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An American National Standard

Designation: 130/98

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

This standard is issued under the fixed designation D 1159; 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 Department of Defense.

1. Scope

1.1 This test method[2] 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 D 86) 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[2]
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 D 2710. If the bromine number is less than 0.5, then Test Method D 2710 or the comparable bromine index methods for industrial aromatic hydrocarbons, Test Methods D 1492 or D 5776 must be used in 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. The inch-pound units given in parentheses are for information purposes 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 practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Sections 7, 8, and 9.

2. Referenced Documents

2.1 *ASTM Standards:*

- D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure[3]
- D 1193 Specification for Reagent Water[4]
- D 1492 Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration[5]
- D 2710 Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration[3]
- D 5776 Test Method for Bromine Index Aromatic of Hydrocarbons by Electrometric Titration[5]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *bromine number*—the number of grams of bromine that will react with 100 g of the specimen under the conditions of the test.

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0D on Physical Methods.

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

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[2] See Dubois, H. D., and Skoog, D. A., "Determination of Bromine Addition Numbers," *Analytical Chemistry*, Vol 20, 1948, pp. 624–7.

[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 06.04.

4. Summary of Test Method

4.1 A known weight of the specimen dissolved in the selected solvent (see 8.1) maintained at 0 to 5°C (32 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.

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 to 5°C (32 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.[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.

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 D 1193.

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 ± 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,
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 ($Na_2S_2O_3{\cdot}5H_2O$) 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.

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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*, BDH Ltd., Poole, Dorset, U.K. and the *United States Pharmacopeia and National Formulary*, U. S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.