

Method 8 Detection Limit Study

Experimental Design and Implementation Plan

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Statement of Problem

There is increasing interest in the utility industry as well as other industries in measuring low levels (1 ppm or less) of sulfur trioxide (SO₃) and sulfuric acid (H₂SO₄) in flue gas streams¹. One of the major factors driving this interest is the widespread installation of selective catalytic reduction (SCR) units for the control of nitrogen oxides (NO_x). The catalyst used in SCR systems also catalyzes the formation of SO₃. This increased SO₃ has attracted the attention of regulators for a variety of reasons including its contribution to increased opacity problems (blue plume) from some units.

In the past, SO₃ emissions have been largely ignored by regulators and permit writers. However, for the reasons stated above, SO₃ emission limits are becoming increasingly common in plant operating permits. 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 SO₃, there are two commonly used measurement methods -- EPA Reference Method 8 and various flavors of ASTM D3326 better known as "Controlled Condensation". This research project will focus on EPA Method 8 since it has been established as the reference method and is commonly required as the method of compliance determination in plant operating permits.

Method 8 was originally developed for and validated on measurement of SO₂ and SO₃ from sulfuric acid plants (Hamil 1974). The stack gas from these plants is quite distinct from typical stack gas from, say, coal-fired utility boilers in that it is virtually free of particulate and moisture. Hamil's initial collaborative study did not address the issue of detection limits for the method. A detection limit of 0.05 mg/m³ (0.03 x 10⁻⁷ lb/ft³) is stated in the method. 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. Based on experience and engineering judgment, it is believed that the actual detection limit in a coal-fired utility boiler gas matrix is significantly higher by as much as two orders of magnitude.

¹ Virtually all of what is sampled in these methods is H₂SO₄. SO₃ is hygroscopic and therefore absorbs vapor-phase moisture at temperatures higher than its dewpoint, forming H₂SO₄. These reactions take place between 370 and 205 °C (about 700 to 400 °F). For any sampling after, say, an air pre-heater, virtually all the SO₃ will have been converted to H₂SO₄. In addition, manual sampling methods do not measure SO₃ directly but rather cool the gas to below the acid dewpoint where all the SO₃ has been converted to H₂SO₄ liquid aerosol. However, for the sake of simplicity, in this paper, SO₃ will be used generically to refer both to SO₃ and H₂SO₄.

Experimental Objectives

The above discussion raises several questions that we will attempt to answer experimentally. These are:

1. What is the Method Detection Limit (MDL) for Method 8 under “ideal” conditions (i.e. clean, dry air)?
2. What are the matrix effects that significantly impact the MDL?
3. What are the matrix effects that significantly impact the precision or accuracy of the method?

Overview of Experimental Procedure

The questions presented above will be answered with a two-phase experimental design as presented below.

Phase 1 - Determination of MDL under ideal conditions.

EPA defines the Method Detection Limit in 40 CFR 136, Appendix B as follows:

“the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.”

The Appendix then goes on to describe a seven-step procedure to determine the detection limit. However, this procedure is highly specific to water laboratories. We have adapted this procedure as follows to be applicable to a stack gas matrix.

1. Make an estimate of the detection limit based on three times the standard deviation of at least seven replicate blank samples.
2. Prepare a test cell to produce an appropriate volume of sample gas that is as free of the target analyte as possible.
3. Spike the sample gas such that the concentration of the target analyte is within the range of one to three times the estimated detection limit.
4. Conduct at least seven replicate runs processing the spiked sample gas through the entire sampling and analytical procedure.
5. The variance (S^2) and standard deviation (S) of the replicate measurements are determined.
6. The MDL is then determined by multiplying the standard deviation (S) by the Student’s t-statistic at a 99th percentile for n-1 degrees of freedom. If seven replicates are used, the Student’s t-value is 3.143.

- Verify the reasonableness of the MDL by spiking the matrix at the MDL that was determined in Step 6 and analyzing another seven replicates spiked at this level. The experimental F-ratio (S^2_A/S^2_B) of the variances is determined and compared with the appropriate reference F-ratio, which is 3.05. If $S^2_A/S^2_B > 3.05$, the analyst is instructed to respike at the most recently calculated MDL and process the samples through the procedure starting with Step 4. If $S^2_A/S^2_B \leq 3.05$, then the pooled standard deviation is used to calculate the MDL as described in the Calculation section of this document.

Phase 2 - Matrix Effects

Once the MDL is determined, the next phase of the project is to identify and quantify any effect the gas matrix has on measurement at or near the MDL. While the Phase 1 study used clean dry air as the matrix, Phase 2 employs a sample gas that more closely simulates the actual stack gas from a combustion source.

The composition of the gas matrix for Phase 2 includes moisture, SO₂, CO₂(?), CO(?), NO_x(?), and NH₃. In addition, the percent O₂ is a variable. The matrix composition and variables are summarized the in Table 1 below. The balance of the sample gas is nitrogen (N₂).

Table 1
Matrix and Variable Summary

Constituent	Fixed/Var	- value	+ value
O ₂	Var	5%	10%
H ₂ O	Var	5%	10%
CO ₂	Fixed		
CO	Fixed		
NO _x	Fixed		
SO ₂	Var	10 ppm	100 ppm
SO ₃	Var	MDL	3 x MDL
NH ₃	Var	0	5 ppm

This phase consists of two rounds of testing. Each round is designed as a 2^k factorial test. The first phase examines the effects of water and oxygen concentration only. This will be done as a separate phase in order to determine if sulfate contamination of the IPA impinger is occurring in the absence of SO₂.

The three variables, SO₃, H₂O, and O₂ are tested according to the 2³ factorial matrix shown in Table 2. Runs will be randomized. There is a belief that O₂ may not have a significant effect on either MDL or precision and accuracy. If the data from this round support that assumption, O₂ will be removed as a variable in the second round of testing. This would significantly shorten the test cycle for the second round.

This test matrix will be executed twice (i.e. one replicate) to allow for a more robust determination of MDL and method precision.

Table 2
2³ Factorial Testing Matrix for Round 1

Run	SO ₃	H ₂ O	O ₂
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

For each run, SO₃ will be determined according to EPA Method 8 using the titration procedure described in the method. Each sample will also be analyzed by ion chromatography (IC). The “true” concentration of SO₃ will be calculated for each run based on the procedure described in the Calculation section of this document. A percent recovery for SO₃ will be determined for each run. Also, the IPA impinger contents will be analyzed for sulfates.

Round 2 of testing will add SO₂ (and possibly NH₃) to the sample matrix. If O₂ is found not to have a significant effect, it will be held at a fixed value during Round 2.

The four variables, SO₃, H₂O, O₂, and SO₂ are tested according to the 2⁴ factorial matrix shown in Table 3. Runs will be randomized.

Table 3
2⁴ Factorial Testing Matrix for Round 2

Run	SO ₃	H ₂ O	O ₂	SO ₂
1	-	-	-	-
2	+	-	-	-
3	-	+	-	-
4	+	+	-	-
5	-	-	+	-
6	+	-	+	-
7	-	+	+	-
8	+	+	+	-
9	-	-	-	+
10	+	-	-	+
11	-	+	-	+
12	+	+	-	+
13	-	-	+	+
14	+	-	+	+
15	-	+	+	+
16	+	+	+	+

If O₂ is eliminated, either the matrix can be reduced to a 2³ factorial design or NH₃ may be added and it may be retained as a 2⁴ factorial design. This test matrix will not be replicated due to the large number of test runs.

As in Round 1, SO₃ will be determined according to EPA Method 8 using the titration procedure described in the method. Each sample will also be analyzed by ion chromatography (IC). The “true” concentration of SO₃ will be calculated for each run based on the procedure described in the Calculation section of this document. A percent recovery for SO₃ will be determined for each run. Also, the IPA impinger will be analyzed for sulfates.