Designation: E256 – 09

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

This standard is issued under the fixed designation E256; 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 (ε) indicates an editorial change since the last revision or reapproval.

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

1. Scope*

1.1 This test method covers the determination of chlorine in organic compounds by sodium peroxide bomb ignition. It is intended for application to samples of organic materials containing more than 0.5 % chlorine. The procedure assumes that compounds containing halogens other than chlorine will not be present.

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 safety precautions, see 6.5.2, Section 7, 8.3, and 8.9.

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

NOTE 1—Other test methods based on oxygen bomb combustion for analysis for chlorine are described in Test Method D808, Test Method D2361, and Test Method D4208.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D808 Test Method for Chlorine in New and Used Petroleum Products (High Pressure Decomposition Device Method)
D1193 Specification for Reagent Water
D2361 Test Method for Chlorine in Coal (Withdrawn 2008)[3]
D4208 Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method
E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]
E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Summary of Test Method

3.1 The sample is heated in a closed bomb with sodium peroxide in the presence of an accelerator (potassium nitrate) and an oxygen-bearing compound (sucrose). The chlorine is converted to chloride. The contents of the bomb are dissolved in water. The solution is acidified and the chloride is determined by titrating the excess of silver nitrate solution used to precipitate the chloride.

4. Significance and Use

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

4.2 This test method may be used on organic materials in which the complete conversion to chloride can be accomplished by sodium peroxide bomb ignition, and which contain no other halogens.

5. Apparatus

5.1 *Sodium Peroxide Bomb,* [4] 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.

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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] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] The sole source of supply of the ignition bomb and assembly known to the committee at this time is Parr Instrument Co., Moline, IL. The 22-mL fusion cup is part No. N-200. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee [1], which you may attend.

***A Summary of Changes section appears at the end of this standard**

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.

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

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.[5] 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 D1193.

6.3 *Ammonium Thiocyanate, Standard Solution* (0.1 meq/mL*)*—Prepare in accordance with Practice E200.

6.4 *Ferric Ammonium Sulfate Indicator Solution* (80 g/L)—Prepare in accordance with Practice E200.

6.5 *Mixture, Bomb Accelerator:*

6.5.1 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.

6.5.2 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 the possibility of an explosion, grind these materials separately.).

6.5.3 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.

6.6 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

6.7 *Nitrobenzene*—The use and disposal of nitrobenzene must be done in accordance with its hazardous properties (see 7.2). Benzyl alcohol may be a safer, but less effective, coagulant than nitrobenzene.

6.8 *Silver Nitrate, Standard Solution* (0.1 meq/mL*)*—Prepare in accordance with Practice E200.

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

7. Safety Precautions

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 Nitrobenzene is very hazardous when absorbed through the skin or when its vapor is inhaled. Do not get nitrobenzene in the eyes, on the skin, or on clothing. Avoid breathing its vapor. Use only with adequate ventilation.

7.3 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.

7.4 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.

7.5 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 chlorine. 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 7.4) should be weighed in a gelatin capsule.

8.2 Weigh approximately 1.0 g of KNO_3-sugar mixture (see 6.5) 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 following 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

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[5] *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.

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 gasket. If the water does not boil, allow the bomb to heat for 7 or 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 250-mL beaker. Add sufficient water to make a volume approximately 50 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 HNO_3 (sp gr 1.42) to the beaker while 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, and then add 2 to 3 mL excess.

8.9 Cool the solution to room temperature and transfer it completely to a conical 250-mL flask provided with a glass stopper. Add 1 to 2 mL of ferric ammonium sulfate indicator solution and 4 to 5 mL of nitrobenzene (**Warning—** Nitrobenzene is very hazardous when absorbed through the skin or when its vapor is inhaled. Do not get nitrobenzene in the eyes, on the skin, or on clothing. Avoid breathing its vapor. Use only with adequate ventilation.).

8.10 Fill a calibrated 10-mL buret to the zero mark with 0.1 meq/mL NH_4SCN solution. Add a few drops from the buret to the flask. Proceed to the next step.

8.11 Fill a calibrated 50-mL buret to the zero mark with 0.1 meq/mL $AgNO_3$ solution. Titrate the contents of the flask with the $AgNO_3$ solution to a colorless end point. Add about 3 mL excess and then record the total volume of $AgNO_3$ solution added, V_1.

8.12 Stopper the flask and shake vigorously for about 20 s to coagulate the AgCl and to form a protective coating on the precipitate. Rinse the stopper into the flask with water.

8.13 Continue the titration from the buret containing the NH_4SCN solution. The end point is characterized by the first persistent reddish-brown color. It should remain colored during vigorous shaking for 50 to 60 s. Record the total volume of NH_4SCN solution used, V_2.

8.14 *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. Proceed according to the foregoing method.

9. Calculation

9.1 Calculate the chlorine content as follows:

$$\text{Chlorine, mass }\% = \frac{(X - Y) \times 3.545}{W} \tag{1}$$

where:

X = $V_1N_1 - V_2N_2$,
Y = $v_1N_1 - v_2N_2$,
V_1 = $AgNO_3$ solution used in the sample, mL,
V_2 = NH_4SCN solution used in the sample, mL,
v_1 = $AgNO_3$ solution used in the blank, mL,
v_2 = NH_4SCN solution used in the blank, mL,
N_1 = milliequivalents per millilitre of the $AgNO_3$ solution,
N_2 = milliequivalents per millilitre of the NH_4SCN solution,
W = sample used, g, and
3.545 = (atomic wt of chlorine × 100)/1000.

10. Report

10.1 Report the percentage of chlorine to the nearest 0.01 mass %.

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 0.261 % absolute at 14 DF. The 95 % limit for the difference between two such runs is 0.73 % 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 0.405 % absolute at 7 DF. The 95 % limit for the difference between two such averages is 1.13 % 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 0.564 % absolute at 6 DF. The 95 % limit for the difference between two such averages is 1.58 % 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 0.096 % absolute at 14 DF. The 95 % limit for the difference between two such runs is 0.27 % 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 0.064 % absolute at 7 DF. The 95 % limit for the difference between two such averages is 0.18 % 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 0.235 % absolute at 6 DF. The 95 % limit for the difference between two such averages is 0.66 % absolute.

NOTE 2—The above precision statements are based on an interlaboratory study performed ca. 1964–1965. For samples in capsule one sample of chlorothiophene (theoretical chlorine = 29.90 %) 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 chlorobenzoic acid (theoretical chlorine = 22.65 %) was used.[6] Practice E180 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.

12. Keywords

12.1 chlorine; organic compounds; silver nitrate titration; sodium peroxide bomb

SUMMARY OF CHANGES

Subcommittee E15.01 has identified the location of selected changes to this standard since the last issue (E256-98(2003)$^{\varepsilon 1}$) that may impact the use of this standard.

(1) Updated units of measure to comply with the International System of Units (SI).

(2) Added numbered paragraph in Scope stating that SI units are to be considered standard.

(3) Added Summary of Changes section.

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1053.