

Gravimetric Analysis of Total Sulfur

1. Scope:

This procedure is to be used for the analysis of total sulfur in solid (dry) fertilizers that contain elemental sulfur.

2. Principle:

Inorganic dry fertilizers may contain sulfur in both elemental (S) and sulfate (SO₄) forms. The sample is dissolved in hydrochloric acid (HCl) and the elemental S is leached from the insoluble residue with carbon disulfide. The amount of sulfur is calculated based on the weight lost. The sulfate in the HCl filtrate is precipitated with 10% barium chloride and gravimetrically determined as barium sulfate. Both forms of sulfur are converted to %sulfur and added together. Samples are prepared as described in RA-SP-SMPL-PREP.

3. Safety:

The SDS for all chemicals shall be read before performing any part of this method. Gloves, safety glasses, and a lab coat shall be worn when handling hazardous materials and reagents.

Hydrochloric acid is highly corrosive and toxic when inhaled. Use in a fume hood.

Use barium chloride in a fume hood and avoid breathing vapors.

Carbon disulfide is highly flammable and toxic. Use in a fume hood and avoid heat and electrical sparks when using.

4. Equipment, Reagents, and Supplies (equivalents are acceptable):

- 4.1 Drying oven, °105 C
- 4.2 Analytical balance
- 4.3 Beaker, 400 mL
- 4.4 Erlenmeyer flask, 125mL
- 4.5 Hot plate or steam bath
- 4.6 Vacuum flask / pump
- 4.7 Gooch crucible
- 4.8 Glass fiber filter paper (GF/F) (Fisher Sci cat# 1825-024)
- 4.9 Whatman #42 filter paper (Fisher Sci cat# 1002-110)
- 4.10 Hydrochloric acid, concentrated (Fisher Sci cat# A144C-212)
- 4.11 Barium chloride (Fisher Sci cat# B34-500)
- 4.12 Carbon disulfide (Fisher Sci cat# C184-500)
- 4.13 Acetone
- 4.14 Elemental sulfur

5. Reagent Preparation:

- 5.1 Prepare 10% barium chloride solution by adding 100g BaCl₂ to a 1000mL volumetric flask and filling to the line with DI water. Filter through Whatman #42 paper.
- 5.2 Prepare 1L of elemental sulfur saturated acetone by filling a 1000mL volumetric flask with acetone then, while stirring, adding elemental sulfur until elemental sulfur collects as a powder at the bottom of the flask and no more will go into solution.

6. Sample Analysis:

See section 7 for sulfur coated urea samples and sulfur formulations > 4%.

- 6.1 Fit a clean Gooch crucible with GF/F paper and dry at 105°C for at least 1 hour. Cool in desiccator and weigh (W_{c1}).
- 6.2 Weigh 0.5g ± 0.001g of sample into a 400mL beaker. Record the weight (W_s).
- 6.3 Add 200mL DI water then 15mL HCl. Cover with a watch glass and boil gently for ~10 minutes on a hot plate.
- 6.4 Filter the solution into a flask with vacuum through the Gooch crucible.
- 6.5 Rinse the beaker and the sides of the crucible with hot water. Pour beaker rinseate through the filter. Repeat as needed until all material is washed onto the filter (the beaker may need to be thoroughly cleaned with a brush then rinsed onto the filter). Set the crucible aside for elemental sulfur analysis (step 6.14).

Sulfate Analysis:

- 6.6 Quantitatively transfer the filtrate back to the original beaker. Cover the beaker with a watch glass and bring nearly to a boil on a hot plate.
- 6.7 Add ~15mL of the 10% BaCl₂ solution dropwise until the solution is well-clouded then slowly add the rest. BaSO₄ forms as the precipitate.
- 6.8 Digest at low temperature (not boiling) for 1 hour.
- 6.9 Let stand ~3 hours or overnight at room temperature to cool.
- 6.10 Fit a clean Gooch crucible with GF/F paper and dry at 105°C for at least 1 hour. Cool in desiccator and weigh (W_{c2}).
- 6.11 Filter the cooled solution into a flask through the crucible using vacuum.
- 6.12 Wash the beaker with hot water and pour rinseate through the filter. Repeat until all the precipitate has been washed out of the beaker.

6.13 Dry the crucible for at least 2 hours at 105°C. Cool in desiccator and weigh (W_{CB})

Elemental Sulfur:

6.14 Wash the crucible that was set aside in step 6.4 with five 10mL portions of sulfur saturated acetone.

6.15 Dry crucible for ~1 hour at 105°C. Cool in desiccator and weigh (W_{C3})

6.16 Place the crucible in a beaker or glass weighing bottle and fill 75% full with carbon disulfide (CS_2). Cover and let stand 1 hour.

6.17 Filter with suction and wash with three 10mL portions of CS_2 .

6.18 Dry crucible for ~1 hour at 105°C. Cool in desiccator and weigh (W_{CE}).

7. Sample Analysis for Sulfur Coated Urea or Elemental Sulfur Formulations (4-100%)

7.1 Fit a clean Gooch crucible with GF/F paper and weigh.

7.2 Weigh 0.5g ± 0.001g sample into 125mL Erlenmeyer flask. Record the weight.

7.3 Add 50mL water to the flask, stopper, and shake vigorously for ~1 minute.

7.4 Filter quantitatively with suction through the crucible.

7.5 Proceed with steps 6.14 – 6.18.

8. Calculations:

$$\% \text{ Sulfur from } SO_4 = \frac{(W_{CB} - W_{C2}) * 0.1374}{W_S}$$

$$\% \text{ Elemental Sulfur} = \frac{(W_{C3} - W_{C1}) * (W_{CE} - W_{C1})}{W_S}$$

$$\% \text{ Total Sulfur} = \% \text{ Sulfur from } SO_4 + \% \text{ Elemental Sulfur}$$

Where (all weights are in grams):

W_{C1} = Weight of crucible from step 6.1

W_S = Weight of sample from step 6.2

W_{C2} = Weight of crucible from step 6.10

W_{CB} = Weight of crucible with $BaSO_4$ precipitate from step 6.13

W_{C3} = Weight of crucible from step 6.15

W_{CE} = Weight of crucible with elemental sulfur from step 6.18

$$0.1374 = \frac{\text{Molecular mass of sulfur}}{\text{Molecular mass of } BaSO_4} = \frac{32.065}{233.38}$$

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9. References:

Official Methods of Analysis of AOAC, 14th ed., 1984, 2.183

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