



# Standard Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration<sup>1</sup>

This standard is issued under the fixed designation D 2710; 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.

## 1. Scope

1.1 This test method covers the determination of the amount of bromine-reactive material in petroleum hydrocarbons and is thus a measure of trace amounts of unsaturates in these materials. It is applicable to materials having bromine indexes below 1000.

1.2 This test method is applicable only to essentially olefin-free hydrocarbons or mixtures that are substantially free from material lighter than isobutane and have a distillation end point under 288°C (550°F).

1.3 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only.

1.4 *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 hazard statements, see Sections 7 and 8.

NOTE 1—This procedure has been cooperatively tested on materials with bromine indexes in the range from 100 to 1000. These materials include petroleum distillates such as straight-run and hydrocracked naphtha, reformer feed, kerosine, and aviation turbine fuel.

NOTE 2—Materials with bromine index greater than 1000 should be tested for bromine number using Test Method D 1159/IP 130.

NOTE 3—Bromine index of industrial aromatic hydrocarbons should be determined using Test Method D 1492 or D 5776.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1159 Test Method for Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration<sup>2</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.OD on Physical Methods.

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

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

D 1492 Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration<sup>3</sup>

D 5776 Test Method for Bromine Index of Aromatic Hydrocarbons by Electrometric Titration<sup>3</sup>

## 3. Terminology

### 3.1 Definition:

3.1.1 *bromine index*—the number of milligrams of bromine that will react with 100 g of sample under the conditions of the test.

## 4. Summary of Test Method

4.1 A known mass of the sample dissolved in a specified solvent is titrated with standard bromide-bromate solution. The end point is indicated by a dead stop electrometric titration apparatus when the presence of free bromine causes a sudden change in the electrical conductivity of the system.

## 5. Significance and Use

5.1 This test method provides a measure of trace amounts of unsaturated hydrocarbons in petroleum distillates boiling up to 288°C (550°F). An estimate of the quantity of these materials is useful in assessing the suitability of the lighter fractions for use as reaction solvents.

## 6. Apparatus

6.1 *Electrometric End Point Titration Apparatus*—Any apparatus designed to perform titrations to pre-set end points (see Note 4) 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 electric titrimeters, including certain pH meters, have also been found to be suitable.

NOTE 4—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.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 06.04.

6.2 *Titration Vessel*—A jacketed glass vessel of approximately 150-mL capacity of such a form that can be conveniently maintained at 0 to 5°C (32 to 41°F). A pair of platinum electrodes spaced not more than 5 mm apart shall be mounted to extend well below the liquid level. Stirring shall be by a mechanical or electromagnetic stirrer and shall be rapid, but not so vigorous as to draw air bubbles down to the electrodes.

6.3 *Burets*, 10 and 50-mL capacity.

6.4 *Iodine Number Flasks*, glass-stoppered, 500-mL capacity.

## 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 American Chemical Society where such specifications are available.<sup>4</sup> Other grades may be used, providing 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 distilled water, or water of equivalent purity.

7.3 *Preparation and Standardization:*

7.3.1 *Bromide-Bromate Standard Solution (0.05 N)*—Dissolve 5.1 g of potassium bromide (KBr) and 1.4 g potassium bromate (KBrO<sub>3</sub>) in water and dilute to 1 L. Standardize to four significant figures as follows: Place 50 mL of glacial acetic acid (**Warning**—See Note 5.) and 1 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) (**Warning**—See Note 6.) in a 500-mL iodine number flask. Chill the solution in an ice bath for approximately 10 min, and with constant swirling of the flask, add from a 50-mL buret 40 to 45 mL of bromide-bromate solution, estimated to the nearest 0.01 mL, at a rate such that the addition takes between 90 and 120 s. Stopper the flask immediately, shake the contents, place it again in the ice bath, and add 5 mL of potassium iodide (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 the standard 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 the disappearance of the blue color. Calculate the normality of the bromide-bromate solution as follows:

$$N_1 = A_2 N_2 / A_1 \quad (1)$$

where:

$N_1$  = normality of the bromide-bromate solution,  
 $A_1$  = millilitres of the bromide-bromate solution,  
 $N_2$  = normality of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, and

$A_2$  = millilitres of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required for titration of the bromide-bromate solution.

NOTE 5—**Warning:** Poison. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

NOTE 6—**Warning:** Poison. Corrosive. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled.

7.3.2 *Potassium Iodide Solution (150 g/L)*—Dissolve 150 g of KI in water and dilute to 1 L.

7.3.3 *Sodium Thiosulfate, Standard Solution (0.05 N)*—Dissolve 12.5 g of sodium thiosulfate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O) in water and add 0.01 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 normality with an error not greater than ±0.0002. Restandardize at intervals frequent enough to detect changes of 0.0005 in normality.

7.3.4 *Starch Indicator Solution*—Mix 5 g of soluble starch with approximately 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 supernatant liquid into glass bottles and seal well. Starch solutions (some preserved with salicylic acid) are also commercially available and may be substituted.

7.3.5 *Sulfuric Acid (1+5)*—Carefully add 1 volume of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84) to 5 volumes of water and thoroughly mix. (**Warning**—See Note 7.)

NOTE 7—**Warning:** Poison. Corrosive. Strong Oxidizer. Contact with organic material may cause fire. May be fatal if swallowed.

7.3.6 *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) (see 7.3.5).

7.4 *Solvents:*

7.4.1 *Acetic Acid*, glacial. (**Warning**—See Note 5.)

7.4.2 *Methanol* (**Warning**—See Note 8.)

NOTE 8—**Warning:** Flammable. Vapor harmful. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

7.4.3 *1,1,1-Trichloroethane* (**Warning**—See Note 9.)

7.4.4 *Dichloromethane* (**Warning**—See Note 9.)

NOTE 9—**Warning:** Harmful if inhaled. High concentrations may cause unconsciousness or death. Contact may cause skin irritation and dermatitis.

NOTE 10—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.

NOTE 11—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, including the preparation of the titration solvent and the dilution of samples, if applicable.

NOTE 12—Commercially available reagents can be used in place of laboratory preparations.

## 8. Procedure

8.1 Switch on the titrimeter and allow the electrical circuits to stabilize in accordance with the manufacturer's instructions.

<sup>4</sup> *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.

8.2 Cool the titration vessel to 0 to 5°C (32 to 41°F) by circulating a suitable coolant through the jacketed titration vessel.

8.3 Introduce 110 mL of titration solvent into the titration vessel and pipet in a quantity of sample as indicated in Table 1. Switch on the stirrer and adjust to a rapid stirring rate, but avoid any tendency for air bubbles to be drawn down into the solution. Allow the contents to cool to 0 to 5°C (32 to 41°F) and maintain at this temperature throughout the titration. (**Warning**—See Note 12.)

8.3.1 Frequently the order of magnitude of the bromine index of a sample is unknown. In this case, a trial test is recommended using an 8 to 10-g sample in order to obtain the approximate magnitude of the bromine index. This exploratory test should be followed with another determination using the appropriate sample size as indicated in Table 1.

8.3.2 The sample mass can be determined by obtaining the density of the sample and calculating the mass of a measured volume.

NOTE 13—**Warning:** Hydrocarbon samples, particularly those boiling below 205°C (400°F), are flammable.

8.4 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.

8.5 Depending on the titrator apparatus, add the bromide-bromate solution manually or by microprocessor control in small increments from the buret. The end point of the titration is achieved when the potential reaches the pre-set value (see 8.4) and persists for more than 30 s.

8.6 *Blanks*—Make duplicate blank titrations on each batch of titration solvent and reagents. Less than 0.10 mL of bromide-bromate solution should be required.

**9. Calculation**

9.1 Calculate the bromine index as follows:

$$\text{Bromine index} = [(A - B)N \times 7990]/W \quad (2)$$

where:

- A = millilitres of bromide-bromate solution required for titration of the sample,
- B = millilitres of bromide-bromate solution required for titration of the blank,
- N = normality of bromide-bromate solution, and
- W = grams of sample.

**10. Precision and Bias**

10.1 *Precision:*

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

10.1.1.1 *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 14 in only one case in twenty.

10.1.1.2 *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 118 in only one case in twenty.

10.2 *Bias:*

10.2.1 The procedure in this test method has no bias because the value of bromine index can be defined only in terms of a test method.

NOTE 14—The precision for this test method was not obtained in accordance with RR:D02-1007.<sup>5</sup>

NOTE 15—It is not known whether the precision estimates are applicable when using dichloromethane as a constituent of the titration solvent.

**11. Keywords**

11.1 bromide-bromate solution; bromine index; electrometric titration; hydrocarbons; petroleum

**TABLE 1 Sample Size**

Bromine Index	Sample Size,g
100 to 500	10 to 8
Over 500 to 1000	8 to 4

<sup>5</sup> Annual Book of ASTM Standards, Vol 05.03.

**ANNEX**
**(Mandatory Information)**
**A1. RESULTS OF BROMINE INDEX COOPERATIVE PROGRAM**

A1.1 See Table A1.1 for the bromine index results.

**TABLE A1.1 Bromine Index**

Sample		1091	1092	1093	1094	1095	Pooled
Lab. 1	1	1064	116	576	391	447	
	2	1064	120	576	392	447	
	avg	1064	118	576	392	447	447
2	1	1081	115	573 <sup>A</sup>	349	467	
	2	1102	119	604 <sup>A</sup>	368	474	
	avg	1092	117	589	359	471	471
3	1	1097	147	688	409	544	
	2	1114	136	688	397	544	
	avg	1106	142	688	403	544	544
4	1	1120	124	582	397	416	
	2	...	118	...	399	...	
	avg	(1120)	121	(582)	398	(416)	(416)
5	1	1039	116	532	388	389	
	2	1049	116	537	388	373	
	avg	1044	116	535	388	381	381
6	1	1055	113	549	395	360	
	2	1055	115	548	390	366	
	avg	1055	114	549	393	363	363
7	1	1063	113	573	365	443	
	2	1061	113	566	385	450	
	avg	1062	113	570	375	447	447
8	1	1277	142	718	449	620	
	2	1274	141	719	451	621	
	avg	1276 <sup>B</sup>	142	719 <sup>B</sup>	450	621 <sup>B</sup>	621 <sup>B</sup>
$\bar{X}$ , average		1078	123	584	395	438	
Repeatability							
Degrees of freedom		13	15	11	15	13	31
$\sigma_r$ , standard deviation		5.5	2.2	1.8	6.1	3.8	5
$r$ , repeatability		16.8	6.6	5.6	18.6	11.6	14
Reproducibility							
Degrees of freedom		6	7	6	7	6	32
$\sigma_r$ , standard deviation		28.5	12.1	49.5	26.3	60.3	41
$R$ , reproducibility		99	40	171	88	208	118

<sup>A</sup>Excluded from repeatability calculations.

<sup>B</sup>Excluded from reproducibility calculations. Table A1.1

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