



Standard Test Method for Total Bromine Number of Unsaturated Aliphatic Chemicals¹

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1. Scope

1.1 This test method covers the determination of total bromine number in various double-bonded aliphatic compounds, using pyridine sulfate dibromide (PSDB), also known as Rosenmund-Kuhnenn reagent.² The total unsaturation is determined, whether conjugated or not.

1.2 *This standard does not purport to address all of the safety problems 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 7 and in paragraphs 5.1.1, 6.4.1, 6.7.1, and 8.1.

2. Referenced Documents

2.1 ASTM Standards:

D 1159 Test Method for Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electro-metric Titration³

D 1193 Specification for Reagent Water⁴

D 1541 Test Method for Total Iodine Value of Drying Oils and Their Derivatives⁵

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁶

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis⁶

3. Terminology

3.1 Definitions:

3.1.1 *total bromine number*—number of centigrams of bromine equivalent to the total unsaturation present in 1 g of

sample. It is a measure of the total ethylenic unsaturation present in the designated aliphatic compound.

4. Significance and Use

4.1 This test method is a good general means for measuring ethylenic (double-bond) unsaturation and is applicable to many compounds because of its speed, convenience, and minimum tendency for substitution. This test method has been applied to alpha-olefins, cyclic unsaturated hydrocarbons such as the cyclopentenes, unsaturated aliphatic side chains on aromatic rings, unsaturated esters and alcohols, acrylic and methacrylic esters, acids, and salts, and other similar compounds. Diisobutylene and some tertiary-substituted hydrocarbons substitute to some extent but probably less by this test method than by most others. It is not satisfactory for such materials as commercial propylene trimer and tetramer, butene dimer, and mixed nonenes, octenes, and heptenes. For the bromine number of petroleum distillates that are substantially free of material lighter than isobutane and that have 90 % distillation points under 620°F (327°C) (such as gasoline), Test Method D 1159, is recommended.

5. Apparatus

5.1 *Iodine Flasks*, glass-stoppered, 500 mL capacity.

5.1.1 **Caution**—The bromination must be run under conditions of *low light intensity*, preferably less than 5.41 m/m² (0.5 foot-candle). This condition is mandatory from the time the mercuric acetate is added until after the potassium iodide has been added. Normally it will be satisfactory to close the blinds on the laboratory windows and turn off the lights in the immediate area. To further minimize the effect of light, wrap the iodine flasks up to the top rim with aluminum foil (or other light-excluding device).

5.2 *Volumetric Pipets*, certified or National Institute of Standards and Technology (NITS) grade, 10, 25, and 50-mL capacity.

5.3 *Buret*, certified or National Institute of Standards and Technology grade, 50-mL capacity, graduated in 0.1-mL divisions.

5.4 *Automatic Buret and Reservoir*^{7,8}—A gravity-filled buret with 2000-mL reservoir, both made of amber glass. This is

¹ This test method is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.22 on Functional Groups.

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² This test method is adapted from the suggested for tung oil by Rowe, Furnas, and Bliss, *Industrial and Engineering Chemistry*, Analytical Ed., IENAA Vol 16, p. 371, using the Rosenmund-Kuhnenn reagent (pyridine sulfate dibromide or PSDB) as the brominating system. For the sake of uniformity, it follows in most respects the principles and format of Test Method D 1541. Some sections have been copied in whole or part from that test method.

³ *Annual Book of ASTM Standards*, Vol 05.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.01.

⁵ *Annual Book of ASTM Standards*, Vol 06.03.

⁶ *Annual Book of ASTM Standards*, Vol 15.05.

⁷ A suitable automatic buret and reservoir may be obtained from the Ace Glass Co., Vineland, NJ. Catalog No. 5753–T.

⁸ Sisco 300 Stopcock Grease, obtainable from the Swedish Iron and Steel Co., 100 Quinby St., Westfield, NJ, has been found satisfactory for lubricating stopcocks.

for storing and dispensing the PSDB (or Rosenmund-Kuhnenn) reagent. In this apparatus, the reagent is reasonably stable for several weeks or even months.

5.5 Aluminum Foil.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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.⁹ 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 *Acid, Glacial*—The glacial acetic acid must pass the ACS dichromate test.⁹ To 10 mL of acid add 1.0 mL of 0.1 *N* potassium dichromate solution and cautiously add 10 mL of sulfuric acid. Cool the solution to room temperature and allow it to stand for 30 min. While mixing the solution, dilute slowly and cautiously with 50 mL of water, cool, and add 1 mL of freshly prepared potassium iodide reagent solution. Titrate the liberated iodine with 0.1 *N* thiosulfate solution, using starch as the indicator. Not more than 0.40 mL of the 0.1 *N* potassium dichromate solution should be consumed (not less than 0.60 mL of the 0.1 *N* thiosulfate solution should be required). Correct for a blank carried through the entire procedure.

6.4 Carbon Tetrachloride (CCl₄).

6.4.1 **Caution**—Carbon tetrachloride is highly toxic. The TLV limit is 10 ppm. Inhaling vapor is hazardous to health. Avoid breathing of vapor or contact with skin or eyes. Use in a hood with adequate ventilation. An alternative, less toxic solvent, namely, 1,1,1-trichloroethane, may be used in place of CCl₄. The method is known to be workable using this solvent; however, insufficient data have been generated to provide precision and accuracy statements for the method using 1,1,1-trichloroethane.

6.5 *Mercuric Acetate Solution (25 g/1000 mL)*—Dissolve 25 g of mercuric acetate (Hg(C₂H₃O₂)₂) in glacial acetic acid and dilute to 1000 mL with glacial acetic acid.

NOTE 1—Because the mercuric acetate solution seems to weaken catalytically with time, it should be prepared daily. Optionally, 0.6 g of dry mercuric acetate may be added to the iodine flask after the sample solution is introduced, but this technique is somewhat inconvenient.

6.6 *Potassium Iodide Solution (300 g/1000 mL)*—Dissolve 300 g of potassium iodide (KI) in water and dilute to 1000 mL.

NOTE 2—Prepare this reagent just prior to use. The freshly prepared reagent should be colorless.

6.7 *PSDB (or Rosenmund-Kuhnenn) Reagent (Caution, see 6.7.1)*—Place 40 mL glacial acetic acid in each of three

250-mL Erlenmeyer flasks. To the first, add slowly 16.0 ± 0.2 g of pyridine, with cooling in an ice bath. To the second flask, add slowly 20.0 ± 0.2 g of concentrated sulfuric acid (H₂SO₄, sp gr 1.84) with cooling as above. When cool, add the contents of the second flask to the contents of the first flask, with further cooling. To the third flask, add 16.0 ± 0.2 g of bromine. Add the bromine solution to the mixture of the first two solutions. Transfer to a 1000-mL volumetric flask with the aid of glacial acetic acid, and make up to 1000 mL with glacial acetic acid. Mix thoroughly and transfer to the overhead amber reservoir of the automatic buret. The reagent is approximately 0.10 *N* with respect to bromine. Preferably it should be adjusted by the addition of glacial acetic acid, if necessary, to slightly less than 0.10 *N* for convenience in titrating. The normality of the reagent can be checked for this adjustment by running a reagent blank titration as described in 9.5, but eliminating the standing time.

6.7.1 **Caution**—The PSDB reagent should be prepared in a fume hood, with great care. All of its components, as well as the reagent itself, must be regarded as hazardous chemicals. To minimize the possibility of getting painful blisters on the skin, acetic acid is preferably dispensed from some such device as an automatic buret¹⁰ with adapter for fitting it to a 2500-mL Winchester bottle. (If CCl₄ is used in this test method, it should also be handled in a hood because of its high toxicity. See 6.4).

6.8 *Sodium Thiosulfate, Standard Solution (0.1 N)*—Prepare and standardize the solution in accordance with Practice E 200.

6.9 *Starch Indicator Solution (10 g/1000 mL)*—Prepare in accordance with Practice E 200.

7. Precautions

7.1 Carbon tetrachloride is extremely toxic. Its TLV limit is 5 ppm (approximately 30 mg/m³). It is toxic by several routes of entry. It irritates mucous membranes, depresses the central nervous system, causes effects on blood cells (perhaps mediated in part by hepatic injury) and metabolic changes. Damage to the liver and kidney is the outstanding result of intoxication by this solvent. Exposure can present an important health hazard either acutely or chronically. The majority of fatal poisonings from carbon tetrachloride have resulted from acute or subacute exposures.¹¹

8. Sampling

8.1 The procedure used in preparing the sample for analysis will depend on its physical form, its solubility, and the magnitude of its bromine number. Most materials, whether liquid or solid, are best handled by preparing a stock solution containing a measured and conveniently larger amount of sample dissolved in acetic acid (or in CCl₄ alone or mixed with acetic acid (**Caution**, see 6.4 and 7.1)), from which an aliquot is taken for analysis. Most compounds are brominated quantitatively if not more than 40 mL of the original 50 mL of PSDB reagent is consumed in the reaction with the sample. For

⁹ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

¹⁰ Ace Glass Catalog No. 5770 has been found satisfactory for this purpose.

¹¹ "Documentation of the Threshold Limit Values," 5th edition, American Conference of Governmental Industrial Hygienists, 1986, p. 109.

practical purposes, the weight of sample contained in the aliquot should be chosen so that 30 to 40 mL of the PSDB reagent is consumed, but sometimes it may be found useful to take a smaller sample so that a larger excess of unreacted reagent remains. The following typical sampling scheme has been found adequate for acrylic and methacrylic esters and acids, or similar compounds, containing one double bond:

Molecular Weight	Volume of Sample, mL
99 or less	1.5
100 to 135	2.0
136 to 200	3.0
201 to 250	4.0
Above 250	5.0

9. Procedure

9.1 To a 100-mL volumetric flask add about 20 mL of glacial acetic acid. Wipe dry the stopper area of the flask, then stopper the flask and weigh it on an analytical balance. Next carefully introduce into the flask by pipet the amount of sample designated in Section 8. Restopper the flask and reweigh it. Then fill to the 100-mL mark with glacial acetic acid and mix well, to give the stock solution from which a 10-mL aliquot is taken for analysis. For compounds of low bromine number, where aliquoting is not practical, the sample may be transferred directly into the reaction flask containing acetic acid (or CCl_4 , or both) and the PSDB reagent, and dissolved before adding the catalyst. In such cases, for liquids a weighing buret may be used to advantage.

9.2 Working in light of low intensity, run into an aluminum foil-covered iodine flask (**Caution**, see 5.1.1), by means of the automatic buret, exactly 50.0 mL of PSDB reagent. Pipet immediately into the flask a 10-mL aliquot of the stock solution of the sample. Next, add at once from a graduate 25 mL of mercuric acetate solution (Note 3) in such a way that the ground-glass area in the neck of the flask is thoroughly wetted with the mercuric acetate solution. Stopper the flask, swirl to mix, then place it in a dark cabinet immediately at a temperature of 23 to 27°C (Note 4 and Note 5).

NOTE 3—Modification of the procedure permits satisfactory bromination of some comparatively unreactive unsaturates that are not amenable to the regular procedure. Thus, by doubling the amount of mercuric acetate catalyst, reducing the amount of sample so as to leave 100 % excess of unreacted PSDB reagent, and stretching the reaction time to 24 h, it is possible to secure essentially quantitative bromination of maleic acid. Sometimes the addition of HCl also seems to be helpful in brominating such slow reacting materials.

NOTE 4—Without catalyst (mercuric acetate), reaction between most eligible unsaturates and the PSDB reagent is quite slow, even in sunlight. However, with catalyst the bromine adds very rapidly to the double bond, even in the dark. Furthermore, in the presence of catalyst, even relatively subdued light promotes *substitution* of hydrogen by bromine, and tends toward low results, because the blank is affected more than the sample. Consequently, the lighting restrictions imposed by 9.2 are necessary for optimum results, and during the reaction period the flask must be kept in absolute darkness.

NOTE 5—Substitution is also accelerated by increase in temperature. As illustrated by chloroform (CHCl_3), usually regarded as inert, substitution is negligible at 15°C, slight at 25°C, and considerable at 35°C. Working in the range between 25 and 27°C is normally prescribed, but when dealing with easily substituted samples, it will be found advantageous to run the reaction at a temperature as low as 18°C. Further, both the PSDB reagent and the sample stock solution have very high coefficients of expansion, so

care must be taken to safeguard against errors caused by the volumetric effects of changes in temperature.

9.3 After exactly 30 min (Note 3) bring the flask out into the dimly lighted laboratory and quickly and immediately add potassium iodide by filling the gutter of the flask with KI solution, then admitting this solution to the flask by loosening and partially removing the stopper. Replace the stopper tightly and shake the flask vigorously for about 30 s. Next, add about 200 mL of water, washing down the stopper and neck of the flask carefully in the process. Then strip the foil cover from the flask.

9.4 Finally, using normal illumination (for example, from a titration lamp) titrate the released iodine with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution, while swirling. Then add 1 to 2 mL of starch solution and proceed slowly with the titration to the disappearance of the purplish starch indicator color.

9.5 With each group of samples, conduct at least two blank determinations, following the same procedure as described in 9.1-9.4, except that no sample shall be added and the sample aliquot shall be replaced by 10 mL of glacial acetic acid. In the titration, run into the flask about 40 mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution before completing the titration as described.

NOTE 6—Small amounts of water do not adversely affect the applicability of this test method.

10. Calculation

10.1 Calculate the total bromine number as follows:

$$\text{Total bromine number} = [(A - B)N \times 7.991]/W \quad (1)$$

where:

A = mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for titration of the blank,

B = mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for titration of the sample,

N = normality of the $\text{Na}_2\text{S}_2\text{O}_3$ solution, and

W = grams of sample in aliquot used.

10.2 In case it is desired to calculate the assay value of the sample analyzed, the calculation becomes:

$$\text{Assay, Weight \% Compound X} = \frac{(A - B) \times N \times M \times 100}{W \times 2000 \times D} \quad (2)$$

where:

M = molecular weight of Compound X, and

D = number of double bonds in Compound X.

11. Report

11.1 Report the bromine number to the nearest 0.1 unit.

12. Precision and Bias

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

12.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 0.514 % relative at 60 DF. The 95 % limit for the difference between two such runs is 1.4 % relative.

12.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability (Formerly called Repeatability))*—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been

estimated to be 0.511 % relative at 30 DF. The 95 % limit for the difference between two such averages is 1.4 % relative.

12.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 1.12 % relative at 9 DF. The 95 % limit for the difference between two such averages is 3.1 relative.

NOTE 7—The above precision statements are based on an interlaboratory study performed in 1962 on three materials (methyl methacrylate, cyclohexene, and undecenoic acid). One analyst in each of 10 laboratories performed duplicate determinations and repeated on a second day, for a

total of 120 determinations.¹² Practice E 180 was used in developing 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 analysis; Rosmund-Kuhnhehn reagent; total bromine number; unsaturated aliphatics; volumetric

¹² Details of the interlaboratory study are available as Research Report E15 - 0013 from ASTM Headquarters.

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