

Source Test Procedure ST-21

TOTAL REDUCED SULFUR

REF: Regulations 12-1-301 thru 303

1. APPLICABILITY

- 1.1 This method is used to quantify emissions of total reduced sulfur compounds (TRS) as H₂S, in the presence of sulfur dioxide. It determines compliance with Regulations 12-1-301, 12-1-302 and 12-1-303.

2. PRINCIPLE

- 2.1 A continuous representative gas sample is extracted from the sampling point and conditioned to remove water and particulate material. A small portion of the conditioned sample is passed through a potassium citrate/citric acid buffer solution to remove sulfur dioxide and then through a combustion tube to oxidize all reduced sulfur to sulfur dioxide. The sulfur dioxide is measured with an ultraviolet analyzer.

3. RANGE AND SENSITIVITY

- 3.1 The minimum measurable concentration of reduced sulfur, as H₂S, is 5 ppm with this method.
- 3.2 The maximum concentration of reduced sulfur is 5000 ppm.
- 3.3 The method has been proven in the presence of up to 3500 ppm sulfur dioxide.
- 3.4 The analyzer sensitivity is +/-2% of the instrument scale.

4. INTERFERENCES

- 4.1 None are known.

5. APPARATUS

- 5.1 Analyzer. Use an E.I. DuPont de Nemours Photometric analyzer Model 400 equipped with a stainless steel sample cell or its equivalent to determine SO₂ concentrations.
- 5.2 Chart Recorder. The recorder monitors and records the continuous output from the analyzer.
- 5.3 Sample conditioning, zero air, and span gas system. The assembly of this system is shown in Figure IV-68. The sample conditioning system provides a dry, particulate free gas flow to the instrument. The zero air system provides clean dry atmospheric air for instrument calibration. The span gas system provides a known concentration of SO₂ for use in calibrating the analyzer. Except as specified, all materials which come in contact with either the sample or span gases must be constructed of Teflon or stainless steel.
- 5.4 Sample Probe. Use a borosilicate glass tube long enough to traverse the stack being tested. If the stack temperature exceeds 425 °C (800 °F), use a quartz probe. Other probes are acceptable subject to approval by the Source Test Section.

- 5.5 Condensers. Use modified Greenberg-Smith impingers with the impaction plates removed and the inlet tube shortened to a length of 10 cm (4 inches), or equivalent.
- 5.6 Cooling System. Immerse the impingers in an ice bath during the test.
- 5.7 Particulate Filter. Use a Balston type 95 holder with a grade B filter, or equivalent, in the sample system.
- 5.8 Pumps. Use leak-free, Teflon-lined, diaphragm pumps in the sample and zero air systems. The pumps must have a free-flow capacity of at least 40 liters/min (1.5 CFM).
- 5.9 Back-pressure Regulator. Use a back-pressure regulator to maintain the sample and zero gas sample pressures to the instrument at five psig.
- 5.10 Gas Scrubber. Use a bed of silica gel, Ascarite (or soda-lime), and charcoal to remove moisture, carbon dioxide, and hydrocarbons from the zero air system.
- 5.11 Span Gas. Use high-pressure cylinder containing a known concentration of SO₂ in nitrogen. The span gas concentration must be in the same range as the source being tested.
- 5.12 Combustor. Use a system to oxidize all reduced sulfur compounds in the sample stream to SO₂. An example of an acceptable combustion tube found adequate by the BAAQMD is shown in Figures IV-69 and IV-70.
- 5.13 Sulfur Dioxide Scrubber. Use three midget impingers containing the scrubbing reagent.
- 5.14 Filter. Use a Balston type 95 holder with a grade B filter following the combustion tube to remove SO₃ and particulate from the effluent.

6. REAGENTS

- 6.1 Potassium Citrate/Citric Acid Buffer. Add 300 grams of potassium citrate and 41.0 grams of citric acid to one liter of distilled water. Check the pH of the solution and adjust as necessary to 5.6 with the appropriate reagents.

7. PRE-TEST PROCEDURES

- 7.1 Warm-up the instrument according to manufacturer's instructions.
- 7.2 Assemble the sampling system as shown in Figure IV-71.
- 7.3 Leak-test the sampling system by starting the pump, plugging the probe, and checking that the pressure to the analyzer falls to zero.
- 7.4 Introduce zero air, into the analyzer and zero the instrument according to manufacturer's instructions.
- 7.5 Introduce span gas into the analyzer and calibrate the instrument according to manufacturer's instructions.
- 7.6 Conduct a preliminary concentration traverse (in accordance with ST-18) to determine if stratification of the stack gases exists. If the concentration of reduced sulfur compounds at any point differs from the average concentration by more than 10%, traverse the stack during the test. If not, sample at any single point.
- 7.7 Prepare the chart recorder according to manufacturer's instructions.
- 7.8 Add approximately 25 ml of the citrate buffer reagent to each of two midget impingers.

- 7.9 Check the scrubber efficiency when the stack SO₂ concentration exceeds 300ppm. Pass SO₂ span gas in the range expected through the sample system at a flow rate of 2 CFH. Breakthrough should not occur in less than 20 minutes. If breakthrough occurs, add 25ml more of the citrate buffer reagent.

8. SAMPLING

- 8.1 Each test run shall be of thirty minute duration when testing from continuous operations. Each test run at a batch operation shall be for 90% of the batch time or thirty minutes, whichever is less.
- 8.2 Introduce sample gas into the analyzer at the same flow rate used to calibrate the analyzer.
- 8.3 Maintain ice in the cooling system throughout the test.
- 8.4 Calibrate the analyzer before and after each test run. Record each step of the process clearly on the chart recording.
- 8.5 Conduct three test runs.
- 8.6 Periodically pass SO₂ span gas through the scrubber and ascertain that the analyzer reads zero. If it doesn't, replace the buffer reagent.

9. AUXILIARY TESTS

- 9.1 Stack flow rate. Determine the stack gas flow rate after each test run in accordance with ST-17.
- 9.2 Moisture. Determine the stack gas moisture content in accordance with ST-23.

10. CALCULATIONS

- 10.1 From the chart recording determine the time-averaged concentration of TRS on a dry basis for each run.
- 10.2 The mass emission rate of TRS, as H₂S, at kraft pulp mills:

$$W = \frac{5.27 \times 10^{-6} C_{RS} Q_{ot}}{T}$$

Where:

- W = Mass emissions of reduced sulfur, as H₂S, in lbs per ton of pulp produced.
- C_{RS} = Time- averaged concentration of reduced sulfur, as H₂S, pp,
- Q_o = Stack flow rate, SDCFM
- t = Time of pulp produced/day, hrs/day
- T = Tons of pulp produced/day
- 5.27 x 10⁻⁶ = Constant based on the above units, standard conditions and molecular weight.

11. REPORTING

- 11.1 The results are reported as shown Figure IV-72.