the sample is directed through an impinger filled with silica gel to remove any remaining moisture. The sample volume is measured using dry gas meter. Once the SO_3 and H_2SO_4 is separated from the SO_2, the samples are analyzed separately via a barium-thorin titration.

Method 8 is currently the only method published by the EPA for measuring sulfur trioxide and sulfuric acid emissions. For this reason, for compliance purposes, the method is often applied to emission sources with conditions for which the method may produce biased or inaccurate results (i.e. high moisture, particulate laden streams). The method was specifically developed for testing emissions from sulfuric acid plants. These emissions are dry and reasonably clean which produce very little interference. However if this method is applied to sources (such as utility boilers) which contain interferences, such as ammonia or moisture, the results can be inaccurate and biased.

Figure 2: Contour plot of titrant indicator efficiency for varying levels of IPA concentration and pH levels (Ref: Haartz et al. *Anal. Chem.*, **1979**, 51, 2293-2295)



Results

Previously Reported Analytical Biases

Haartz et al. have reported endpoint shift for the Barium-Thorin titration method.[7] The sharpness and shift of the endpoint is dependent on the concentration of IPA and the pH of the solution. The endpoint tends to be obscured and delayed for IPA concentrations that are below 70%; e.g. while analyzing a solution with IPA concentration below 70%, the volume of titrant needed to reach the endpoint is greater than the volume required for reaction with the sulfate. This means the titrant is less efficient at reacting with the sulfate at these conditions. Figure 2 shows a contour plot of the reaction efficiencies as a function of IPA concentration and pH. From the figure it can be seen that when pH falls below 3.5 the titration results will suffer unless the IPA concentration is maintained at or above 80%. Method 8 only requires an IPA concentration of 80% so, if any water is added to the impinger, or heat causes evaporation of IPA from the impinger, the concentration will fall below this critical value. For this reason, the concentration of IPA and pH of the Impinger 1 solution was recorded and evaluated during several tests.

Table 2 lists the results of this analysis. The table shows how low the concentration of IPA can get during a test. Even at moisture levels of 5% the IPA concentration can drop to 24%. The efficiencies at these concentration values are not even indicated in Figure 2.

Table 3 compares the concentration measurements between conducting USEPA titration procedures and following procedure outlined by Haartz. For the Haartz method, the solution was diluted with IPA until the concentration was 80%. The table indicates what Haartz et al. had stated: a positive bias for low concentrations of IPA due to larger titrant volumes.

Table 2: Concentration of IPA in solution at different points of testing, compared to moisture concentration in gas steam

	Concentration of IPA			
Moisture	Beginning of run	End of Run	Front half rinse	pH
10%	80%	13%	46%	2.95
5%	80%	24%	55%	3.00

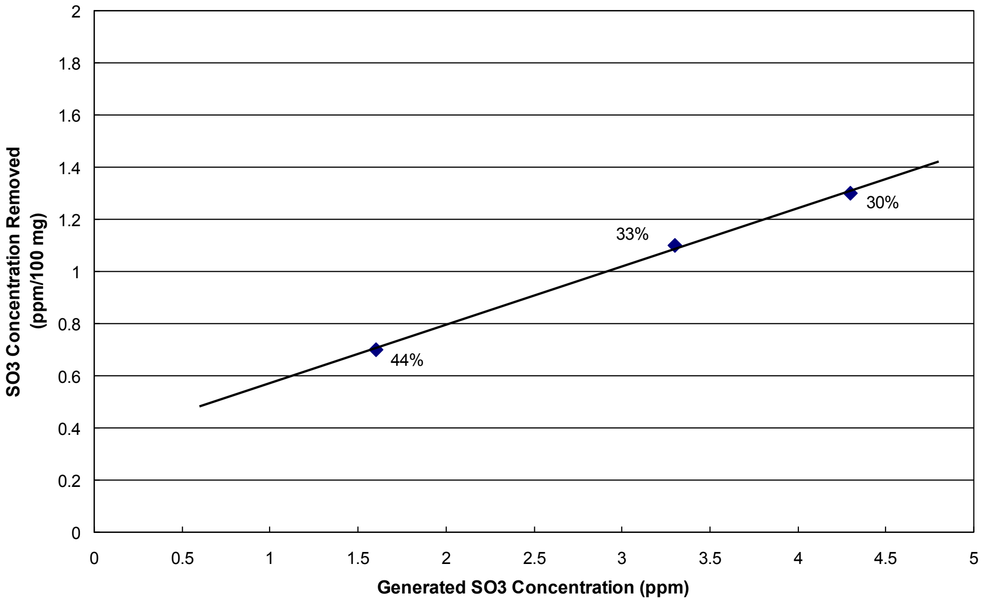
Table 3: Comparison between Method 8 specified titration method and parameters defined by Haartz et al.

Titration Method	Average (ppm)	Recover (%)	Standard Deviation
Method 8	0.49	428%	0.048
Haartz et al.	0.34	297%	0.0243

Although not measured in this study, interaction with particulate matter is also a source of bias in this Method. Daugherty reported a bias in SO_3 measurements due to particulate interaction.[8] Figure 3 shows the experimentally determined SO_3 concentration that was removed by Western Low-Sulfur Fly Ash. The figure indicates at low levels of SO_3 there still exists a large percentage of SO_3 that is adsorbed by the particulate (~50%). This percentage only gets larger as the SO_3 concentration gets smaller. Daugherty also reported that fly ash could be a potential “neutralizing agent” in the IPA impinger, but the effect as a scrubbing agent is much more detrimental.

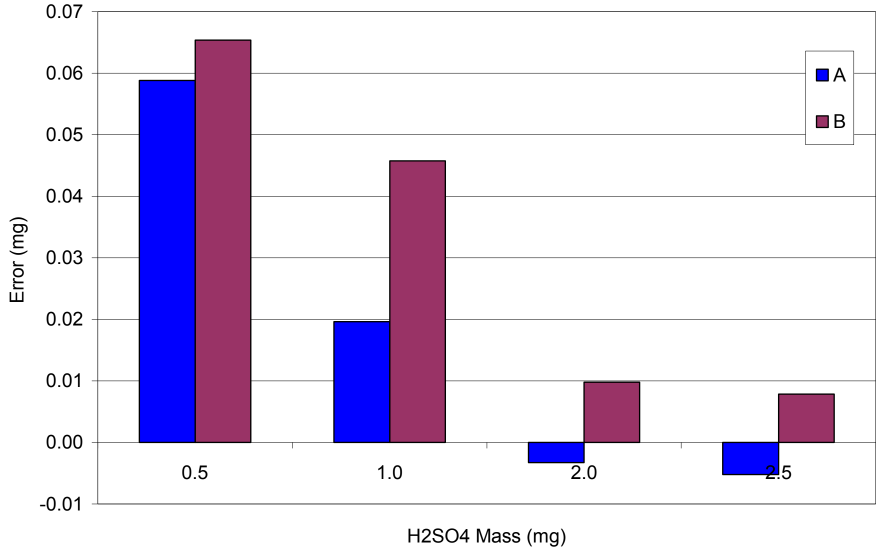
Koebel and Elsener also report a bias associated with SO_3 recovery.[9] The results of the investigation of SO_3 absorption in IPA found that a systematically low measurement of SO_3 can occur. This bias occurs when there is a reaction between SO_3 and IPA, forming esters. This reaction occurs when the temperatures are sufficiently high enough, or the SO_3 concentration is high enough. The existence of water in this reduces the reaction of SO_3 and IPA.

Figure 3: SO3 concentration removed by particulate



With the reporting of biases associated with sulfate recovery in the IPA impinger Clean Air Engineering conducted a study of titration analysis accuracy vs. analyst. The study was conducted using 20 samples containing 5 different concentrations of sulfate. The analysts measured the concentration of each sample separately by following EPA methods and using two aliquots for each sample. Figure 4 shows the results of the study, indicating analyst A conducts measurements with less error than Analyst B. It should be noted that the lowest concentration analyzed in Figure 4 is almost a full order of magnitude greater than the EPA reported detection limit of Method 8. The result indicated in the figure show an error of more than 10% at this concentration. Therefore a sample with a concentration equivalent to the published detection limit would have an analyst error greater than 10%.

Figure 4: Titration accuracy at low concentrations of sulfate



Since ion chromatography (IC) is a commonly used alternative technique for sample analysis for Method 8, a study was conducted comparing the results between using a glass filter and a quartz filter using IC analysis. Table 4 shows the results of the study, indicating a bias when glass filters are used. The borosilicate glass filter contains the interferant sodium, which gives a high biased reading for the sulfate results. This bias was not apparent when analysis was conducted with titration.

There is always a concern when conducting sulfate tests that the SO_2 in the gas stream will be scrubbed out in the IPA impinger due to either the absorption in the solution, the oxidation due to gas stream, or the oxidation due to the post test purge. Due to this concern, an analysis was completed on 8 samples varying the dilution gas, purge gas, and concentration of SO_2 in the dilution gas. All of these runs were accomplished without the addition of SO_3.

Figure 5 shows the results of the analysis. The two windows in the figure separate the test conditions of varying purge gas and dilution gas.

Table 4: Comparison between quartz filter and glass fiber filter IC analysis

	Reagent Blank	Reagent Blank w/ Glass Filter	Reagent Blank w/ Quartz Filter	Preliminary Run	Prelim. Run w/ Glass Filter
as H2SO4 (mg)	0.02	0.91	<0.023	<0.010	0.156
as H2SO4 (ppm)	0.004	0.22	<0.005	<0.002	0.037

The right window indicates the SO_3 concentration is higher for air dilution than for nitrogen dilution, while the right frame does not show an appreciable difference between air or nitrogen purge. This indicates that purging with nitrogen does not have a significant advantage. The SO_2 that is oxidized and captured in the IPA impinger as SO_3 is also seen to have an average concentration of 0.086 mg/dscm (0.026 ppm). This concentration is of the same order of magnitude as the EPA published detection limit and can be considered a significant bias to the system. These results may have been more significant if moisture were included in the carrier gas stream.

Figure 5: SO_3 concentration comparing air and nitrogen effects on SO_2 oxidation when used as purge or dilution gas

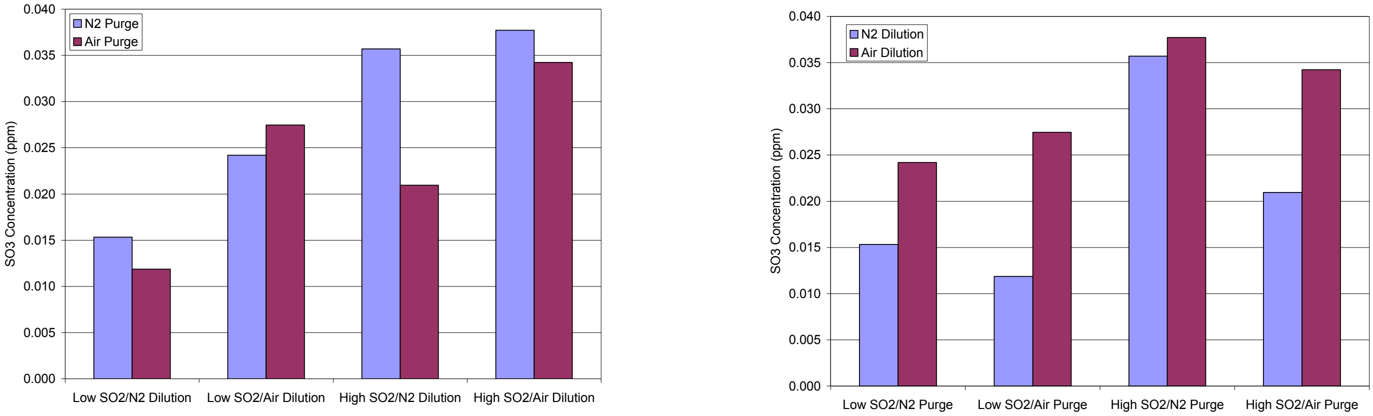
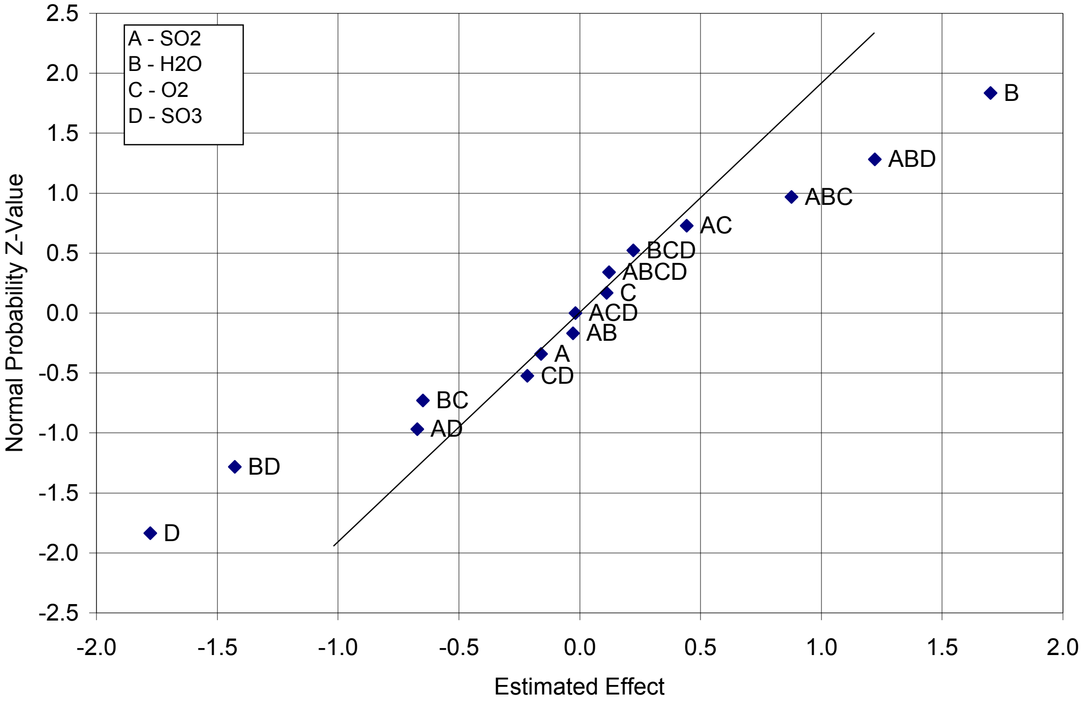


Figure 6: Probability plot of significant effects for 2^4 factorial experiment



Matrix Effects

A Design of Experiments (DOE) study was conducted using the gas matrix listed in Table 1. The objective of the study was to determine the gas constituents that contribute to the greatest bias when using Method 8 to test coal fired boiler exhaust. The gas test matrix was designed to simulate "typical" boiler operations. Figure 6 shows a normal probability plot for the 16 runs conducted in the study. The four variables in the study are listed in the figure. The combined effects are noted in the figure by the data points with multiple letters. Any data points that stray from the "best fit" line can be assumed to stray from a normal distribution. Therefore concentrations of H_2O and SO_3 are apparent to be furthest from the linear trend. Combined effects of these two variables are also seen to stray from the norm in the figure. Because of this trend a second analysis was conducted using 3 variables as opposed to 4, in an analysis of variance (ANOVA) experiment. Table 5 shows the results of this analysis.

The percent contribution shown in Table 5 indicates which factors are significant. The P-value is the quantification of this contribution. A P-value of 0.01 corresponds to a 99% confidence interval of being significant. The table then indicates that H_2O and SO_3 are the significant factors in the matrix. SO_3 has a negative effect, as shown in the table, while H_2O has a positive effect. Therefore, the more moisture there is in the system, the higher the bias due to water, and vice versa for the SO_3 concentration. The H_2O bias could be due to interaction with SO_2 or due to the dilution of the IPA in Impinger 1. The SO_3 bias is potentially due to the interaction between the acid and the experimental apparatus. The authors found that running the acid at low concentrations introduced many problems due to the potential for the acid to adhere to the quartz walls of the flow tube.

Table 5: Analysis of variance for 2^3 factorial experiment

Factor*	Effect Estimate	Sum of Squares	Percent Contribution	Degrees of Freedom	MS	F_o	P-value
A	1.721	11.851	30.811%	1	11.85	32.20	0.0005
B	-1.799	12.942	33.648%	1	12.94	35.16	0.0003
C	0.071	0.020	0.053%	1	0.02	0.06	0.8202
AB	-1.631	10.644	27.673%	1	10.64	28.92	0.0007
AC	0.119	0.056	0.147%	1	0.06	0.15	0.7057
BC	-0.031	0.004	0.010%	1	0.00	0.01	0.9205
ABC	-0.014	0.001	0.002%	1	0.00	0.00	0.9650
Pure Error		2.945	7.7%	8	0.37		
Total		38.46		15	2.56		

* A=H_2O, B=SO_3, C=SO_2

Because very low levels of SO_3 in the experimental apparatus (<0.1 ppm) had the propensity for problems, the final MDL is calculated using a concentration of SO_3 of 0.5 ppm. The average and standard deviation for 7 replicates is found in Table 6. The MDL is calculated by multiplying the t-value (3.146) by the standard deviation, as outlined in 40 CFR part 136 App. B.[5] The average blank concentration is added to the result.

$$MDL = s \times t_{6,99\%} + (\overline{X}_{blank})$$

The MDL for Method 8 in simulated boiler flue gas is therefore estimated to be 0.6 mg/m^3, an order of magnitude greater than published by the EPA.[6] The MDL can be reduced to ~0.3 mg/m^3 if the Haartz titration procedure, outlined previously, is used.

Table 6: Results of MDL calculation

Titration Procedure	Average	Recovery	Standard Deviation, s	MDL	
	(ppm)	(%)	(ppm)	ppm	mg/m^3
Method 8	0.49	428%	0.0480	0.159	0.598
Haartz et al.	0.34	297%	0.0243	0.084	0.317

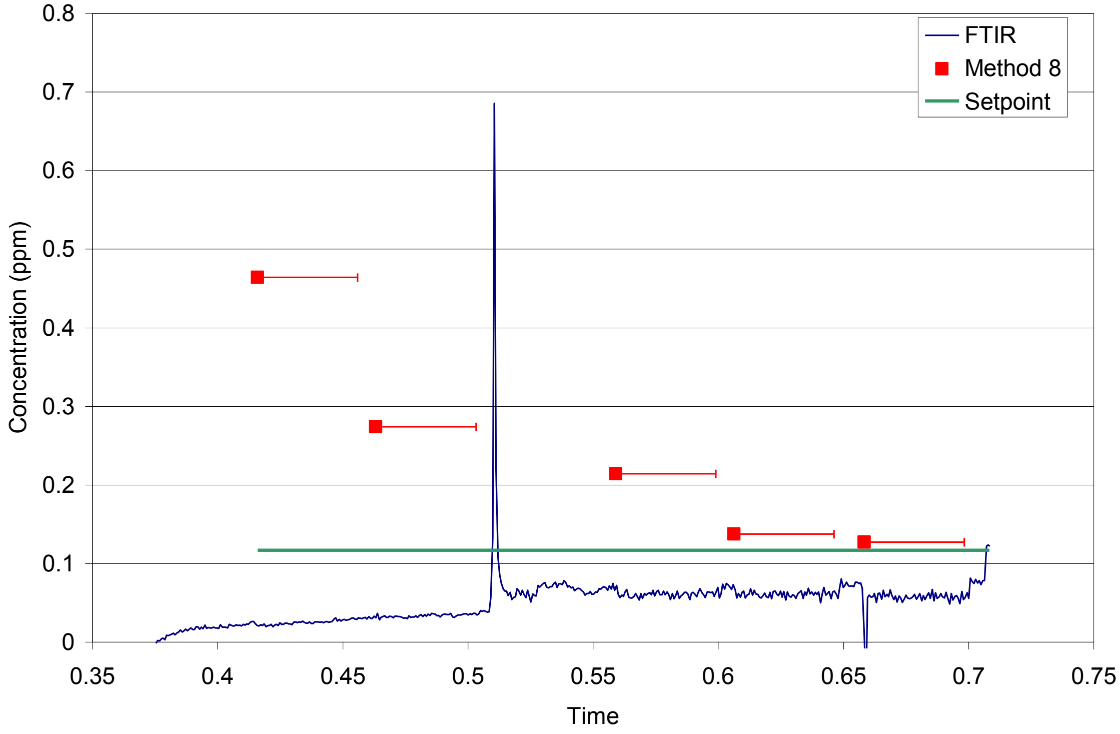
Lastly, Figure 7 shows the results of simultaneously sampling using Method 8 and an extractive FTIR. The acid concentration was set to a level of 0.1 ppm and Method 8 runs were conducted over a period of seven hours. It can be seen from the figure the Method 8 run results have an exponential decay which decreases to the setpoint of the system. This phenomenon happens due to the equilibration of the experimental system. The experimental system is time consuming to operate in this way, it takes ~8 hours of conditioning before a stable sample can be extracted. The FTIR signal in the figure is provided to show how much of the SO_3 signal is lost when extracting the sample gas stream. The sulfur compounds are not stable at the temperatures that the FTIR must operate, much of the sulfate occurs as H_2SO_4 vapor, and some of this is yet aerosol – a phase the FTIR is incapable of detecting accurately. In addition to this, any small change in the system creates great perturbations in the FTIR signal, as seen in the spike in the figure.

Conclusions

EPA Method 8 used for determination of H_2SO_4 and SO_3 in the flue gas was originally developed for testing at sulfuric acid plants, but has been applied to coal fired boiler utility plants. There is no record of any collaborative detection limit study being done at a utility boiler facility. Preliminary results indicate the MDL of USEPA method 8 is approximately 0.6 mg/m^3 under controlled conditions for simulated coal fired boiler exhaust (not including particulate or ammonia). This limit does not take into account any biases, but is based on typical method variability in a controlled environment.

Factors that may bias results include: SO_2 oxidation in the sampling system, analyst errors during titrations, sulfate recovery inefficiencies during sampling, interference in chemical analysis from filter material, and scrubbing of SO_3 by the particulate matter collected on the filter. These biases may all contribute to inaccuracies in the system and many are a function of time, which constrains sampling to the minimum time limit possible, i.e. increasing the sampling duration will not necessarily provide lower detection limits.

Figure 7: H_2SO_4 signal from different measurement methods (corrected to dry conditions)



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