

METHOD 10

DETERMINATION OF SULFUR IN FUEL OIL

REF: Reg. 9-1-304
10-2-501.2

1. PRINCIPLE

The fuel oil sample is oxidized by combustion in a Schöninger Oxygen Combustion Flask. The sulfur dioxide formed during the combustion is absorbed in a dilute solution of sodium hydroxide containing hydrogen peroxide. The sodium hydroxide solution is then filtered and the formed sulfate is determined turbidimetrically as barium sulfate.

2. APPARATUS

- 2.1 Schöninger Oxygen Combustion Flask, 1 liter, available from A. Thomas Co., Philadelphia, PA.
- 2.2 Filter paper carrier for (2.1), available from A. Thomas Co., Philadelphia, PA.
- 2.3 Special filter paper for (2.2), available from A. Thomas Co., Philadelphia, PA.
- 2.4 Special screw clamp to attach (2.2) to (2.1), available from A. Thomas Co., Philadelphia, PA.
- 2.5 Safety Oxygen Flask Igniter, Thomas-Ogg Model 11, available from A. Thomas Co., Philadelphia, PA.
- 2.6 Spectrophotometer.
- 2.7 Analytical Balance.
- 2.8 25 ml Graduated Test Tubes

3. REAGENTS

- 3.1 Cylinder Oxygen. U.S.P. Grade.
- 3.2 Sodium Hydroxide (0.05 N). Dissolve 2 g of sodium hydroxide in distilled water and dilute to 1 liter.
- 3.3 30% Hydrogen Peroxide

- 3.4 HCl (6 N). Dilute concentrated hydrochloric acid 1:1 with distilled water.
- 3.5 Sulfa Ver IV Pillows, Cat. #12065-00. Available from Hach Chemical Co., Ames, Iowa.

4. ANALYTICAL PROCEDURE

- 4.1 Place 20 ml of 0.05 N NaOH and 5 drops of 30% H₂O₂ in the Schöninger Oxygen Combustion Flask.
- 4.2 Weigh a sample of fuel oil directly onto a tared special filter paper, adding the oil dropwise from a capillary pipette. Record the weight of the oil. The weight of the sample required depends on the sulfur content of the fuel oil. As a general guide, for samples containing 5 to 10% sulfur, a 10 to 15 mg sample is taken; for 2 to 5% sulfur, 15 to 30 mg; for 0.5 to 2% sulfur, 30 to 40 mg; for 0.1 to 0.5% sulfur, 40 to 50 mg; for samples containing less than 0.1%, 60 to 70 mg. The maximum weight of oil which may be taken is in the 60 to 70 mg range using a one liter combustion flask. Larger weights will result in incomplete combustion, evidenced by soot formation during the burning of the sample.
- 4.3 Fold the filter paper containing the fuel oil sample and attach it to the filter paper carrier (2.2).
- 4.4 The Schöninger flask is then thoroughly flushed with oxygen.
- 4.5 Quickly insert the filter paper carrier in the combustion flask and attach the screw clamp and tighten. Place the flask in the safety igniter and position so that the filter paper will be in line with the infra-red beam. Push igniter button until the filter paper ignites.
- 4.6 After combustion is complete, allow the sample to stand 10 to 15 minutes to permit complete absorption of sulfur dioxide and then shake vigorously. If combustion is incomplete (large amount of soot formed) sample must be re-run.
- 4.7 Filter, if necessary, and pipette a 10 ml aliquot of the filtrate into a 25 ml graduated test tube.
- 4.8 Make up volume to 19 ml with distilled water. Add 1 ml of 6 N HCl and the contents of a Sulfa Ver IV pillow.
- 4.9 Cover the test tube with parafilm and invert several times to mix thoroughly and dissolve the reagent.
- 4.10 Read after 10 minutes at 500 nm using 25 mm cuvettes. Determine the μgm sulfate in the aliquot from the standard curve prepared in Section 5.

4.11 Run a blank and standards with each sample.

5. STANDARD CURVE

- 5.1 Standard Stock Sulfate Solution. Weigh and transfer 0.1480 g of dry sodium sulfate to a 1 liter flask. Dissolve and dilute to mark with distilled water. This solution contains 100 microgram of sulfate per ml.
- 5.2 Prepare a standard curve from the 100 µgm/ml standard sulfate solution by pipetting respectively 0, 2, 4, 6, 8 and 10 ml into a series of 25 ml graduated test tubes.
- 5.3 Make up to 19 ml with distilled water. Add 1 ml 6 N hydrochloric acid and the contents of a Sulfa Ver IV pillow.
- 5.4 Cover the test tube with parafilm and invert several times to mix.
- 5.5 Read after 10 minutes at 500 nm using 25 mm cuvettes. Plot % transmittance vs. concentration on semi-log graph paper. The standard curve is non-linear in the 0 to 400 micrograms range.

6. CALCULATION

$$\text{Total mg Sulfur} = \frac{(\mu\text{gm from Std Curve}) (20 \text{ ml}) (32)}{(1000) (\text{ml aliquot}) (96)}$$

Where: 32 = the mol. wt. of sulfur
96 = the mol. wt. of sulfate

$$\% \text{ Sulfur} = \frac{\text{Total mg Sulfur} \times 100}{\text{Wt. of Sample (mg)}}$$

7. REFERENCE

- 7.1 Levaggi, D.A., Feldstein, M., "A Rapid Method for the Determination of Sulfur in Fuel Oil by the Schöninger Flask Method," J. Air Poll. Cont. Assoc. 13, 380, 1963.6.