METHOD 8 – DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

Applicability

This method is applicable to the determination of sulfuric acid (including sulfuric acid mist and sulfur trioxide) and gaseous sulfur dioxide emissions from stationary sources.

Principle

A stack sample is withdrawn isokinetically from the stack. The sulfuric acid mist (including sulfur trioxide) and sulfur dioxide are separated and both fractions are measured separately by barium-thorin titration.

Interferences

Possible interferents are free ammonia, dimethyl aniline and fluorides. If free ammonia is present, alternate procedures must be used (see Special Situations Section).

Based on the above we (appropriate box checked):

_____ Do not expect any interference.

_____ Do expect interference. The description and discussion of the anticipated interference follows.

In–Stack Detection Limits & Sample Times

The minimum detection limit of the method has been determined to be 0.05 mg/m^3 (0.03E-07 lb/ft^3) for H_2SO_4/SO_3 and 1.2 mg/m^3 (0.75E-07 lb/ft^3) for SO_2 for a standard 60-minute sample. Actual in-stack method detection limits (ISDL) are based on actual source sampling parameters and analytical results. Actual detection limits can be improved through increased stack gas sampled (sample time). For this source, the in-stack concentration is:

Allowable(s) = _____ lbs/hr (SO_2), and _____ lbs/hr (H_2SO_4)
Stack flow = _____ dscfm

lb/ft^3 = (lb / hr) / (dscfm x 60) = _____ lb/ft^3 (SO_2), and _____ lbs/hr (H_2SO_4)

Therefore, the sample time will be _____ minutes.

Sample Train & Recovery Components & Supplies

A schematic of the sampling train is shown in Figure 8-1 of the method. Specifically, the sampling train will be constructed with components specified under EPA Method 8, Section 6.0, (similar to a Method 5 train), with the following exceptions and/or highlights.

Sample Train

1) **Probe liner** will be constructed of Borosilicate or quartz glass and heated.
2) **Filter Holder** will be borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials (*e.g.*, Teflon or Viton) may be used, subject to BTS approval. The holder design will provide a positive seal against leakage from the outside or around the filter. The filter holder will be placed between the first and second impingers and be unheated.
3) The **impinger train** will consist of four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Silicone grease may be used if necessary. The first and third impingers must have the standard tips and the second and fourth will be modified to be non-restricted. The first impinger contains 100 ml 80% isopropanol (IPA), 100 ml of 3% H_2O_2 in the second and third impingers and about 200 g of silica gel in the fourth impinger.
4) **Pump** - leak-free diaphragm pump, or equivalent, with a small surge tank between the pump and rate meter.
5) **Dry Gas Meter** (DGM) - sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F).
6) A **nozzle**, **pitot tube**, **differential pressure gauge** and **metering system** as described in Method 5.
7) A Method 8 train may be combined with a particulate matter train (see Special Situations Section).

Sample Recovery

1) **Wash bottles** (glass or polyethylene), two 500 ml.
2) **Storage bottles** (polyethylene), two 1000 ml per sample run.
3) **Graduated cylinders**, 250 ml and 1 liter.
4) **Trip balance** (for moisture determination), accurate to $\pm$0.5 g.

Sampling

Pre-test leak checks and post-test leak checks will be conducted by following the same basic procedure in Method 5, Section 8.4.2 noting that the probe heater will be adjusted to the minimum temperature to prevent condensation and adjusting the temperature upward if condensation is observed.

The sampling train will be assembled as indicated above. Crushed ice and water will be placed around the impingers. The initial DGM reading and barometric pressure will be recorded. Sample isokinetically, following the general procedures given in Method 5, Section 8.5. For each run, the required data should be recorded on a data sheet such as the one shown in Method 5, Figure 5-3. Maintain sampling rate at or below 0.030 m^3/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If condensation does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation.

Post-Test Purge

At the conclusion of an acceptable post leak check, remove the probe and purge the remainder of the sampling train with clean ambient air (optionally passed through a charcoal filter) for 15 minutes at the average sampling rate during the test run.

Sample Recovery

Container No. 1

The first impinger (plus contents) will be cleaned and weighed to the nearest 0.5 g, and the weight recorded for the moisture determination. The contents of the first impinger will be transferred to a 250-ml graduated cylinder. The probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder will be rinsed with 80 percent IPA. The IPA rinse solution will be added to the graduated cylinder. The contents of the graduated cylinder will be diluted to 225 ml with 80 percent IPA, and the cylinder contents transferred to the storage container. The graduated cylinder will be rinsed with 25 ml of 80 percent IPA, and the rinse transferred to the same storage container. The filter will be added to the solution in the storage container and the container will be mixed. The container will be sealed to protect the solution against evaporation. The container will be sealed, the level of liquid on the container will be marked, and the sample container will be identified.

Container No. 2

The second and third impingers (plus contents) will be cleaned and weighed to the nearest 0.5 g, and the weights recorded for moisture determination. Likewise, the spent silica gel (or silica gel plus impinger) will be weighed to the nearest 0.5 g, and the weight recorded for moisture determination. The solutions from the second and third impingers will be transferred to a 1-liter graduated cylinder. All connecting glassware (including back half of filter holder) between the filter and silica gel impinger will be rinsed with water, and this rinse water will be added to the graduated cylinder. The contents of the graduated cylinder will be diluted to 950 ml with water, and the cylinder contents will be transferred to a storage container. The graduated cylinder will be rinsed with 50 ml of water, and the rinse transferred to the storage container. The container will be sealed, the level of liquid on the container will be marked, and the sample container will be identified.

Sample Preparation & Analysis

The level of the fluid in the container will be noted. If significant leakage occurred, either the run will be voided or methods will be used to correct the results, subject to BTS approval.

Container No. 1

The container holding the IPA solution and the filter will be shaken. If the filter breaks up, the fragments will be allowed to settle for a few minutes before removing a sample aliquot. A 100-ml aliquot of this solution will be pipetted into a 250-ml Erlenmeyer flask, 2 to 4 drops of thorin indicator will be added, then titrated to a pink endpoint using 0.0100 N barium standard solution. The titration will be repeated with a second aliquot of sample, and the titration values averaged. Replicate titrations will agree to within 1 percent or 0.2 ml, whichever is greater.

Container No. 2

The solution in the container holding the contents of the second and third impingers will be thoroughly mixed. A 10-ml aliquot of sample will be pipetted into a 250-ml Erlenmeyer flask. 40 ml of 100 percent IPA and 2 to 4 drops of thorin indicator will be added, then titrated to a pink endpoint using 0.0100 N barium standard solution. The titration will be repeated with a second aliquot of sample, and the titration values averaged. Replicate titrations will agree to within 1 percent or 0.2 ml, whichever is greater.

Blanks

Two blanks are required. The first blank will be 100 ml of 80 percent IPA. 2 to 4 drops of thorin indicator will be added, then titrated as indicated above for Container No. 1.

The second blank will be prepared by combining 2 ml of 3% H_2O_2, 8 ml of water and 40 ml of 100 percent IPA. 2 to 4 drops of thorin indicator will be added, then titrated as indicated above for Container No. 2.

Calculations

All calculations will be performed as per Method 8, including blank corrections. Please note that the correct Vsoln values in Section 12.1 of the method should be 1000 ml for SO_2 and 250 ml for H_2SO_4. Detailed sample calculations will be included in the final report.

Emissions will be presented in the following units:
_____.

Audit Samples

If provided, audit samples will be analyzed consistent with Section 11.3 of the method and the results will be provided in the final test report. It is recognized that failure to achieve method acceptance criteria for the audit could result in the requirement to repeat the stack test program

Proposed Deviations from this BTS Template or the Method

(Insert any proposed deviations here)

Special Situations Section – If either of these two situations is relevant, they will be checked in the checkbox located prior to the procedure.

(_) 1. **Alternative Procedures for Method 8 when Ammonia is Present**:

Sampling Procedures
SOx must be determined using Method 8, utilizing the sampling procedures specified in Section 16.3.1 of Method 6, which are as follows:

The probe will be maintained at 275°C (527°F) and equipped with a high-efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material will be unreactive to SO_2. Whatman 934AH (formerly Reeve Angel 934AH) filters treated as described in Reference 10 in Section 17.0 of Method 5 is an example of a filter that has been shown to work. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter will be heated above the moisture dew point but below 225°C (437°F)."

Procedure for analysis of Container #1
Same as described above.

Procedure for analysis of Container #2
The SO_2 analysis of Container #2 is analyzed per Section 11.2.2 of Method 8 (including replicate titrations), except add 0.5 ml of 0.1N HCl prior to adding the indicator.

The SO_2 concentration determined from Container # 1 is summed with the SO_2 concentration from Container #2 to determine the total SO_2 concentration.

(_) 2. **Combining the Method 8 train with the Particulate Matter Sampling Train:**

EPA Method 8 allows for determination of particulate in conjunction with SO_x. However, if these procedures are followed the H_2SO_4 mist does not get measured as part of the SO_x.

To address these concerns, the following procedures should be employed.

SAMPLE TRAIN

1. A heated glass fiber filter is added to the Method 8 sampling train between the probe and the IPA impinger. This filter is maintained at the temperature specified by NJATM1 and is in addition to (not a replacement for) the filter between the 1st and 2nd impingers called for in Method 8.

2. The impingers are as described in Method 8.

3. Moisture determination must be made by weight, not volume. The impingers (plus absorbing solutions) and the weight of the silica gel (or silica gel plus container) must be weighed to the nearest 0.5 g and recorded prior to testing. These items are weighed again at the end of the test to determine the moisture content, prior to sample recovery.

SAMPLE RECOVERY

1. The heated filter is recovered per NJATM1 (CONTAINER 1).

2. The probe nozzle, fitting, liner and front half of filter holder are recovered with acetone into a container (CONTAINER 2), per NJATM1.

3. The above components are then recovered with IPA into a container, with the contents of the first impinger and impinger rinses per Method 8 (CONTAINER 3). The remaining sample recovery continues per Method 8 (CONTAINER 2 from Method 8 becomes CONTAINER 4).

4. The post-test 15 minute purge (after a successful leak check) is conducted after removal of the probe AND the heated particulate filter assembly, through the rest of the sample train.

ANALYSIS

1. The filter and acetone probe wash are analyzed for particulate per NJATM1.

2. The acetone residue is solubilized with the IPA wash (CONTAINER 2). The particulate filter is then added to this container. Analysis for SO_x continues per Method 8.