



# Standard Test Method for Phosphorus in Organic Compounds by Sodium Peroxide Bomb Ignition<sup>1</sup>

This standard is issued under the fixed designation E 357; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope

1.1 This test method<sup>2</sup> covers the determination of phosphorus in organic compounds by sodium peroxide bomb ignition. It is applicable to samples of organic materials containing more than 1.0 % phosphorus.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *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.* Specific precautionary statements are given in Section 8, and Note 1, Note 2, and Note 6.

1.4 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 1193 Specification for Reagent Water<sup>3</sup>

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>4</sup>

## 3. Summary of Test Method

3.1 A sample is heated in a closed bomb with sodium peroxide in the presence of an accelerator mixture consisting of potassium nitrate and sucrose. The phosphorus is converted to phosphate. The melt is dissolved in water and acidified with nitric acid. Phosphorus is determined gravimetrically on an

aliquot of the solution by precipitation as quinolinium phosphomolybdate,  $(C_9H_7N)_3H_3PO_4 \cdot 12MoO_3$ .

## 4. Significance and Use

4.1 This test method is applicable to the determination of phosphorus in organic materials containing at least 1.0 % phosphorus. It can be used as an assay procedure for known phosphorus organic compounds.

## 5. Interferences

5.1 Interfering substances include elements such as arsenic which form insoluble precipitates with the quinoline molybdate reagent, and those which yield insoluble phosphates. Interference from silica is reduced by addition of citric acid to the reagent. Citric acid forms a complex with molybdic acid, of such stability that its reaction with silicic acid is avoided.

## 6. Apparatus

6.1 *Sodium Peroxide Bomb Apparatus*, consisting of a 22-mL fusion cup of 99 % nickel, a 99 % nickel cup cover, lead gaskets, a bomb body and screw cap, a wrench, a bomb socket, and a measuring dipper holding approximately 15 g of sodium peroxide. A less expensive nickel plated brass cup cover may be substituted.<sup>5</sup>

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

6.3 *Burner*, blast, for use with natural gas and oxygen.

6.4 *Capsules*, gelatin, Size No. 0.

6.5 *Crucibles*, Gooch, Coors porcelain, with perforated bottoms, Size No. 3, 25-mL capacity.

6.6 *Filter Pads*, glass-fiber, 2.1-cm diameter.

## 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

<sup>5</sup> Available from Parr Instrument Co., 211 Fifty-Third St., Moline, IL., Catalog No. 2102. The 22-mL fusion cup is part No. N-200.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.21 on Elements.

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<sup>2</sup> Official Methods of Analysis of the Association of Official Agricultural Chemists, Tenth Ed., 1965, p. 12, and Perrin, C. H., *Journal, Association of Official Agricultural Chemists, JOACA*, Vol 41, 1959, p. 758.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 15.05.

all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>6</sup> 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.

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

7.3 *Sodium Peroxide* ( $\text{Na}_2\text{O}_2$ ), calorific grade, 30 to 40 mesh granular, minimum assay of 96.0 %  $\text{Na}_2\text{O}_2$ . Store in a wide-mouth metal can with tight-fitting resealable lid. Label with safety precautions from the original metal container.

7.4 *Mixture, Bomb Accelerator*:

7.4.1 Dry 450 g of potassium nitrate ( $\text{KNO}_3$ ) crystals in an oven at 110 to 120°C for 2 days. Grind the crystals to a powder.

7.4.2 Dry 150 g of granulated sucrose in an oven at 50 to 60°C for 2 days. Grind the dried sugar to a powder.

NOTE 1—**Caution:** Do not grind  $\text{KNO}_3$  with sugar. To avoid the possibility of an explosion, grind these materials separately.

7.4.3 Mix the powdered  $\text{KNO}_3$  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.

7.5 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ( $\text{HNO}_3$ ).

7.6 *Nitric Acid* (1 + 9)—Mix 1 volume of nitric acid ( $\text{HNO}_3$ , sp gr 1.42) with 9 volumes of water.

7.7 *Synthetic Quinoline*.

7.8 *Sodium Molybdate Dihydrate*,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ .

7.9 *Acetone*.

7.10 *Quinoline Molybdate Reagent*—Dissolve 70 g of sodium molybdate dihydrate in 150 mL of water. Dissolve 60 g of citric acid in a mixture of 85 mL of  $\text{HNO}_3$  (sp gr 1.42) and 150 mL of water and cool. Slowly add the molybdate solution to the citric acid solution while stirring. Dissolve 5 mL of synthetic quinoline, with stirring, in a mixture of 35 mL of  $\text{HNO}_3$  (sp gr 1.42) and 100 mL of water. Gradually add this solution to the molybdate-citric- $\text{HNO}_3$  solution, mix, and allow to stand for 24 h. Filter the solution, add 280 mL of acetone, and dilute to 1 L with water. Mix thoroughly and store in a stoppered polyethylene container.

## 8. Safety Precautions

8.1 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.

8.2 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.

8.3 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.

8.4 Samples of unknown or unfamiliar composition or samples suspected of containing water or other material reactive with  $\text{Na}_2\text{O}_2$  should be tested before mixing with  $\text{Na}_2\text{O}_2$ . Place the  $\text{Na}_2\text{O}_2$  in an empty fusion cup to a depth of 5 mm cautiously wearing safety glasses and gloves, add approximately 25 mg of the sample and mix. If the sample ignites spontaneously upon contact with the  $\text{Na}_2\text{O}_2$ , use a gelatin capsule for weighing the sample and introducing it into the bomb mixture. If the sample does not react with  $\text{Na}_2\text{O}_2$ , then proceed with the weighing of the sample, omitting the use of a gelatin capsule.

## 9. Procedure

9.1 Weigh a sample containing 60 to 120 mg of phosphorus to the nearest 0.1 mg. In any case, do not exceed a sample weight of 0.5 g. Solid samples should be pulverized before weighing. Liquid samples or samples that react on contact with  $\text{Na}_2\text{O}_2$  (see 8.4) should be weighed in a gelatin capsule.

9.2 Weigh approximately 1.0 g of  $\text{KNO}_3$ -sugar accelerator mixture into a clean, dry fusion cup. Add one dipper (approximately 15 g) of  $\text{Na}_2\text{O}_2$  to the fusion cup and mix the contents with a clean, dry, glass stirring rod.

9.3 Transfer approximately one half of the mixture from the fusion cup above to a second fusion cup. Place the weighed sample in the first fusion cup (Note 2). 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 1.5 by 3.0-cm piece of dry filter paper. Add the paper to the contents of the fusion cup and press into the mixture with the glass rod. 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 lead gasket, cover, bomb body, and cap. Tighten the screw cap first by hand and then with a wrench, supporting the bomb in the bench socket. Proceed promptly with the following ignition step.

NOTE 2—**Caution:** During the charging procedure, the analyst should be prepared for a premature ignition. The use of gloves, safety glasses, and a protective shield is recommended.

9.4 Place the bomb on a tripod behind a safety shield. Place several millilitres of water in the well at the top of the bomb. Adjust the gas-air burner to produce a narrow, hot flame striking the base of the fusion cup and position the flame so that the water comes to a vigorous boil in approximately 50 to 70 s. Do not rotate or rock the bomb to prevent contact of the peroxide with the lead gasket. Release the bomb immediately into a container of cold water.

<sup>6</sup> *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.

NOTE 3—The base of the fusion cup may get a dull red during heating. Overheating causes excessive oxidation of the nickel cup and dark green solutions. Underheating will leave unoxidized matter in the bomb. Do not allow the water to evaporate to dryness during heating to prevent overheating of the top of the bomb and melting of the lead gasket. The lead gasket must not come into contact with the peroxide melt as this will dissolve lead and produce troublesome precipitates.

9.5 After the bomb has cooled to room temperature, rinse with water and disassemble. Remove the cover and wash the lower surface of the cover briefly with a stream of hot water, collecting the washings in a 400-mL beaker. Add additional cold water to the beaker to bring the volume to approximately 50 mL. Place the fusion cup on its side in the beaker and cover with a watch glass. After the initial effervescence has subsided, place the covered beaker on a steam bath and warm gently, stirring occasionally until dissolution of the melt is complete. Remove the cup and rinse thoroughly inside and out with water. Rinse the inside of the cup twice with HNO<sub>3</sub> (1 + 9). Collect all rinsings in the beaker. Cautiously neutralize the solution by addition of HNO<sub>3</sub> until a drop of the solution on a stirring rod just turns litmus paper red. A vigorous effervescence is observed just before the equivalence point is reached and subsides as soon as the solution becomes acid. After neutralizing, add 25 mL of HNO<sub>3</sub> in excess. Heat the solution to boiling on a hot plate, then boil for 5 min. Cool the solution, transfer quantitatively to a 250-mL volumetric flask, dilute to volume with water, and mix thoroughly.

9.6 If the solution is not clear, filter through a general-purpose, acid-washed, medium-retention filter paper, collecting the filtrate in a dry beaker. Transfer a 25.00-mL aliquot to a 400-mL beaker and dilute to approximately 100 mL with water.

NOTE 4—The sample aliquot should contain no more than 12 mg of phosphorus. For samples containing less than 10 % phosphorus, a 0.4 to 0.5 g sample may be used, and a 50.00-mL aliquot taken for analysis.

NOTE 5—The presence of carbonaceous matter in the solution does not necessarily indicate incomplete decomposition and fixation of the desired element.

9.7 Add 50 mL of quinoline molybdate reagent to the solution slowly from a graduate while stirring. Cover the beaker with a watch glass, place on a hot plate in a well ventilated hood, and boil for 1 min.

NOTE 6—**Caution:** Quinoline molybdate reagent contains acetone and is flammable. Keep away from fire and boil only in a well ventilated hood.

9.8 Cool the solution to room temperature, stirring occasionally while cooling. Filter the solution through a tared Gooch crucible containing a glass fiber filter pad which has been previously dried at 250 ± 10°C. Wash the precipitate five times with 25-mL portions of water and dry in an oven at 250 ± 10°C for 30 min. Cool in a desiccator and reweigh.

9.9 Run a blank through the entire procedure by igniting the specified amounts of Na<sub>2</sub>O<sub>2</sub> and accelerator mixture. If a gelatin capsule was employed for the sample, add an empty

capsule to the blank fusion cup. Use the same size aliquot for the blank determination as was used for the sample determination.

## 10. Calculation

10.1 Calculate the phosphorus content of the sample as follows:

$$\text{Phosphorus, weight \%} = (A - B) \times 0.01400 \times F \times 100 W \quad (1)$$

where:

*A* = grams of precipitate, obtained from sample aliquot,

*B* = grams of precipitate, obtained from identical blank aliquot,

*F* = dilution factor = 250/aliquot size, mL, and

*W* = grams of sample used.

## 11. Report

11.1 Report the percentage of phosphorus to the nearest 0.01 %.

## 12. Precision and Bias

12.1 The following criteria shall be used in judging the acceptability of results (Note 7):

12.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.105 % absolute at 58 DF. The 95 % limit for the difference between two such runs is 0.31 % absolute.

12.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability, Formerly Called Repeatability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.100 % absolute at 29 df. The 95 % limit for the difference between two such averages is 0.28 % absolute.

12.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.184 % absolute at 8 df. The 95 % limit for the difference between two such averages is 0.51 % absolute.

NOTE 7—The preceding precision statements are based on an interlaboratory study performed in 1967 on one sample each of triphenylphosphine, triphenylphosphite, and trimethylphosphate. One analyst in each of 10 laboratories performed duplicate determinations and repeated them on a second day.<sup>7</sup> Practice E 180 was used in obtaining these precision estimates.

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

## 13. Keywords

13.1 organic compounds; phosphorous; quinoline molybdate; sodium peroxide bomb

<sup>7</sup> Details of the interlaboratory study are available as Research Report E15-1004 from ASTM Headquarters.

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