Standard Test Method for Sulfur in Organic Compounds by Sodium Peroxide Bomb Ignition[1]

ϵ^1 NOTE—Warning notes were editorially moved into the standard in May 2003.

1. Scope

1.1 This test method covers the determination of sulfur in organic compounds by sodium peroxide bomb ignition. It is intended for application to samples of organic materials containing more than 0.5 % sulfur. The presence of iron may require a separation such as is described.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 6.6.2, Section 7 and 8.3.

NOTE 1—A test method based on an oxygen bomb combustion of petroleum products is described in Test Method D 129.

1.3 Review the current Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions

2. Referenced Documents

2.1 *ASTM Standards:*

D 129 Test Method for Sulfur in Petroleum Products (General Bomb Method)[2]

D 1193 Specification for Reagent Water[3]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[4]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[4]

3. Summary of Test Method

3.1 The sample is oxidized with sodium peroxide in the presence of an accelerator (potassium nitrate) and an oxygen-bearing compound (sucrose), and the sulfur is converted to sulfate. The contents of the bomb are dissolved in water. The solution is acidified, filtered, and barium chloride solution added to precipitate the sulfate present. The barium sulfate is removed by filtration, ignited to constant weight, and calculated to percentage sulfur.

4. Significance and Use

4.1 This test method may be used to determine the total sulfur content of unknown organic samples or to assay known sulfur containing organic compounds.

4.2 This test method may be used on organic materials in which the complete conversion of sulfur to sulfate can be accomplished by sodium peroxide bomb ignition.

4.3 This test method assumes that sulfate is quantitatively measured by precipitation with barium chloride solution.

5. Apparatus

5.1 *Sodium Peroxide Bomb,* [5] flame ignition type, 22-mL capacity. This consists of a 99 % nickel fusion cup, 99 % nickel cap cover, lead gaskets, a bomb body, a screw cap, a wrench, an ignition housing, a bomb socket, glass mixing rod, and a sodium peroxide measuring dipper. A less expensive nickel-plated brass cap cover may be substituted.

5.2 *Safety Shield*—Any heavy-duty commercially available shield should suffice to confine the results of an explosion in the event of bomb body rupture during flame ignition.

5.3 *Burner,* blast-type, using gas and air. For some bomb work, the cheaper bunsen burner has been found to be satisfactory. The final ignition of crucibles may be done with a

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[1] This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.01 on General Standards.

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[2] *Annual Book of ASTM Standards,* Vol 05.01.

[3] *Annual Book of ASTM Standards,* Vol 11.01.

[4] *Annual Book of ASTM Standards,* Vol 15.05.

[5] A suitable ignition bomb and assembly is available from the Parr Instrument Co., 211 Fifty-Third St., Moline, IL. The 22-mL fusion cup is part No. N-200.

blast burner, a Meker-type burner, or a muffle furnace operating at approximately 800°C.

5.4 *Capsules*, gelatin, size No. 00, for liquid samples.

5.5 *Crucible*, filtering, 25-mL capacity, porcelain filtering crucible, fine porosity.

6. Reagents

6.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water conforming to Specification D 1193.

6.3 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

6.4 *Barium Chloride Solution* (10 %)—See Practice E 200, 96.7.

6.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

6.6 *Mixture, Bomb Accelerator*:

6.6.1 Dry 900 g of potassium nitrate (KNO_3) crystals in a 110 to 120°C oven for 2 days. Grind the dried crystals to a powder.

6.6.2 Dry 300 g of granulated sucrose in a 50 to 60°C oven for 2 days. Grind the dried sugar to a powder (**Warning—**Do not grind potassium nitrate with sugar. To avoid possible explosion, each must be ground separately.).

6.6.3 Mix the powdered KNO_3 and powdered sugar in a ball mill for 20 to 30 min. Balls should be omitted from the mill during this blending operation. Store in a closed jar kept in a desiccator.

6.7 *Sodium Peroxide*, 30 to 40 mesh, calorific grade. See the safety precautions on the label concerning this strongly caustic oxidant.

7. Hazards

7.1 This test method should not be applied to samples containing appreciable amounts of water (0.1 % or greater). Water reacts spontaneously with sodium peroxide and may cause premature reaction of the sample and peroxide. Also, oxygen is released, which may develop dangerously high internal bomb pressure.

7.2 Sodium peroxide is a potentially dangerous chemical. Avoid scattering the reagent or leaving the container exposed to the air or moisture. Spilled sodium peroxide should be washed down with large amounts of water, and not wiped up with paper or cloth.

7.3 Fusion cups may develop holes or cracks at any time (even when relatively new, but especially after long and continued use) and should be examined before use; cups not suitable for use should be discarded promptly. Fusion cup cover gaskets must be replaced when damaged. Bomb bodies and screw caps must be discarded when the threads become worn. This must be checked frequently.

7.4 Samples of unknown or unfamiliar composition or samples suspected of containing water or other material reactive with sodium peroxide should be tested before mixing with sodium peroxide. Place sodium peroxide in an empty fusion cup to a depth of 5 mm. Cautiously (wear gloves and safety glasses) add small quantities (approximately 25 mg) of the sample and mix. If the sample ignites spontaneously upon contact with the sodium peroxide, use a gelatin capsule for weighing the sample and introducing it into the bomb mixture. If the sample does not react with sodium peroxide, then proceed with the weighing of the sample, omitting the use of a gelatin capsule.

8. Procedure

8.1 Weigh (to the nearest 0.0001 g) a sample containing the equivalent of 0.1 g of sulfur. In any case, do not exceed a sample weight of 0.5 g. Solid samples should be pulverized before weighing. Liquid samples and samples that react on contact with sodium peroxide (see 7.3) should be weighed in a gelatin capsule.

8.2 Weigh approximately 1.0 g of KNO_3-sugar mixture (see 6.6) into a clean, dry fusion cup. Add one dipper (approximately 15 g) of sodium peroxide to the fusion cup and mix the contents with a clean, dry, glass stirring rod.

8.3 Transfer approximately one half of the mixture momentarily from the fusion cup above into a second fusion cup (**Warning—**During the charging procedure, the analyst should be prepared for a premature ignition. The use of gloves, safety spectacles, and a protective shield is urged.). Place the weighed sample (see 8.1) into the first fusion cup. In the case of a sample that is not in a capsule, stir the contents of the first cup with a clean, dry, glass rod while slowly returning the balance of the peroxide-accelerator mixture from the second cup. Wipe the lower part of the rod with a 15 by 30-mm piece of dry filter paper. Add the paper to the contents of the fusion cup and proceed promptly to the assembly operation. In the case of a sample that is in a capsule, return the balance of the peroxide-accelerator mixture to the first fusion cup. Promptly assemble the bomb with a gasket, cover, bomb body, and screw cap. Tighten the screw cap first by hand (wear gloves) and then with the wrench, supporting the bomb in the bench socket. Proceed promptly to the next step.

8.4 Place the bomb on a tripod behind a safety shield. About 1 or 2 mL (avoid excess) of water may be placed in the reservoir formed on top of the bomb by the surrounding screw cap. Adjust the blast burner to produce a narrow, hot flame striking the bottom of the bomb. Do not expose anyone to possible injury should the bomb explode. Heat the bomb until the contents are ignited, as indicated by the boiling of the water or a slightly perceptible dull red heat or an audible click. If possible, do not continue to heat after the water has evaporated to dryness, as the top of the bomb will overheat and destroy the

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[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

gasket. If the water does not boil, allow the bomb to heat for 7 to 8 min or until the water has evaporated.

8.5 Following ignition, drop the bomb into a water bath (shielded) to cool. Remove the bomb from the water bath and rinse the outside of the bomb with water.

8.6 Disassemble the bomb, carefully remove the cover from the fusion cup, and rinse the cover with water into a 400-mL beaker. Add sufficient water to make a volume approximately 125 to 150 mL. Place the fusion cup upright in the beaker. Turn the cup on its side with a stirring rod and immediately cover with a watch glass. Allow to stand until effervescence ceases. The fusion mass should be examined for evidence of a poor fusion, such as the presence of carbon or unfused peroxide granules, or both. Poor fusions cause results to be low.

8.7 Heat the contents of the beaker, if necessary, to dissolve the peroxide melt. Rinse the watch glass and the fusion cup with warm water and remove. Collect the rinsings in the beaker.

8.8 Cautiously acidify by adding HCl (sp gr 1.19) to the beaker with stirring. When the solution approaches neutralization, as indicated by a decrease in effervescence, place a piece of blue litmus paper in the solution. Slowly continue the addition of the acid until the litmus paper turns red.

8.9 At this point, if ferric ion is present, it should be removed to prevent erroneously high results. The presence of ferric ion is detected during the previous step by observing a red-brown precipitate of ferric hydroxide which dissolved on acidification. Remove the iron by adding an excess of NH_4OH (sp gr 0.90) and filtering off the ferric hydroxide through filter paper. Acidify the filtrate with HCl (sp gr 1.19) to a red litmus test.

8.10 Add about 2 mL of HCl (sp gr 1.19) in excess, but no more. Filter the contents of the beaker through a filter paper into a 600-mL beaker. Wash the filter paper and the 400-mL beaker with several portions of hot water, adding the rinses to the 600-mL beaker until the volume approximates 300 to 400 mL.

8.11 Place the beaker on a hot plate and heat to a gentle boil. Add dropwise, with stirring, about 10 mL of hot 10 % $BaCl_2$ solution (based on 0.1 g of sulfur). Cover the beaker with a watch glass.

8.12 Digest the contents of the beaker on a steam plate, or its equivalent, for 1 or 2 h. Remove the beaker from the steam plate and allow to stand overnight at room temperature.

8.13 Filter the contents of the beaker through a previously ignited, cooled, and weighed (to 0.0001 g) porcelain filtering crucible of fine porosity. Use a stream of hot water and a rubber policeman to effect the complete transfer of precipitate to the filtering crucible. Wash the precipitate in the crucible several times with hot water until a negative test for chlorides is obtained when $AgNO_3$ solution is added to the washings.

8.14 Dry the crucible at about 100°C for 1 h and finally ignite to constant weight at about 800°C (do not exceed 1100°C). Cool in a desiccator and weigh to 0.0001 g.

8.15 *Blank*—For the blank, measure the specified amount of sodium peroxide and accelerator into a bomb cup. If a gelatin capsule was used, add an empty capsule to the cup. Follow the usual procedure including a ferric ion removal step if it was applied. Subtract the weight of $BaSO_4$ obtained in the blank from that observed in the sample.

9. Calculation

9.1 Calculate the sulfur content as follows:

$$\text{Sulfur, wt \%} = \frac{(A - B) \times 13.736}{W} \tag{1}$$

where:

A = $BaSO_4$ from the sample, g,
B = $BaSO_4$ from the blank, g,
W = sample used, g, and
13.736 = (atomic weight of sulfur × 100)/formula of $BaSO_4$.

10. Report

10.1 Report the percentage of sulfur to the nearest 0.01 %.

11. Precision and Bias

11.1 *For Samples in Capsule*—The following criteria should be used in judging the acceptability of results (Note 2):

11.1.1 *Repeatability (Single Analyst)* —The standard deviation for a single determination has been estimated to be 0.274 % absolute at 14 DF. The 95 % limit for the difference between two such runs is 0.77 % absolute.

11.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.236 % absolute at 7 DF. The 95 % limit for the difference between two such averages is 0.66 % absolute.

11.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.432 % absolute at 6 DF. The 95 % limit for the difference between two such averages is 1.21 % absolute.

11.2 *For Samples Not in Capsule*—The following criteria should be used in judging the acceptability of results (Note 2):

11.2.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.155 % absolute at 14 DF. The 95 % limit for the difference between two such runs is 0.43 % absolute.

11.2.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.138 % absolute at 7 DF. The 95 % limit for the difference between two such averages is 0.39 % absolute.

11.2.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.287 % absolute at 6 DF. The 95 % limit for the difference between two such averages is 0.80 % absolute.

NOTE 2—The above precision statements are based on an interlaboratory study conducted ca. 1964 - 1965. For samples in capsule one sample of chlorothiophene (theoretical sulfur = 27.04 %) was used. One analyst in each of 7 laboratories performed duplicate determinations and repeated on a second day, for a total of 28 determinations. For samples not in capsule the same design was followed except that one sample of mercaptobenzothiazole (theoretical sulfur = 38.35 % was used[7]. Practice E 180 was used in developing these precision estimates.

11.3 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: E15–1054.

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