Source Test Method **ST-20**

SULFUR DIOXIDE, SULFUR TRIOXIDE, SULFURIC ACID MIST

(Adopted January 20, 1982)

REF: Regulations 6-320, 6-330, 9-1-302,
9-1-304 thru 310, 10-1-301, 12-6-301

1. APPLICABILITY

1.1 This method is used to quantify emissions of sulfur dioxide, sulfur trioxide and sulfuric acid mist. It determines compliance with Regulations 6-320 and 6-330 for SULFUR TRIOXIDE and SULFURIC ACID MIST, and 9-1-302, 9-1-304 thru 310 and 10-1-301 and 12-6-301 for SULFUR DIOXIDE.

1.2 This method, modified with a glass fiber disc filter as the back-up SO_3 filter, has been given alternate status by the EPA to EPA Method 8. It may be used to determine compliance with oxides of sulfur regulations under Regulation 9.

2. PRINCIPLE

2.1 Sulfuric acid mist, sulfur trioxide and sulfur dioxide are collected in a single extractive sampling train. Acid mist is trapped in a quartz wool plug in the sample probe and is subsequently analyzed with an acid-base titration. Sulfur trioxide is absorbed in an 80% isopropyl alcohol (IPA)/water solution with a quartz wool back-up filter and is analyzed using analytical procedure Lab-12. Sulfur dioxide is absorbed in an aqueous hydrogen peroxide solution and is analyzed using analytical procedure Lab-12.

3. RANGE

3.1 The minimum measurable concentration using this method listed below are:

      3.1.1 Acid mist - 0.0002 gr/ft^3 as H_2SO_4

      3.1.2 Sulfur trioxide - 7 ppm

      3.1.3 Sulfur dioxide - 7 ppm

3.2 The maximum measurable concentrations using this method listed below are:

      3.2.1 Acid mist - undetermined

      3.2.2 Sulfur trioxide - 350 ppm

      3.2.3 Sulfur dioxide - 2.5 %

4. INTERFERENCES

4.1 Acid mist and sulfur dioxide. The presence of strong acids or salts such as hydrochloric acid or sodium bisulfite give erroneously high results. The presence of alkaline gases or reactive basic solids such as ammonia or calcium oxide give erroneously low results.

4.2   Sulfur Trioxide. Sulfur dioxide at 2000 ppm or over may oxidize to sulfur trioxide in the IPA/H_2O solution. for this reason, two IPA/H_2O impingers are used in series. The sample concentration of SO_3 as indicated by the second impinger is regarded as a blank analysis and is subtracted from the analysis of the first impinger.

5.   APPARATUS

5.1   Probe. Use a borosilicate glass probe long enough to extend across the stack diameter. If stack temperatures exceed 800 ^{O}F, use a quartz probe. The probe entrance shall be enlarged to approximately 20 mm I.D. for a length of 10 cm. The downstream end should be fitted with a 90 ^{O} elbow and a ball joint. The probe shall be heat-traced and insulated if necessary to prevent sample condensation.

5.2   Acid mist filter. Insert approximately 3 grams of quartz wool in the probe entrance.

5.3   Absorbers. Use four Greenberg-Smith impingers, one with the inlet fitted with a ball joint to receive the probe.

5.4   Filter. Approximately 10 grams of quartz or quartz wool are packed into a glass holder of the same specifications as the filter holders used in ST-15.

5.5   Cooling system. An ice bath is used to contain the impingers.

5.6   Sample Pump. Use a leak-free vacuum pump capable of at least 0.5 CFM flow rate at 15 inches of mercury-vacuum. The pump has a flow control valve and vacuum gauge attached to the inlet.

5.7   Silica gel tube. Use approximately 500 cc of silica gel (with a Drierite indicator) to insure that the gas entering the dry test meter is dry.

5.8   Dry test meter. Use a dry gas test meter accurate within $\pm$2% of the true volume and equipped with a thermometer to measure the outlet temperature.

5.9   Connections. Use Teflon tubing in making all connection that come in contact with the sample. Vinyl tubing is acceptable for all other connections.

5.10   Barometer. Use a barometer that is accurate to within $\pm$0.2 inches of mercury.

5.11   Rotameter. use a calibrated rotameter to measure the sampling rate.

6.   REAGENTS

6.1   Isopropanol, 80%. Prepare an 80% by volume solution of isopropanol (IPA) in distilled water. Check the solution for contamination using Analytical Procedure Lab-10.

6.2   Hydrogen peroxide, 3%. Prepare a 3% by volume solution of hydrogen peroxide in distilled water.

7.   PRE-TEST PROCEDURES

7.1   Add 100 ml of the 80% IPA to each of the first two impingers.

7.2 Add 100 ml of the hydrogen peroxide solution to each of the second two impingers.

7.3 Stopper the impingers.

7.4 Retain 100 ml of each solution to analyze as a blank.

7.5 Assemble the sampling train as shown in Figure 20-1.

7.6 If condensation is expected, heat trace the sample line.

7.7 Leak-test the sampling train by starting the pump, plugging the probe, and adjusting the pump inlet vacuum to 10 inches Hg. The leak rate must not exceed 0.02 CFM through the dry test meter. Before stopping the pump, carefully release the plug in the sample probe to avoid backflow of the impinger solution.

7.8 Record the initial dry test meter reading and barometric pressure on a data sheet as shown in Form 20-1.

Figure 20-1

Sulfur Oxide and Acid Mist Sampling Train
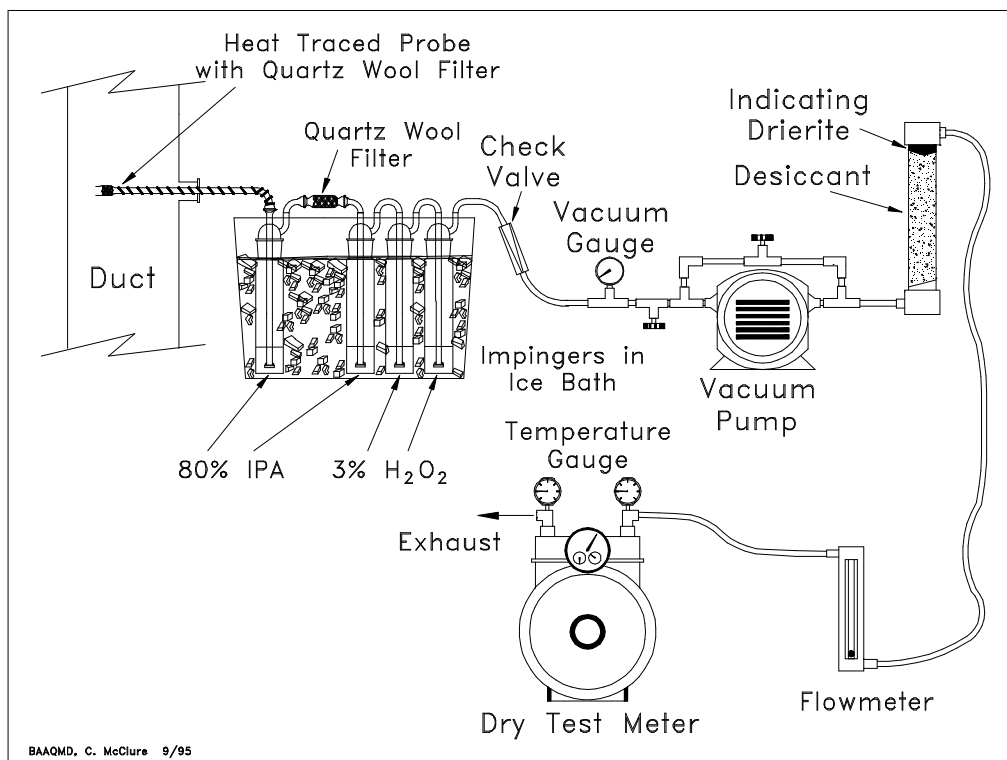
8. SAMPLING

8.1 Sample at continuous operations for a period of thirty minutes for each test run. Sample at batch processes for a period of thirty minutes or 90% of batch process time, whichever is less.

8.2 Position the probe at the sampling point and start the pump.

8.3   Sample at a constant rate of 14.3 liter/min (0.5 CFM) during the test as determined by the rotameter.

8.4   Record the following information at five-minute intervals on Form 20-1:

> Dry Test Meter Temperature
> Impinger Outlet Temperature
> Dry Test Meter Reading

8.5   Check the sample probe periodically for condensate.   If condensation occurs, stop the test until the problem is rectified.

8.6   Add ice as necessary to maintain the temperature exiting the last impinger at $7^{\text{o}}C$ ($45^{\text{o}}F$) or less.

8.7   At the conclusion of each run, stop the pump, remove the probe from the stack, and record the final meter volume.

8.8   Take three consecutive samples.

9.   POST-TEST PROCEDURES

9.1   Immediately after sampling, purge the impinger train with ten cubic feet of SO_2-free ambient air at a rate of 0.5 CFM.

9.2   Keep the two IPA solutions on ice and stoppered until they are analyzed.

9.3   Analyze the IPA solution within 24 hours after sampling.

9.4   Individually analyze each train for acid mist, sulfur trioxide, and sulfur dioxide using Analytical Procedure Lab-12.

10.   AUXILIARY TESTS

10.1   Stack velocity.   Determine the stack gas velocity after each run in accordance with ST-17.

10.2   Moisture Content. Determine the moisture in the stack gases in accordance with ST-23.

10.3   Production Rate. Determine the sulfuric acid or sulfur production from plant data based on a 24 hour, daily production rate in tons per day, if the test is being conducted on a sulfur recovery plant.

10.4   Oxygen Concentration. Use ST-14 to determine the oxygen concentration of the stack gas.

11.   CALCULATIONS

11.1   The standard sample volume:

$$V_o = \frac{17.71 V_m P_b}{T_m}$$

Where:

V_o =   Standard dry sample volume, SDCF @ $70^{\text{o}}F$ and 29.92 inches Hg

Vm = Actual Metered Volume, ft^3

Pb = Barometric Pressure, Inches Hg

Tm = Average Meter Temperature, ^{O}R

17.71 = Constant correcting to $70^{O}F$ and 29.92 inches Hg

11.2   Acid mist concentration:

$$C_{H_2SO_4} = \frac{15.4W}{V_o}$$

Where:

$C_{H_2SO_4}$ = Concentration of acid mist, grains/SDCF

W = Weight of acid on the probe filter, grams

15.4 = Correction from grams to grains

11.3   Sulfur trioxide concentration, as sulfuric acid:

$$C_{SO_3}(\text{impinger \#1}) = \frac{15.4W_1}{V_o}$$

$$C_{SO_3}(\text{impinger \#2}) = \frac{15.4W_2}{V_o}$$

$$C_{SO_3}(\text{filter}) = \frac{15.4W_F}{V_o}$$

Where:

W_1 = Weight of SO_3 (as H_2SO_4) in impinger #1.

W_2 = Weight of SO_3 (as H_2SO_4) in impinger #2.

W_F = Weight of SO_3 (as H_2SO_4) in the filter.

11.4   Total sulfur trioxide content of the sample:

$$C_{SO_3} = C_{SO_3}(\text{impinger \#1}) - C_{SO_3}(\text{impinger \#2}) + C_{SO_3}(\text{filter})$$

Where:

C_{SO_3} = Concentration of SO_3, as H_2SO_4, grains/SDCF

11.5   Total of acid mist and sulfur trioxide concentration:

$$C_{H_2SO_4}(\text{total}) = C_{H_2SO_4} + C_{SO_3}$$

11.6   The concentration of sulfur dioxide:

$$C_{SO_2} = \frac{1.33 \times 10^4 \, W}{V_o}$$

Where:

C_{SO_2} = Concentration of SO_2, ppm (dry)

W = Total impinger catch of SO_2 for each run, grams.

1.33×10^4　=　A constant derived from the molar volume and molecular weight of SO_2.

11.7　The total sample concentration of sulfur dioxide:

$$C_{SO_2} = C_{SO_2}(\text{impinger \#3}) + C_{SO_2}(\text{impinger \#4})$$

11.8　Mass emission rate of SO_2:

$$M_{SO_2} = K C_{SO_2} Q_o$$

Where:

M_{SO_2}　=　Mass emission rate of SO_2 kg/hr (lb/hr)

Q_o　=　Stack gas flow rate $SDM^3/min (SDFT^3/min)$

K　=　$9.92 \times 10^{-6} \dfrac{lb}{ppm - ft^3 - hr}$　for English units

　=　$1.59 \times 10^{-4} \dfrac{kg}{ppm - m^3 - hr}$　for Metric units

11.9　Mass emissions based on production rate:

$$M_{tp} = \frac{M_{SO_2}}{M_d}$$

Where:

M_{tp}　=　Mass emission per ton of product, $\dfrac{Kg}{\text{metric ton}}\left(\dfrac{lbs}{\text{short ton}}\right)$

M_{SO_2}　=　Mass emission rate of SO_2, $\dfrac{Kg}{hr}\left(\dfrac{lbs}{hr}\right)$

M_d　=　Production Rate per hour (based on up to 48 hour average)

11.10　Oxygen correction factor:

$$F = \frac{20.95 - X_{O_2}}{20.95 - P_{O_2}}$$

Where:

F　=　Oxygen correction factor

X_{O_2}　=　Oxygen concentration to be corrected to; 0% for Sulfur Recovery Plants and 12% for Sulfuric Acid Plants

P_{O_2}　=　Oxygen content present in stack gas.

11.11　SO_2 concentration corrected for oxygen content:

$$C_{SO_2}F = F \times C_{SO_2}$$

Where:

$C_{SO_2}F$ =　SO_2 concentration corrected for oxygen content.

12.   REPORTING

12.1   Report the data indicated on Form 20-2.

Plant # _____

Source I.D. _____

Sample Type _____

Process Cycle _____

Duct Size _____

Duct Shape _____

Duct Pressure _____

Assumed %H_2O _____

Bay Area Air Quality Management District
939 Ellis Street, San Francisco, CA 94109

Form 20-1
Source Test Data Sheet

Run # _____

Temp Meter # _____

Mag. Gauge # _____

Date: _____

Box ΔH@ _____

Meter (Y) _____

Nozzle Diameter _____

Pitot Tube I.D., Cp _____

Gas System _____

Pbar, Barometer _____

Leak Test Rate _____

Time @ Point _____

# of Points _____

Time/Run (Min.) _____

Sampling Train: Probe # _____ Filter # _____ Imp. # _____ Imp. # _____ Pump/Box # _____

Initial Traverse Data					Sampling Data									
Trav. Point I.D.	Dist. from Wall	Duct Temp. ^{0}F	ΔP "H_2O	Angle of Flow	Traverse Point I.D.	ΔP "H_2O	Duct Temp. ^{0}F	Vs FPS	Time (minutes)	Meter Rate CFH	Meter Temp. ^{0}F	Meter Volume Ft^3	Train Vacuum "Hg	Sat'd Gas Temp. ^{0}F

Post Run Impinger Catch (ml) = _____

Assumed O_2 = _____

Assumed CO_2 = _____

Post Run Calculated %H_2O = _____

Source Test Team

_____

_____

_____

Comments:

_____

_____

_____

ST-20-8

Form 20-2

<table>
<tr><td rowspan="2">Distribution:

Firm
Permit Services
Enforcement Services
Technical Services
Planning
Requester
DAPCO</td><td>BAY AREA
AIR QUALITY MANAGEMENT DISTRICT
<i>939 Ellis Street
San Francisco, California 94109
(415) 771-6000</i>

Summary of
Source Test Results</td><td>Report No.: _____

Test Date: _____

Test Times:

Run A: _____

Run B: _____

Run C: _____</td></tr>
</table>

Source Information		**BAAQMD Representatives**
Firm Name and Address	Firm Representative and Title Phone No. ( )	Source Test Engineers
Permit Conditions:	Source: Plant No. Permit No. Operates	Permit Services Division/Enforcement Division Test Requested By:
Operating Parameters:		
Applicable Regulations:		**VN Recommended:**

Source Test Results and Comments:

<u>METHOD</u>	<u>TEST</u>	<u>RUN A</u>	<u>RUN B</u>	<u>RUN C</u>	<u>AVERAGE</u>	<u>LIMIT</u>
ST-17	Stack Volume Flowrate, SDCFM					
	Stack Gas Temperature, ^{0}F					
ST-23	Water Content, Volume %					
ST-14	Oxygen, Volume %					
ST-5	Carbon Dioxide, Volume %					
ST-6	Carbon Monoxide, ppmv					
	Carbon Monoxide, lb/hr					
ST-20	Sulfur dioxide, ppmv					
	Sulfur dioxide, lb/hr					
	Sulfur trioxide, as acid, gr/SDCF					
	Sulfuric acid mist, gr/SDCF					
	Total acid, gr/SDCF					
	SO_2, lbs/ton product					

Air Quality Engineer II Date	Supervising Air Quality Engineer Date	Approved by Air Quality Engineering Manager