



Designation: D 1159 – 9801

An American National Standard

Designation: 130/98

## Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee ~~D-2~~ 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.

Current edition approved ~~Apr. 10, 1998~~ Nov. 10, 2001. Published ~~September 1998~~ November 2001. Originally published as D 1159 – 51 T. Last previous edition D 1159 – 938.

## 1. Scope

1.1 This test method<sup>2</sup> 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 <sup>2</sup>
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 ~~Note 3 through Note 11~~. Sections 7, 8, and 9.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure<sup>3</sup>

D 1193 Specification for Reagent Water<sup>4</sup>

D 1492 Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration<sup>5</sup>

D 2710 Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration<sup>3</sup>

D 5776 Test Method for Bromine Index Aromatic of Hydrocarbons by Electrometric Titration<sup>5</sup>

## 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.

## 4. Summary of Test Method

4.1 A known weight of the specimen dissolved in the selected solvent (see ~~Note 9~~ 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 ~~10~~ 2) may be used in conjunction with a high-resistance polarizing current supply capable of maintaining approximately 0.8 V

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

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 06.04.

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.<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 reagent water as defined by Type III of Specification D 1193.

7.3 *Acetic Acid, Glacial*—(**Warning—See Note 3.**)

NOTE 3—**Warning: Poison;—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<sub>2</sub>)*— Dissolve 51.0 g of potassium bromide (KBr) and 13.92 g of potassium bromate (KBrO<sub>3</sub>) 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—See Note 4—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 KI solution in the lip of the flask. After 5 min remove the flask from the ice bath and allow the KI 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<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) 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:

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

where:

$M_1$  = molarity of the bromide-bromate solution, as Br<sub>2</sub>,

$A$  = millilitres of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required for titration of the bromide-bromate solution, and,

$M_2$  = molarity of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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. ~~NOTE 4—**Warning: Poison corrosive. May be fatal if swallowed. Liquid and vapor causes severe burns. Harmful if inhaled; relative density 1.19.**~~

7.5 *Methanol*—(**Warning—See Note 5.**)

NOTE 5—**Warning: Flammable;—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 (KI) in water and dilute to 1 L.

<sup>6</sup> *Annual Book Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of ASTM reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory*, Vol 05-02; BDH Ltd., Poole, Dorset, U.K. and the *United States Pharmacopeia and National Formulary*, U. S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

7.7 *Sodium Thiosulfate, Standard Solution* (0.1 M)—Dissolve 25 g of sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O) in water and add 0.1 g of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) 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 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 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<sub>2</sub>SO<sub>4</sub>, rel dens 1.84) with five volumes of water.

~~NOTE 6—Warning: Poison. 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<sub>2</sub>SO<sub>4</sub>(1 + 5).

7.11 *1,1,1-Trichloroethane*—(Warning—See Note 7.)

~~NOTE 7—Warning: Harmful—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. A program to identify and evaluate candidate solvents is currently underway in Subcommittee D02.04.)

~~NOTE 8—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 3—Commercially available reagents can be identified and adopted by ASTM. A program to identify and evaluate candidate solvents is currently underway in Subcommittee D02.04.~~

~~NOTE 9—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 place of the titration solvent, for the dilution of samples, and as the titration blank—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—See Note 9.)—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 to 1 g freshly purified cyclohexene or diisobutene (see Table 1) or 6 to 10 g of 10 mass percent solutions of these materials in 1,1,1-trichloroethane.

~~NOTE 10—Warning: Flammable. 1,1,1-trichloroethane. (Warning—Flammable.)~~

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

Standard	Bromine Number
Cyclohexene, purified (see 7.4.1, 9.3, and Note 11) — Note 10)	487 to 499 (see 9.5)
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 Note 11) — Note 10)	436 to 444 (see 9.5)
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.

**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 <sup>A</sup>	101 to 102.5	0.7175 ±0.0015	1.4112

<sup>A</sup> Only the 2,4,4-trimethyl-1-pentene isomer.

8.3 Purified samples of cyclohexene and diisobutene can be prepared from cyclohexene and diisobutene,<sup>7</sup> by the following procedure:

8.3.1 Add 65 g of activated silica gel, 75 to 150  $\mu\text{m}$  (100 to 200 mesh) manufactured to ensure minimum olefin polymerization<sup>8</sup> to<sup>9</sup> 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.

~~NOTE 11—~~**Caution:** If 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—**See Note 12.)

~~NOTE 12—~~**Warning:** Hydrocarbons;—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 10 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 to 5°C (32 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.

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.

~~Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed~~

~~<sup>7</sup> Available from Eastman, Rochester, NY, by the American Chemical Society, see *Analar Standards for Laboratory*, BDH Ltd., Poole, Dorset, U.K. specifying No. 13019 (cyclohexene) and the *United States Pharmacopeia and National Formulary*, U. S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD: No. P2125 (diisobutene).~~

~~<sup>8</sup> Available from W.R. Grace~~

~~<sup>9</sup> Refer to ASTM Research Report RR: D02-1290 covering the round robin data and Company, Davison Chemical Division, Baltimore, MD 21203, by specifying Code 923, statistical analysis for products having 90 % distillation points under 205°C.~~

~~<sup>9</sup> Available from Eastman, Rochester, NY; W.R. Grace and Company, Davison Chemical Division, Baltimore, MD 21203, by specifying No. 13019 (cyclohexene) and No. P2125 (diisobutene); Code 923.~~

**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

## 10. Calculation

10.1 Calculate the bromine number as follows:

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

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  $\text{Br}_2$ ,
- $W$  = 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  $\text{Br}_2$ ) and conversion of mL to L.

## 11. Precision and Bias <sup>8</sup>

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:

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

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

where:  $X$  = sample mean.

Commercial olefins:

$$r = 3 \quad (5)$$

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:

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

$$90 \% \text{ distillation point between } 205 \text{ and } 327^\circ\text{C } R = 0.78 (X^{0.67}) \quad (7)$$

where:  $X$  = sample mean.

Commercial olefins <sup>10</sup>

$$R = 12 \quad (8)$$

11.2 *Bias*—The procedure for measuring bromine number has no bias because the value of bromine number can be defined only in terms of a test method.

**NOTE 13**—~~The 4~~—The precision of this test method was determined using 1,1,1-trichloroethane as the sample dilution solvent and as a component of the titration solvent. It is not known whether the precision estimates are applicable when using dichloromethane in place of 1,1,1-trichloroethane.

## 12. Keywords

12.1 aliphatic olefins; bromine number; electrometric titration; petroleum distillates

<sup>8</sup> Refer to ASTM Research Report RR: D02-1290 covering the round robin data and statistical analysis for products having 90 % distillation points under 205°C.

<sup>10</sup> Provisional value obtained from a limited amount of data.



**ANNEXES**
**(Mandatory Information)**
**A1. REPORTED BEHAVIOR OF COMPOUNDS BY THE ELECTROMETRIC BROMINE NUMBER METHOD**

A1.1 Technically, the bromine number is the number of grams of bromine reacting with 100 g of the sample under prescribed conditions. By this definition, bromine consumed by addition, substitution, oxidation, and reactions with sulfur, nitrogen, and oxygen-containing compounds is included in the bromine number of the material. The use of the bromine number under determination in the estimation of olefinic unsaturation depends on the fact that the addition reaction proceeds rapidly and completely under most conditions. The addition of bromine proceeds readily at temperatures down to or below 0°C. Decreasing temperature of reaction, time of contact, and concentration of free bromine tend to retard both substitution and oxidation reactions. Other factors, such as solvent medium, extent of agitation, and exposure to actinic light, also influence the rate of the various reactions.

A1.2 Experience has shown that no single set of test conditions will direct the reaction of bromine in one manner to the exclusion of the others. For this reason, the conditions of bromine number tests are usually established on an empirical basis to give reasonable values with representative materials.

A1.3 The possibility of multiple reactions occurring concurrently and the variable behavior to certain materials in the presence of bromine imposes an element of uncertainty in the interpretation of results. A knowledge of the material being handled and its response to bromine greatly reduces the risk of misinterpretation.

A1.4 Bromine number data have been obtained for a variety of petroleum hydrocarbons and certain nonhydrocarbons associated with petroleum, by the electrometer bromine number procedure. These data, which were submitted by cooperators, are presented in Table A1.1.

A1.5 It is intended that this information serve as a general guide in the interpretation of bromine numbers on petroleum products. It is recognized that the bromine number data recorded in this table are of limited value owing to incompleteness; however, it is considered that their usefulness will be amplified as more bromine number data are contributed by cooperators.

**TABLE A1.1 Reported Behavior of Compounds by the Electrometric Bromine Number Method**

Compound	Purity, % <sup>A</sup>	Bromine Number		
		Theory	Found	Deviation
Paraffins				
Hexane	99.96 <sup>B</sup>	0.0	0.0	0.0
2-Methylhexane	99.88	0.0	0.0	0.1
Heptane	<sup>C</sup>	0.0	0.1	+ 0.1
Octane	99.94	0.0	0.0	0.0
2,2,4-Trimethylpentane	99.96	0.0	0.1	+ 0.1
Straight Chain Olefins				
1-Pentene	99.7	228.0	208	-20
<i>trans</i> -2-Pentene	99.91	228.0	235	+ 7
1-Hexene	99.80	189.9	181	-9
<i>cis</i> -2-Hexene	99.83	189.9	189	-1
<i>trans</i> -2-Hexene	99.87	189.9	189	-1
<i>cis</i> -3-Hexene	99.94	189.9	193	+ 3
<i>trans</i> -3-Hexene	...	189.9	191.4	+ 1.5
1-Heptene	99.8	162.8	136	-27
<i>trans</i> -2-Heptene	99.85	162.8	163	0
<i>trans</i> -3-Heptene	99.80	162.8	163	0
1-Octene	99.7	142.4	132	-10
2-Octene	...	142.4	139	- 3
<i>trans</i> -4-Octene	99.84	142.4	149	+ 7
1-Decene	99.89	114.1	111.4	- 2.7
1-Dodecene	99.9	95.1	82.9	-12.2
1-Tridecene	99.8	87.7	81.4	-6.3
1-Tetradecene	99.7	81.4	70.8	-10.6
1-Pentadecene	99.8	76.0	62.9	-13.1
1-Hexadecene	99.84	71.2	62.8	- 8.4
Branched Chain Olefins				
2-Methyl-1-butene	99.90	228.0	231.8	+ 3.8
2-Methyl-2-butene	99.94	228.0	235	7
2,3-Dimethyl-1-butene	99.86	189.9	194	+ 4

**TABLE A1.1** *Continued*

Compound	Purity, % <sup>A</sup>	Bromine Number		
		Theory	Found	Deviation
3,3-Dimethyl-1-butene	99.91	189.9	167	- 23
2-Ethyl-1-butene	99.90	189.9	198	+ 8
2,3-Dimethyl-2-butene	99.90	189.9	191	+ 1
2-Methyl-1-pentene	99.92	189.9	182	- 8
3-Methyl-1-pentene	99.70	189.9	152	- 38
4-Methyl-1-pentene	99.82	189.9	176	- 14
2-Methyl-2-pentene	99.91	189.9	190	0
3-Methyl- <i>cis</i> -2-pentene	99.85	189.9	193.7	+ 3.8
3-Methyl- <i>trans</i> -2-pentene	99.86	189.9	191	+ 1
4-Methyl- <i>cis</i> -2-pentene	99.92	189.9	190	0
4-Methyl- <i>trans</i> -2-pentene	99.75	189.9	190	0
2,3,3-Trimethyl-1-butene	99.94	162.8	161	- 2
3-Methyl-2-Ethyl-1-butene	99.8	162.8	165.4	+ 2.6
2,3-Dimethyl-1-pentene	99.80	162.8	158.5	- 4.3
2,4-Dimethyl-1-pentene	99.87	162.8	152.8	- 10.0
2,3-Dimethyl-2-pentene	99.6	162.8	162.3	- 0.5
4,4-Dimethyl- <i>cis</i> -2-pentene	99.79	162.8	159	- 4
4,4-Dimethyl- <i>trans</i> -2-pentene	99.91	162.8	158	- 5
3-Ethyl-1-pentene	99.85	162.8	173.1	+ 10.3
3-Ethyl-2-pentene	99.80	162.8	165	+ 2
2-Methyl-1-hexene	99.88	162.8	161	- 2
5-Methyl-1-hexene	99.80	162.8	154	- 9
3-Methyl- <i>cis</i> -2-hexene	99.8	162.8	163.6	+ 0.8
2-Methyl- <i>trans</i> -3-hexene	99.9	162.8	163.4	+ 0.6
2-Methyl-3-Ethyl-1-pentene	99.81	142.4	139.8	- 2.6
2,4,4-Trimethyl-1-pentene	99.91	142.4	137.0	- 5.4
2,4,4-Trimethyl-2-pentene	99.92	142.4	141.2	- 1.2
Diisobutene	<i>D</i>	142.4	139.8 <sup>D</sup>	- 2.6
2-Ethyl-1-hexene	<i>E</i>	142.4	140.2	- 2.2
2,3-Dimethyl-2-hexene	99.71	142.4	143	+ 1
2,5-Dimethyl-2-hexene	99.8	142.4	142.8	+ 0.4
2,2-Dimethyl- <i>trans</i> -3-hexene	99.80	142.4	139	- 3
Triisobutene	99.0 <sup>F</sup>	95	57.5	- 37.5
Nonconjugated Cyclic Diolefins				
4-Ethenyl-1-cyclohexene (4-vinyl-1-cyclohexene)	99.90	295.5	210 <sup>G</sup>	(- 85)
di-1,8(9)- <i>p</i> -Menthadiene (dipentene)	98-100 <sup>H</sup>	234.6	225.2	- 9.4
Conjugated Diolefins				
2-Methyl-1,3-butadiene (isoprene)	99.96	470	235.7	- 234
<i>cis</i> -1,3-Pentadiene	99.92	470	285.3	- 185
<i>trans</i> -1,3-Pentadiene	99.92	470	234	- 236
2-Methyl-1,3-Pentadiene	95 + <sup>I</sup>	389	197.3	- 192
2,3-Dimethyl-1,3-Butadiene	99.93	389	186.1	- 203
Nonconjugated Diolefins				
1,2-Pentadiene	99.66	470	230	- 240
1,4-Pentadiene	99.93	470	185	- 285
2,3-Pentadiene	99.85	470	227	- 243
1,5-Hexadiene	99.89	389	352	- 37
Aromatics with Unsaturated Side Chains				
Phenylethylene (styrene)	<i>J</i>	153.4	123.6	- 29.8
Methylphenylethylene ( $\alpha$ -methylstyrene)	<i>J</i>	135.3	133.2	- 2.1
Amylbenzene	97.8 <sup>K</sup>	135.2	0.0	135.2
Cyclic Olefins				
Cyclopentene	99.97	234.6	237	+ 2
Cyclohexene	99.98	194.6	193.2	- 1.4
Cyclohexene	<i>D</i>	194.6	192.8 <sup>D</sup>	- 1.8
1-Methylcyclopentene	99.86	194.6	209	+ 14
1-Methylcyclohexene	99.82	166	162	- 4
Ethenylcyclopentane (Vinylcyclopentane)	99.91	166	164	- 2
Ethylidenecyclopentane	99.96	166.2	167.7	+ 1.5
1,2-Dimethylcyclohexene	99.94	145.0	150.9	+ 5.9
3-Cyclopentyl-1-propene	99.87	145.0	140.9	- 4.1
Ethylidenecyclohexane	99.86	145.0	147.0	+ 2.0
Ethenylcyclohexane (Vinylcyclohexane)	99.95	145	139	- 6
1-Ethylcyclohexene	99.83	145	146.6	+ 1.6
Indene	...	137.7	134	- 4
Aromatics, Monocyclic				
Benzene	99.98	0.0	0.1	+ 0.1



**TABLE A1.1** *Continued*

Compound	Purity, % <sup>A</sup>	Bromine Number		
		Theory	Found	Deviation
Toluene	99.97	0.0	0.1	+ 0.1
o-Xylene	99 + <sup>L</sup>	0.0	0.0	0.0
m-Xylene	99 + <sup>L</sup>	0.0	0.0	0.0
p-Xylene	99 + <sup>L</sup>	0.0	0.0	0.0
isopropylbenzene (Cumene)	99.95	0.0	0.0	0.0
1,2,4-Trimethylbenzene (Pseudocumene)	99.67	0.0	0	0
1,3,5-Trimethylbenzene (Mesitylene)	<sup>M</sup>	0.0	0.3	+ 0.3
1,3-Dimethyl-4-ethylbenzene	99.9	0.0	0.0	0.0
1,2,4,5-Tetramethylbenzene (Durene)	99.86	0.0	0.1	+ 0.1
1,2,3,5-Tetramethylbenzene (Isodurene)	<sup>M</sup>	0.0	0.3	+ 0.3
<i>t</i> -Butylbenzene	99.73 <sup>B</sup>	0.0	0.0	0.0
<i>t</i> -Amylbenzene	<sup>F</sup>	0.0	0.7	+ 0.7
Aromatics, Bicyclic				
Phenylbenzene (Biphenyl)	<sup>M</sup>	0.0	0.0	0.0
Naphthalene	99.96	0.0	0	0
1, 2,3,4-Tetrahydronaphthalene (Tetralin)	99.9	0.0	0.2	+ 0.2
1-Methylnaphthalene	99.78	0.0	0.0	0.0
2-Methylnaphthalene	99.91	0.0	0.0	0.0
2,3-Dihydroindene (Indan)	99.9	0.0	0.0	0.0
Cyclohexylbenzene	99.93	0.0	0	0
Aromatics, Polycyclic				
Athracene	<sup>M</sup>	0.0	11.8	+ 11.8
Phenanthrene	<sup>M</sup>	0.0	3.9	+ 3.9
Cycloparaffins				
Methylcyclopentane	99.99 <sup>B</sup>	0.0	0.0	0.0
Methylcyclohexane	99.97	0.0	0	0
Isopropylcyclopentane	99.8	0.0	0.0	0.0
<i>cis</i> -Hexahydroindan ( <i>cis</i> -Hydrindan)	99.94	0.0	0.0	0.0
<i>trans</i> -Hexahydroindan ( <i>trans</i> -Hydrindan)	99.71	0.0	0.0	0.0
<i>tert</i> -Butylcyclohexane	99.95	0.0	0	0
Cyclopentylcyclopentane	99.95	0.0	0.0	0.0
<i>cis</i> -Decahydronaphthalene ( <i>cis</i> -decalin)	98 + <sup>I</sup>	0.0	0.11	+ 0.11
<i>trans</i> -Decahydronaphthalene ( <i>trans</i> -decalin)	98 + <sup>I</sup>	0.0	1.64	+ 1.64
Sulfur Compounds				
Ethanethiol (ethyl mercaptan)	99.95	0.0	209	+ 209
3-Thiapentane (ethyl sulfide)	99.94	0.0	184	+ 184
2,3-Dithiabutane (methylsulfide)	99.97	0.0	1.1	+ 1.1
Thiacyclobutane (trimethylene sulfide)	99.95	0.0	214	+ 214
Thophene	99.99	0.0	0.4	+ 0.4
Thiacyclopentane (tetrahydrothiophene)	99.95	0.0	183	+ 183
3,4-Dithiahexane (diethylsulfide)	99.90	0.0	0.4	+ 0.4
2-Methyl 2-propanethiol ( <i>tert</i> -butyl mercaptan)	99.92	0.0	141	+ 141
1-Pentanethiol (amyl mercaptan)	99.92	0.0	83	+ 83
Nitrogen Compounds				
Brodine	99.85	0.0	11.8	+ 11.8
iodine	<sup>N</sup>	0.0	1.4	+ 1.4
2-Methylpyridine	99.90	0.0	0.9	+ 0.9
4-Methylpyridine	99 + <sup>O</sup>	0.0	1.7	+ 1.7
2,4,6-Trimethylpyridine	99 + <sup>O</sup>	0.0	2.7	+ 2.7
2-(5-nonyl) pyridine	<sup>M</sup>	0.0	1.4	+ 1.4
Pyrrrole	99.99	0.0	873	+ 873
2-Methylpyrrrole	98 + <sup>N</sup>	0.0	708	+ 708
2,4-Dimethylpyrrrole	98 + <sup>N</sup>	0.0	484	+ 484
2,5-Dimethylpyrrrole	99.9 <sup>P</sup>	0.0	869	+ 869
2,4-Dimethyl-3-ethylpyrrrole	98 + <sup>N</sup>	0.0	248	+ 248
1-Butyl 1-(1) pyrrrole	98 + <sup>N</sup>	0.0	472	+ 472
Oxygen Compounds				
Acetone	<sup>O</sup>	0.0	0.0	0.0
Methylethylketone	<sup>R</sup>	0.0	0.0	0.0

**TABLE A1.1** *Continued*

Compound	Purity, % <sup>A</sup>	Bromine Number		
		Theory	Found	Deviation
Miscellaneous				
Ethanolamine	<i>M</i>	0.0	1.5	+ 5
Ethylene dichloride	<i>O</i>	0.0	0.0	0.0
Ethylene dibromide	<i>O</i>	0.0	0.0	0.0
Tetraethyllead (TEL)	<i>S</i>	(49.5) <sup>T</sup>	52.7	(+ 3.2)
Tetramethyllead (TML)	<i>S</i>	(59.8) <sup>T</sup>	62.6	(+ 2.8)
AK 33X	<i>S</i>	(73.4) <sup>T</sup>	0.6	(-72.8)
"Ethyl" orange dye	<i>S</i>	...	0.0	...

<sup>A</sup> API Standard Samples, unless otherwise noted.

<sup>B</sup> Phillips research grade product.

<sup>C</sup> Phillips pure grade product, distilled, heart-cut percolated through Si gel.

<sup>D</sup> Average value obtained in September 1957 Cooperative Program on purified Eastman product.

<sup>E</sup> Dow Research Chemical.

<sup>F</sup> Purity not stated.

<sup>G</sup> Approximate value.

<sup>H</sup> Hercules Inc., experimental sample.

<sup>I</sup> From Penn State University.

<sup>J</sup> Eastman white label product, distilled, 50-mm pressure just prior to test.

<sup>K</sup> M C and B chemical. Purity determined by GC, impurities not identified.

<sup>L</sup> Phillips pure grade product.

<sup>M</sup> Eastman white label product.

<sup>N</sup> Samples supplied by API Project 52.

<sup>O</sup> Purity estimated by spectra and GLC.

<sup>P</sup> Purity estimated from freezing point.

<sup>Q</sup> B and A Reagent chemical (Code No. 1004).

<sup>R</sup> M C and B chemical (Code No. 2609).

<sup>S</sup> Ethyl Corporation products.

<sup>T</sup> Calculated values based on the reaction of one mole of bromine with the organometallic compound.

## A2. CALCULATION OF OLEFIN CONTENT

### A2.1 Scope

A2.1.1 This procedure covers the calculation of the volume percentage of olefins from the bromine number in straight-run, reformed, cracked gasolines and commercial gasolines that have a 90 % boiling point below 200°C (392°F); and turbine fuel and kerosine etc., boiling below 315°C (600°F) and having a bromine number of less than 20.

A2.1.2 The procedure is not intended for synthetic olefinic blends of pure or nearly pure compounds having a boiling range of less than 14°C (25°F).

A2.1.3 Sulfur, nitrogen, or oxygen compounds, if present in concentrations of 1 volume % or greater will reduce the accuracy (see Note A2.1).

### A2.2 Procedure

A2.2.1 Determine the bromine number in accordance with this test method.

NOTE A2.1—For information on types of compounds that may yield anomalous data in the bromine number test, see Annex A1. In the case of special samples that contain high concentrations of certain hydrocarbon types, caution in the interpretation of the bromine number is needed.

A2.2.2 Calculate the concentration of olefins from the bromine number as follows :

$$\text{olefins, mass \%} = f BM/160 \quad (\text{A2.1})$$

where:

*f* = boiling range correction (see Fig. A2.1 and Table A2.1),

*B* = bromine number expressed as grams of bromine/100 g of sample, and

*M* = molecular weight (relative molecular mass) of olefins (see Table A2.2).

NOTE A2.2—The boiling range correction is needed for cracked naphthas since it is an empirical fact that the percentage by volume of olefins is higher in the lower boiling fractions and that these olefins are also of lower relative molecular mass (molecular weight).

A2.2.3 Using the 50 % boiling point (see Test Method D 86), estimate the average density of the olefins using Fig. A2.2. Multiply the mass percentage of olefins (as calculated in A2.2.2) by the ratio of the density of the original sample to the density of the olefins to obtain percentage by volume as follows:

$$\text{olefins, volume \%} = (A/B) \times C \quad (\text{A2.2})$$

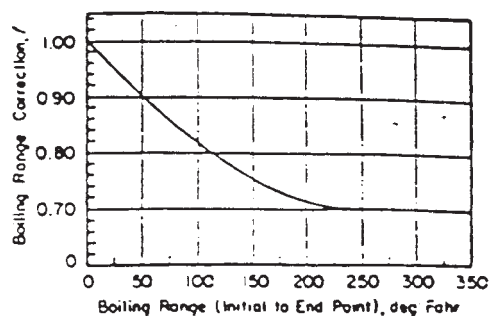


FIG. A2.1 Boiling Range Correction

TABLE A2.1 Boiling Range Corrections for Olefins

Boiling Range Correction, f	Boiling Range, °C (°F) Initial to End, (see Test Method D 86)
1.00	0 (0)
0.975	7 (13)
0.950	14 (25)
0.925	21 (38)
0.900	28 (50)
0.875	38 (68)
0.850	43 (78)
0.825	53 (95)
0.800	62 (112)
0.775	72 (130)
0.750	95 (152)
0.725	99 (178)
0.700	125 or greater (225)

TABLE A2.2 Relation of Average Relative Molecular Mass (Molecular Weight) to 50 % Boiling Point by Test Method D 86

50 % Boiling Point, °C (°F)	Average Molecular Weight of Olefins
38 (100)	72
66 (150)	83
93 (200)	96
121 (250)	110
149 (300)	127
177 (350)	145
204 (400)	164
232 (450)	186

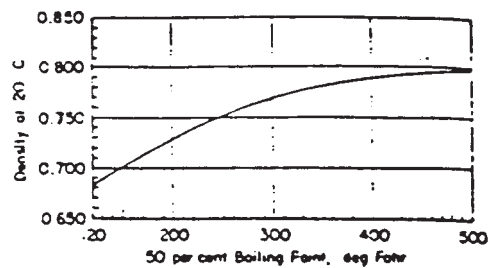


FIG. A2.2 Relation of Density to the 50 % Boiling Point

where:

- A = density of the sample,
- B = average density of the olefins, and
- C = mass percentage of olefins.

### A2.3 Precision<sup>11</sup>

A2.3.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

<sup>11</sup>Provisional value obtained from a limited amount

A2.3.1.1 *Repeatability*— The difference between successive test 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:

Straight-Run Fuels  
(less than 1 volume % olefins)  
0.2

Cracked Gasolines  
(1 to 25 volume % olefins)  
0.6

A2.3.1.2 *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, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Straight-Run Fuels  
(less than 1 volume % olefins)  
0.4

Cracked Gasolines  
(1 to 25 volume % olefins)  
3

A2.3.2 *Bias*—The procedure for calculating olefin content has no bias because the value obtained can be defined only in terms of a procedure.

NOTE A2.3—The precision for this test method was not obtained in accordance with RR: D02-1007.

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<sup>11</sup> The results of cooperative data were last published in the *1996 Annual Book of ASTM Standards, Part 17*, and are filed at ASTM International Headquarters as Research Report No. RR36:D-2.

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