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Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration[1,2]

This standard is issued under the fixed designation D1159; 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~~ Scope*

1.1 This test method[3] covers the determination of the bromine number of the following materials:

1.1.1 Petroleum distillates that are substantially free of material lighter than isobutane and that have 90 % distillation points (by Test Method D86) under 327 °C (626 °F). This test method is generally applicable to gasoline (including leaded, unleaded, and oxygenated fuels), kerosine, and distillates in the gas oil range that fall in the following limits:

90 % Distillation Point, °C (°F)	Bromine Number, max[3]
Under 205 (400)	175
205 to 327 (400 to 626)	10

1.1.2 Commercial olefins that are essentially mixtures of aliphatic mono-olefins and that fall within the range of 95 to 165 bromine number (see Note 1). This test method has been found suitable for such materials as commercial propylene trimer and tetramer, butene dimer, and mixed nonenes, octenes, and heptenes. This test method is not satisfactory for normal alpha-olefins.

NOTE 1—These limits are imposed since the precision of this test method has been determined only up to or within the range of these bromine numbers.

1.2 The magnitude of the bromine number is an indication of the quantity of bromine-reactive constituents, not an identification of constituents; therefore, its application as a measure of olefinic unsaturation should not be undertaken without the study given in Annex A1.

1.3 For petroleum hydrocarbon mixtures of bromine number less than 1.0, a more precise measure for bromine-reactive constituents can be obtained by using Test Method D2710. If the bromine number is less than 0.5, then Test Method D2710 or the comparable bromine index methods for industrial aromatic hydrocarbons, Test Methods D1492 or D5776 must be used in

[1] This test method is under the jurisdiction of ASTM International Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of ASTM Subcommittee D02.06 on Analysis of Liquid Fuels and Lubricants. The technically equivalent standard as referenced is under the jurisdiction of the Energy Institute Subcommittee SC-G-2.

~~In the IP, this test method is under the jurisdiction of the Standardization Committee.~~

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[2] This test method has been developed through the cooperative effort between ASTM and the Energy Institute, London. ASTM and IP standards were approved by ASTM and EI technical committees as being technically equivalent but that does not imply both standards are identical.

[3] Dubois, H. D., and Skoog, D. A., "Determination of Bromine Addition Numbers," *Analytical Chemistry*, Vol 20, 1948, pp. 624–627.

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

accordance with their respective scopes. The practice of using a factor of 1000 to convert bromine number to bromine index is not applicable for these lower values of bromine number.

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

1.4.1 *Exception*—The values given in parentheses are for information only.

1.5 *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~~safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see Sections 7, 8, and 9.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[4]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure
D1193 Specification for Reagent Water
D1492 Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration
D2710 Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
D5776 Test Method for Bromine Index of Aromatic Hydrocarbons by Electrometric Titration

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *bromine ~~number—~~number, n—*the number of grams of bromine that will react with 100 g of the specimen under the conditions of the test.

4. Summary of Test Method

4.1 A known weight of the specimen dissolved in the selected solvent (see 8.1) maintained at 0 °C to 5 °C (32 °F to 41 °F) is titrated with standard bromide-bromate solution. The end point is indicated by a sudden change in potential on an electrometric end point titration apparatus due to the presence of free bromine.

5. Significance and Use

5.1 The bromine number is useful as a measure of aliphatic unsaturation in petroleum samples. When used in conjunction with the calculation procedure described in Annex A2, it can be used to estimate the percentage of olefins in petroleum distillates boiling up to approximately 315 °C (600 °F).

5.2 The bromine number of commercial aliphatic monoolefins provides supporting evidence of their purity and identity.

6. Apparatus

6.1 *Electrometric End Point Titration Apparatus*—Any apparatus designed to perform titrations to pre-set end points (see Note 2) may be used in conjunction with a high-resistance polarizing current supply capable of maintaining approximately 0.8 V across two platinum electrodes and with a sensitivity such that a voltage change of approximately 50 mV at these electrodes is sufficient to indicate the end point. Other types of commercially available electronic titrimeters, including certain pH meters, have also been found suitable.

[4] 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.

NOTE 2—Pre-set end point indicated with polarized electrodes provides a detection technique similar to the dead stop technique specified in previous versions of this test method.

6.2 *Titration Vessel*—A jacketed glass vessel approximately 120 mm high and 45 mm in internal diameter and of a form that can be conveniently maintained at 0 °C to 5 °C (32 °F to 41 °F).

6.3 *Stirrer*—Any magnetic stirrer system.

6.4 *Electrodes*—A platinum wire electrode pair with each wire approximately 12 mm long and 1 mm in diameter. The wires shall be located 5 mm apart and approximately 55 mm below the level of the titration solvent. Clean the electrode pair at regular intervals with 65 % nitric acid and rinse with distilled water before use.

6.5 *Buret*—Any delivery system capable of measuring titrant in 0.05 mL or smaller graduations.

7. Reagents

7.1 *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.[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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type III of Specification D1193.

7.3 *Acetic Acid, Glacial*—(**Warning—**Poison, corrosive-combustible, may be fatal if swallowed. Causes severe burns, harmful if inhaled.)

7.4 *Bromide-Bromate, Standard Solution*(0.2500 *M* as Br_2)—Dissolve 51.0 g of potassium bromide (KBr) and 13.92 g of potassium bromate ($KBrO_3$) each dried at 105 °C (220 °F) for 30 min in water and dilute to 1 L.

7.4.1 If the determinations of the bromine number of the reference olefins specified in Section 8 using this solution do not conform to the prescribed limits, or if for reasons of uncertainties in the quality of primary reagents it is considered desirable to determine the molarity of the solution, the solution shall be standardized and the determined molarity used in subsequent calculations. The standardization procedure shall be as follows:

7.4.1.1 To standardize, place 50 mL of glacial acetic acid and 1 mL of concentrated hydrochloric acid (**Warning—**Poison corrosive. May be fatal if swallowed. Liquid and vapor causes severe burns. Harmful if inhaled; relative density 1.19.) in a 500 mL iodine number flask. Chill the solution in a bath for approximately 10 min and, with constant swirling of the flask, add from a 10 mL calibrated buret, 5 mL ± 0.01 mL of the bromide-bromate standard solution at the rate of 1 or 2 drops per second. Stopper the flask immediately, shake the contents, place it again in the ice bath, and add 5 mL of Kl solution in the lip of the flask. After 5 min remove the flask from the ice bath and allow the Kl solution to flow into the flask by slowly removing the stopper. Shake vigorously, add 100 mL of water in such a manner as to rinse the stopper, lip and walls of the flask, and titrate promptly with sodium thiosulfate ($Na_2S_2O_3$) solution. Near the end of the titration, add 1 mL of starch indicator solution and titrate slowly to disappearance of the blue color. Calculate the molarity of the bromide-bromate solution as follows:

$$M_1 = \frac{AM_2}{(5)\,(2)} \tag{1}$$

where:

M_1 = molarity of the bromide-bromate solution, as Br_2,
A = millilitres of $Na_2S_2O_3$ solution required for titration of the bromide-bromate solution, and,

[5] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, DC. For ~~Suggestions~~suggestions on the testing of reagents not listed by the American Chemical Society, see ~~*Annual*~~*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.

TABLE 1 Physical Properties of Purified Olefins

Compound	Boiling Point, °C	Density at 20 °C, g/mL	Index of Refraction, *D* Line at 20°C
Cyclohexene	82.5 to 83.5	0.8100	1.4465
Diisobutene[A]	101 to 102.5	0.7175 ± 0.0015	1.4112

[A] Only the 2,4,4-trimethyl-1-pentene isomer.

M_2 = molarity of $Na_2S_2O_3$ solution,
5 = millilitres of bromide—bromate solution, and
2 = number of electrons transferred during redox titration of bromide-bromate solution.

Repeat the standardization until duplicate determinations do not differ from the mean by more than ±0.002 M.

7.5 *Methanol*—(**Warning—**Flammable. Vapor harmful. Can be fatal or cause blindness if swallowed or inhaled. Cannot be made non-poisonous.)

7.6 *Potassium Iodide Solution* (150 g/L)—Dissolve 150 g of potassium iodide (Kl) in water and dilute to 1 L.

7.7 *Sodium Thiosulfate, Standard Solution* (0.1 *M*)—Dissolve 25 g of sodium thiosulfate ($Na_2S_2O_3·5H_2O$) in water and add 0.1 g of sodium carbonate (Na_2CO_3) to stabilize the solution. Dilute to 1 L and mix thoroughly by shaking. Standardize by any accepted procedure that determines the molarity with an error not greater than ±0.0002. Restandardize at intervals frequent enough to detect changes of 0.0005 in molarity.

7.8 *Starch Indication Solution* — Mix 5 g of soluble starch with about 3 mL to 5 mL of water. If desired, add about 0.65 g salicylic acid as preservative. Add the slurry to 500 mL of boiling water and continue boiling for 5 min to 10 min. Allow to cool, and decant the clear, supernatant liquid into glass bottles and seal well. Starch solutions (some preserved with salicylic acid) are also commercially available and may be substituted.

7.9 *Sulfuric Acid* (1 + 5)—Carefully mix one volume of concentrated sulfuric acid (H_2SO_4, rel dens 1.84) with five volumes of water. (**Warning—**Poison. Corrosive. Strong oxidizer. Contact with organic material can cause fire. Can be fatal if swallowed.)

7.10 *Titration Solvent*—Prepare 1 L of titration solvent by mixing the following volumes of materials: 714 mL of glacial acetic acid, 134 mL of 1,1,1-trichloroethane (or dichloromethane), 134 mL of methanol, and 18 mL of H_2SO_4(1 + 5).

7.11 *1,1,1-Trichloroethane*—(**Warning—**Harmful if inhaled. High concentrations can cause unconsciousness or death. Contact may cause skin irritation and dermatitis.)

7.12 *Dichloromethane*—(**Warning—**The replacement of 1,1,1-trichloroethane, an ozone-depleting chemical, is necessary because its manufacture and import has been discontinued. Dichloromethane is temporarily being allowed as an alternative to 1,1,1-trichloroethane until a permanent replacement can be identified and adopted by ASTM International. A program to identify and evaluate candidate solvents is currently underway in Subcommittee D02.04.)

NOTE 3—Commercially available reagents can be used in place of laboratory preparations.

8. Check Procedure

8.1 In case of doubt in applying the procedure to actual samples, the reagents and techniques can be checked by means of determinations on freshly purified cyclohexene or diisobutene. (**Warning—**The user of this test method may choose to use either 1,1,1-trichloroethane or dichloromethane to the exclusion of the other solvent. The selected solvent is to be used for all operations, that is, in the preparation of the titration solvent, for the dilution of samples, and as the titration blank.) Proceed in accordance with Section 9, using a sample of either 0.6 g to 1 g freshly purified cyclohexene or diisobutene (see Table 1) or 6 g to 10 g of ~~10 mass percent~~ 10 % by mass solutions of these materials in 1,1,1-trichlorethane. (**Warning—**Flammable.)

8.2 If the reagents and techniques are correct, values within the following should be obtained:

TABLE 2 Specimen Size

Bromine Number	Specimen Size, g
0 to 10	20 to 16
Over 10 to 20	10 to 8
Over 20 to 50	5 to 4
Over 50 to 100	2 to 1.5
Over 100 to 150	1.0 to 0.8
Over 150 to 200	0.8 to 0.6

Standard	Bromine Number
Cyclohexene, purified (see 7.4.1, 9.3, and 8.1)	187 to 199 (see 9.5)
Cyclohexene, 10 % solution	18 to 20
Diisobutene, purified (see 7.4.1, 8.3, and 8.1)	136 to 144 (see 9.5)
Diisobutene, 10 % solution	13 to 15

The reference olefins yielding the above results are characterized by the properties shown in Table 1. The theoretical bromine numbers of cyclohexene and diisobutene are 194.6 and 142.4, respectively.

8.3 Purified samples of cyclohexene and diisobutene can be prepared from cyclohexene and diisobutene,[6] by the following procedure:

8.3.1 Add 65 g of activated silica gel, ~~75 to 150 µm~~ 75 µm to 150 µm (100 to 200 mesh) manufactured to ensure minimum olefin polymerization[7] to a column approximately 16 mm in inside diameter and 760 mm in length, that has been tapered at the lower end and that contains a small plug of glass wool at the bottom. A 100 mL buret, or any column that will give a height-to-diameter ratio of the silica gel of at least 30:1, will be suitable. Tap the column during the adding of the gel to permit uniform packing.

8.3.2 To the column add 30 mL of the olefin to be purified. When the olefin disappears into the gel, fill the column with methanol. Discard the first 10 mL of percolate and collect the next 10 mL that is the purified olefin for test of the bromine number procedure. Determine and record the density and refractive index of the purified samples at 20 °C. Discard the remaining percolate. (**Warning—**If distillation of impure olefins is needed as a pre-purification step, a few pellets of potassium hydroxide should be placed in the distillation flask and at least 10 % residue should remain to minimize the hazards from decomposition of any peroxides that may be present.)

9. Procedure

9.1 Place 10 mL of 1,1,1-trichloroethane or dichloromethane in a 50 mL volumetric flask and, by means of a pipet, introduce a test specimen as indicated in Table 2. Either obtain the weight of specimen introduced by difference between the weight (to the nearest 1 mg) of the flask before and after addition of specimen or, if the density is known accurately, calculate the weight from the measured volume. Fill the flask to the mark with the selected solvent and mix well. (**Warning—**Hydrocarbons, particularly those boiling below 205 °C (400 °F), are flammable.)

9.1.1 Frequently, the order of magnitude of the bromine number of a specimen is unknown. In this case, a trial test is recommended using a 2 g specimen in order to obtain the approximate magnitude of the bromine number. This exploratory test shall be followed with another determination using the appropriate specimen size as indicated in Table 2.

9.1.2 The test specimen taken shall not exceed 20 mL and the volume of bromide-bromate titrant used shall not exceed 10 mL and no separation of the reaction mixture into two phases shall occur during the titration. Difficulty may be experienced in dissolving specimen of the high boiling ranges in the titration solvent; this can be prevented by the addition of a small quantity of toluene.

9.2 Cool the titration vessel to 0 °C to 5 °C (32 °F to 41 °F) and maintain the contents at this temperature throughout the titration. Switch on the titrimeter, and allow the electrical circuit to become stabilized.

[6] The sole source of supply of No. 13019 (cyclohexene) and No. P2125 (diisobutene) known to the committee at this time is Eastman, Rochester, NY. 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.

[7] The sole source of supply of the apparatus known to the committee at this time is Code 923, available from W.R. Grace and Company, Davison Chemical Division, Baltimore, MD 21203. 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.

9.3 Introduce 110 mL of titration solvent into the vessel and pipet in a 5 mL aliquot of the sample solution from the 50 mL volumetric flask. Switch on the stirrer and adjust to a rapid stirring rate, but avoid any tendency for air bubbles to be drawn down to the solution.

9.4 Set the end point potential. With each instrument, the manufacturer's instructions should be followed for end point setting and to achieve the sensitivity in the platinum electrode circuit specified in 6.1.

9.5 Depending on the titrator apparatus, add the bromide-bromate solution manually or by microprocessor control in small increments from the buret. The endpoint of the titration is achieved when the potential reaches the pre-set value (see 9.4) and persists for more than 30 s.

9.6 *Blanks*—Perform duplicate blank titrations of each batch of titration solvent. Do this by repeating 9.3 through 9.5 for each blank determination, substituting 5 mL of the selected solvent (1,1,1-trichloroethane or dichloromethane) in place of the sample solution. Less than 0.1 mL of bromide-bromate solution should be required. If more than 0.1 mL is used, discard the analysis, prepare fresh titration solvent and fresh reagents and repeat the analysis.

10. Calculation

10.1 Calculate the bromine number as follows:

$$bromine\ number = \frac{(A - B)\,(M_1)\,(15.98)}{W} \tag{2}$$

where:

A = millilitres of bromide-bromate solution required for titration of the test aliquot,
B = millilitres of bromide-bromate solution required for titration of the blank,
M_1 = molarity of the bromide-bromate solution, as Br_2,
W = grams of test specimen in the aliquot, and
15.98 = factor for converting g of bromine per 100 g of specimen and incorporating molecular weight of bromine (as Br_2) and conversion of mL to L.

11. Precision and Bias[8]

11.1 *Precision*—The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:

11.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty.
Petroleum distillates:

$$90\,\%\ \text{distillation point under } 205°C\ r = 0.11\ (X^{0.70}) \tag{3}$$

$$90\,\%\ \text{distillation point between 205 and } 327°C\ r = 0.11\ (X^{0.67}) \tag{4}$$

where: X = sample mean.
Commercial olefins:

$$r = 3 \tag{5}$$

11.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty:
Petroleum Distillates:

$$90\,\%\ \text{distillation point under } 205°C\ R = 0.72\ (X^{0.70}) \tag{6}$$

[8] Supporting data (round robin data and statistical analysis for products having 90 % distillation points under ~~205°C)~~205 °C) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1290. Contact ASTM Customer Service at service@astm.org.