22102	***Quality System Procedure*** **[Office of the Texas State Chemist]**	**Issue Date:**	**Rev.:** *2*
Title: **Sulfur in Fertilizers by Gravimetric Analysis AOAC 980.02**			**Page #:** ***1 of 10***

CONTROLLED DOCUMENT

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Purpose

Sulfate sulfur and elemental sulfur are determined separately using gravimetric methods. The results are combined and reported as total sulfur (%S).

The sulfate sulfur analysis is a gravimetric method in which the sulfate is precipitated as barium sulfate by the addition of 10% barium chloride. Reaction of Ba^{2+} with SO_4^{2-} in acid produces the very insoluble precipitate of barium sulfate which is weighed. The mechanism of precipitation involves the formation of three dimensional particles which grow to a macro size. For liquid fertilizers hydrogen peroxide is used to oxidize sulfur to sulfate prior to the precipitation step.

In the elemental sulfur analyses, sulfur-saturated acetone removes all organics that could be rinsed by carbon disulfide without removing sulfur. Carbon disulfide is then used to dissolve and remove elemental sulfur, leaving behind only the insoluble sample residue. The percent free sulfur is calculated using the difference in weights.

Scope / Field of Application

This procedure is appropriate for the analyses of fertilizers for total sulfur

Definitions and Acronyms

NA

Responsibilities

Technicians -prepare and analyze samples following SOP, enter data into Nautilus, prepare and submit reports.
Managers -review and authorize results, ensure SOP and QA procedures are followed.

Materials Required

REAGENTS, SOLUTIONS AND CONTROLS:

All reagents are analytical grade or higher unless otherwise indicated. All acid used is trace metal grade. All water used for solutions is OTSC R.O. water unless otherwise noted.
Refer to the ICN database for information about manufacturers and stock numbers for the reagents and standards used in this protocol. Refer to MSDSs for warnings and hazards for each reagent and standard.

Disposal of Reagents, Solutions and Controls:

Any bulk reagent needing to be disposed of must be identified with a "hazardous waste disposal" tag, and a request must be processed for it to be picked up by Environmental Health and Safety personnel.

The control material is considered as non-hazardous. It may go into the dumpster along with the lab's other non-hazardous waste.

Dispose of waste carbon disulfide filtrate by pouring into labeled waste bottles in room 126. Once a waste bottle is filled it should be tagged and processed the same as unused bulk reagents (see above).

Dispose of all unused sulfur saturated acetone and waste sulfur saturated acetone filtrate in organic waste barrel in room 122.

Unused 10% barium chloride solution may be poured down the sink with running water.

Reagents List:

Barium Chloride Dihydrate ($BaCl_2 \cdot 2H_2O$)

Carbon Disulfide (CS_2)

Hydrochloric Acid (HCl) 12 N –concentrated

Hydrogen Peroxide (H_2O_2) 30% -use manufacturer's expiration date.

Sodium Hydroxide (NaOH) 50%

Sulfur (S) elemental

Water (H_2O) reverse osmosis.

Acetone (C_3H_6O)

Solutions List:

Free sulfur saturated acetone solution: Add 2,000 mL of acetone to approximately 20 g of elemental sulfur. Invert at least 10 times to mix. Filter undissolved sulfur using Whatman #934 filter paper.

10% Barium Chloride (w/v): Accurately weigh 117.3xxx g $BaCl_2 \cdot 2H_2O$ and dissolve in 1 liter of water.

Controls List:

Dry Sulfur Control: Commercial fertilizer, ground and mixed at OTSC, 12.0% total sulfur guarantee. (2 bottles)

Liquid Sulfur Control: Commercial fertilizer, 12-0-0-26, ammonium thiosulfate, prepared April, 2005 by SMW, 23.4% sulfur guarantee (3 bottles)

Free Sulfur Control: Commercial fertilizer, Scott's ProTurf NPK, turf fertilizer, ground and mixed at OTSC, 5.7 % free sulfur guarantee. (4 bottles)

EQUIPMENT:

Analytical balance, readability to 0.0001 g

Beakers, glass, ranging from 100 mL to 400 mL

Boiling chips, inert carbon

Brinkman Dosimat with 15 mL burette (or equivalent) for dispensing $BaCl_2$

Desiccators with color indicating silica gel desiccant

Erlenmeyer Flasks, 125 mL

Glass dome vacuum filtration device

Buchner Funnel, 3.5 in.

Rubber crucible holders with glass stems for use with glass dome vacuum device

Glass fiber filter paper, Whatman #934-AH or equivalent, 2.4 cm

Glass fiber filter paper, Whatman #934 -AH or equivalent, 70 mm

Glass stirring rods

Ceramic Gooch Crucibles

Graduated Cylinders, 15 mL

Hotplates

Oven, 250° ± 5.0° C

Oven, 100-105° C

Plastic transfer pipettes, for weighing liquids

Pump dispensers, capable of dispensing 5 mL, 50 mL, and 100 mL

Squeeze bottles

Vacuum apparatus with Gooch crucible holders (Aspirator)

Vacuum flask, 1000 mL, with Buchner funnel

Watch glasses

Water bath

Timers

Procedure

INTERFERENCES AND TROUBLESHOOTING

Interferences and Troubleshooting of Sulfate Sulfur Analyses

1.Surface Adsorption: The lattice ion, $Ba^{2+}$is the primary adsorbed ion, but some others like NO_2^- and Cl^- may also be adsorbed. Because of primary adsorption the surface of the precipitate will have a plus or minus charge, depending on whether the lattice cation or anion is in excess. To balance this charge, ions of opposite charge are attracted; these are counter ions. The counter ion layer is diffuse and contains other cations and anions. The counter ion is mostly adsorbed by a precipitate, which has the highest charge. Among ions of like charge, the counter ion is usually that which forms the least soluble compound. Digestion after addition of barium chloride reduces amount of surface area and makes it denser, thereby reducing adsorption. Thorough rinsing of precipitate also helps reduce amount of surface adsorption.

2. Occlusion: This is a type of co-precipitation in which impurities are trapped within a growing crystal. During the precipitation, sulfate is in excess and a positive ion, K^+ or Na^+, is adsorbed as a counter ion. As more reagent is added, Ba^{2+} replaces those adsorbed cations, and the growth of

particles continues. If the particles grow too fast, not all the cations will be replaced by Ba^{2+} and will be enclosed within. Again digestion aids in reducing the amount of occlusion but washing has no effect.

3.The 15 mL of 10% $BaCl_2$ contains about 7.2 mmol of $BaCl_2$, and no more than ~7.2 mmol of sulfur can be precipitated with this amount of $BaCl_2$. Results that are approximately double the guarantee (i.e. 2% for a 1% guarantee, 4% for a 2% guarantee, etc.) may be low due to the exhaustion of the $BaCl_2$ titrant. If [Wt(g)*Result(%)*10]/32 approaches the limit of 7.2 mmol, then the P1 result should be reassigned and the sample reanalyzed adjusting the sample weight accordingly.

4. With liquid samples, age and strength of hydrogen peroxide can cause low results. Always use hydrogen peroxide before manufacturer's expiration date. Always keep refrigerated.

5. To prevent loss of sample due to erratic boiling, add a boiling chip to each one before bringing to a full boil. (Step 2 of "Sample Preparation for Determination of Sulfate Sulfur in Dry Fertilizer" section and Step 1 of "Determination of Sulfate in Liquid and Dry Fertilizers" section)

Interferences and Troubleshooting of Free Sulfur Analyses

1. If the acetone is not previously saturated with S, low results may be obtained.

2. Low results also occur if inadequate amounts of CS_2 are used on high guarantee samples. Thorough rinsing is required.

3. If after thoroughly rinsing high guarantee samples with CS_2, elemental sulfur still is not completely removed, the product may be a micro prill sulfur sample. During the manufacture of this product, all of the elemental sulfur does not change to S_8 or rhombic sulfur. Up to 10% of it can remain as polymeric sulfur. If a sulfur residue remains after the carbon disulfide wash, heat the remaining residual to 100° C for three hours, allow it to cool to ambient and then repeat steps 7 through 10 of the "Determination of Free Sulfur". This extra heating step will allow the remaining sulfur to convert to rhombic sulfur, and the carbon disulfide will then extract the rest of the sulfur.

SAMPLE PREPARATION

Sample Preparation for Determination of Sulfate Sulfur in Liquid Fertilizer (see note below)

NOTE: Two liquid sulfur controls are weighed and analyzed for sulfur content along with the samples in each liquid sulfur set. The placement of the controls within the set is determined by Nautilus. They should be treated the same as the liquid samples during each step of the preparation and determination processes.

1. Accurately weigh sample according to Table 1 (Appendix) into a 400 mL beaker.

2. Add 50 mL water, 2 mL 50% NaOH and 2 mL 30% H_2O_2.

3. Cover with a watch glass and reflux for 1 hour using a low hotplate setting, (~200° C) adding 1 mL of H_2O_2 every 15 minutes. Samples should not boil during the 1 hour period, but they should effervesce with the H_2O_2 reaction. Add no more than five, 1 mL additions of H_2O_2.

4. After 1 hour, rinse off each watch glass, add 100 mL of water and acidify with 5 mL concentrated HCl. Proceed to section "Determination"

Sample Preparation for Determination of Sulfate Sulfur in Dry Fertilizer.

NOTE: Two dry sulfur controls are weighed and analyzed for sulfur content along with the samples in each dry sulfur set. The placement of the controls within the set is determined by Nautilus. They should be treated the same as the dry samples during each step of the preparation and determination processes.

1. Accurately weigh sample according to Table 1 (Appendix) into a 400 mL beaker.

2. Add 150 mL water and one boiling chip.

3. Note any presence of elemental ("free") sulfur at this time. If yellow flakes of free sulfur are observed floating on surface after the addition of water to the beakers, then the sample must also be analyzed for free sulfur. In this case, once the sulfate sulfur content is determined for the sample, proceed with the method for determination of free sulfur for the sample. (Below)

4. Add 15 mL concentrated HCl to each sample. Place all samples on hotplate(s), cover with watch glasses, and heat to the boiling point. Time boil for 10 minutes.

5. Using the glass dome vacuum filtrator fitted with Buchner funnel and glass fiber paper, filter each sample as follows: Pour the sample through the filter, and then rinse the beaker out into the filter with hot (~100° C) water. Rinse the surface of the filter with the hot water. Discard each glass fiber paper and rinse out the Buchner funnel well with the hot water between each sample filtration to avoid cross contamination. Proceed to "Determination" section

DETERMINATION

Determination of Sulfate in Liquid and Dry Fertilizers

1. Place one boiling chip in each beaker, cover with watch glass, and bring back to a boil.

2. Once each sample has begun boiling, it should be removed from the hotplate as quickly as possible. Quickly remove boiling chip from beaker and rinse off into beaker with hot (~100° C)

water. Using the Dosimat, quickly add 15 mL of 10% $BaCl_2$ while vigorously agitating with stirring rod. Place beaker in heated water bath (> 90° C) immediately following addition of $BaCl_2$.

3. Heat for 1 hour using the timer connected to the water bath, and then allow to stand in water bath overnight. Leave stirring rod in the beaker overnight.

4. Place Gooch crucibles containing 2.4 cm filter papers in the 250° C oven to dry at least one hr.

5. When crucibles have dried at least 1 hr. transfer them to desiccators to cool. Time the cooling for 1 hr. 15 min.

6. Boil water for rinsing samples during filtration step later.

7. After crucibles have cooled for 1 hr. 15 min. weigh each crucible, and record weights

8. Arrange crucibles in order on aspirator.

9. Remove each beaker containing precipitate from water bath, and arrange in front of aspirator adjacent appropriate crucible.

10. Apply vacuum, and filter entire contents of each beaker through respective crucible. Rinse each beaker thoroughly with hot water (~100° C), making sure all precipitate is transferred to crucible.

11. Wash down the sides of the crucibles, and thoroughly rinse precipitate in each with 10 portions (~15 mL) of hot water (~100° C).

12. Dry at 250 ± 5° C for 1 hour, cool in desiccator for 1 hr. 15 min. and weigh.

13. Record weights.

Determination of Elemental (Free) Sulfur in Fertilizers

NOTE: Two free sulfur controls are weighed and analyzed for free sulfur content along with the samples in each free sulfur set. They should be treated the same as the samples during each step of the determination processes.

1. Weigh an amount of sample containing ~250 mg (0.25 g) elemental S into 125 mL Erlenmeyer flask. To estimate the weight of sample needed, assume the sulfur guarantee is correct and subtract the known amount of sulfate sulfur derived from above sulfate analysis. This yields percent elemental sulfur from which sample weight can be figured. For example, if the guarantee is 18% sulfur and you find 8% sulfate sulfur, then assume the sample has 10% free sulfur (0.10 percentage factor). Therefore you weigh out 2.5xxx g (0.25 g / 0.10). EXCEPTION: It is neither necessary nor practical to weigh out more than 10g of sample for the elemental sulfur analysis.

2. Add 50 mL water and swirl vigorously for 30 seconds.

3. Filter through a Gooch crucible containing 2.4 cm glass fiber paper. Rinse Erlenmeyer flask thoroughly with water making sure all sample is transferred.

4. Wash down sides of each crucible, and rinse precipitate 4 times with water

5. Transfer each crucible to glass dome filtration device, and wash with five 10 mL portions of free sulfur saturated acetone.

6. Dry 1 hour at 100-105° C, cool in a desiccator for 1 hr. 15 min. and weigh. Record weights

7. In a hood, within a spark-proof room with a vacuum filtration device, rinse each crucible with four 15 mL portions CS_2.

8. Dry crucibles 1 hour at 100-105° C.

9. Cool crucibles in a desiccator for 1 hour 15 min.

10. Weigh crucibles. Record weights.

CALCULATIONS

Percent Sulfate Sulfur Calculation

%Sulfate Sulfur = [(CRWT2 - CRWT1) * 0.1374 * 100%] / SMPWT

where: CRWT2 = weight (g) of crucible and barium sulfate, CRWT1 = weight (g) of empty crucible, SMPWT = sample weight (g), and 0.1374 converts %$BaSO_4$ to % S

Percent Free Sulfur Calculation

%Free Sulfur = [(CRWT1 -CRWT2) * 100%] / SMPWT

where: CRWT1 = weight (g) of crucible and sample pre CS_2 wash, CRWT2 = weight (g) of crucible and sample post CS_2 wash, and SMPWT = sample weight (g)

Total Sulfur Calculation

% Total Sulfur = % Free Sulfur + % Sulfate Sulfur

Documentation

The following Quality Records shall be generated and managed:

Required Record	Custodian
ICN Database	QA Manager
Laboratory Notebook	Chemist/QA Manager
Control Charts	Chemist/QA Manager
Completed Nautilus Worksheets	Chemist/ Production Manager
Equipment Logs and Calibration Certificates	Chemist/QA Manager/ Production Manager

Reference Procedures

AOAC 980.02

References

NA

Revision History

June 2, 2005 Version 003-Previous format-

August 8, 2010 Version 004-Previous format- Changes in Format, Changes in Procedure, Changes in Wording for Clarification and Simplification, Correction of Typographical Errors, Addition of Important Information

October 11, 2012-New format-

May 27, 2014 Version 002-Changes in Wording for Clarification and Simplification, Addition of Important Information
Page 3 acetone added to reagents, silica gel to desiccators
Page 4 Gooch, cylinders, dispensers edited
Page 5 step 5 edited
Page 6 step 5 edited
Page 8 step 7 edited

Appendix

Table 1-Weighing Schedule for Sulfur

TABLE 1	
WEIGHING SCHEDULE FOR SULFUR	
Guarantee amount (%)	**Weight (g)**
≤1	12.0xxx
≤2	6.0.xxx
≤3	4.0xxx
≤4	3.0xxx
≤5	2.5xxx
≤7.0	2.0xxx
≤9.0	1.4xxx
≤ 12.0	1. 1xxx
≤ 15.0	0.9xxx
≤ 18.0	0.75xx
≤ 22.0	0.6xxx
≤ 29.0	0.5xxx
≤ 100	(13.74/guarantee)