



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

This standard is issued under the fixed designation D 5776; 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 determines the amount of bromine-reactive material in aromatic hydrocarbons and is thus a measure of trace amounts of unsaturates in these materials. It is applicable to materials having bromine indexes below 500.

1.2 This test method is applicable to aromatic hydrocarbons containing no more than trace amounts of olefins and that are substantially free from material lighter than isobutane and have a distillation end point under 288°C (550°F).

1.3 The following applies to all specified limits in this standard: For purposes of determining conformance with this standard, an observed value shall be rounded off “to the nearest unit” in the last right hand digit used in expressing the specification limit, in accordance with the rounding off method of Practice E 29.

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 a specific hazard statement see Section 8.

### 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>

D 1193 Specification for Reagent Water<sup>3</sup>

D 3437 Practice for Sampling and Handling Liquid Cyclic Products<sup>4</sup>

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications<sup>5</sup>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>5</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>4</sup> Annual Book of ASTM Standards, Vol 06.04.

<sup>5</sup> Annual Book of ASTM Standards, Vol 14.02.

### 2.2 Other Document:

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200<sup>6</sup>

### 3. Terminology

#### 3.1 Definition:

3.1.1 *bromine index*—the number of milligrams of bromine consumed by 100 g of sample under given conditions.

### 4. Summary of Test Method

4.1 The specimen dissolved in a specified solvent is titrated with standard bromide-bromate solution. The end point is indicated by a fixed end-point electrometric titration apparatus, when the presence of free bromine causes a sudden change in the polarization voltage of the system.

### 5. Significance and Use

5.1 This test method is suitable for setting specification, for use as an internal quality control tool, and for use in development or research work on industrial aromatic hydrocarbons and related material. This test method gives a broad indication of olefinic content. It does not differentiate between the types of aliphatic unsaturation.

### 6. Apparatus

6.1 *Fixed End Point Electrometric Titration Apparatus*—Any fixed end-point apparatus may be used incorporating a high resistance polarizing current supply capable of maintaining approximately 10 to 50  $\mu$ A across two platinum plate electrodes or a combination platinum electrode and with a sensitivity such that a voltage change of approximately 50 mV at these electrodes is sufficient to indicate the end point (see Note 1).

NOTE 1—The reagents and techniques may be checked by determining the bromine index of a 100 mg/kg cyclohexene in heptane. This is expected to give a bromine index of 18 to 20 mg/100 g sample. Refer to Table A2.1 of Test Method D 1159.

6.2 *Titration Vessel*—A tall form glass beaker of approximately 250-mL capacity or a water jacketed titration vessel of approximately 250-mL capacity connected to a refrigerated

<sup>6</sup> Available from Superintendent of Documents U.S. Government Printing Office, Washington, DC 20402.

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

circulating water bath controlling the temperature at 0 to 5°C. 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 *Iodine Number Flasks*, glass-stoppered, 500-mL capacity.

## 7. Reagents and Materials

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>7</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 reagent water conforming to Type III of Specification D 1193.

7.3 *Bromide-Bromate Standard Solution (0.10 N)*<sup>8</sup>—Dissolve 10.1 g of potassium bromide (KBr) and 2.8 g potassium bromate (KBrO<sub>3</sub>) in water and dilute to 1.0 L. Standardize to four significant figures as follows: Place 50 mL of glacial acetic acid and 1.0 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) 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 5.0 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 flask, and titrate promptly with the standard sodium thiosulphate (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.

7.4 *Electronic Standardization of Bromide-Bromate Solution*—Standardize to four significant figures as follows: Place 50 mL of glacial acetic acid and 1.0 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) in a 500-mL iodine number flask. Chill the solution in an ice bath for approximately 10 min with constant swirling of the flask, add 4.00 mL of bromide bromate solution from the auto buret. Stopper the flask immediately and, shake the contents, then cool it in a ice bath for 5 min. Add 4.0 mL of potassium iodide (KI) to the lip of the flask, remove the flask from the ice bath and allow the KI solution to slowly flow into the flask by removing the stopper.

<sup>7</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.

<sup>8</sup> The 0.10 N bromide-bromate standard solution is available commercially from laboratory chemical suppliers.

Shake vigorously, transfer to a chilled beaker and rinse the flask including stopper with 100 mL of water. Immerse the electrodes into the solution, titrate with standard sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) to an end point indicated by a significant change in potential that persists for 30 s (see Note 2).

NOTE 2—With commercial titrators, a sudden change in potential is indicated on the meter or dial of the instrument as the endpoint is approached. When this change persists for 30 s it marks the end of the titration. With each instrument, the manufacturer's instructions should be followed to achieve the sensitivity achieved in the platinum electrode circuit.

7.5 *Potassium Iodide Solution (150 g/L)*—Dissolve 150 g of potassium iodide (KI) in water and dilute to 1.0 L.

7.6 *Sodium Thiosulphate, Standard Solution (0.10 N)*—Dissolve 25.0 g of sodium thiosulphate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O) in water and add 0.02 g of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) to stabilize the solution. Dilute to 1.0 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.

7.7 *Starch Solution*<sup>9</sup>—Mill 5 g of arrow-root starch with 3 to 5 mL of water. Add the suspension to 2 L of boiling water. As a preservative, 5 to 10 mg of mercuric iodide (HgI<sub>2</sub>) or 0.2 g of salicylic acid can also be added. Boil for 5 to 10 min, then allow to cool and decant the clear supernatant liquid into glass stoppered bottles.

7.8 *Sulphuric Acid (1 + 5)*—Carefully add 1 volume of concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub> sp gr 1.84) to 5 volumes of water and thoroughly mix.

7.9 *Acetic Acid*, glacial.

7.10 *1-Methyl-2-Pyrrolidinone*.

7.11 *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-Methyl-2-Pyrrolidinone, 134 mL of methanol and 18 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 5).

## 8. Hazards

8.1 Consult current OSHA regulations, suppliers' Material Safety Data Sheets, and local regulations for all materials used in this test method.

## 9. Sampling

9.1 Sample the material in accordance with Practice D 3437.

## 10. Procedure

10.1 Switch on the titrator and allow the electrical circuits to stabilize according to the manufacturer's instructions.

10.2 Introduce 150 mL of titration solvent into the titration vessel and pipet or weigh in a quantity of sample as indicated in Table 1 (Note 3). The sample must be completely dissolved in the titration solvent. 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.

<sup>9</sup> Arrow-root starch indicator solution may also be purchased prepared from chemical suppliers.

**TABLE 1 Sample Size**

Bromine Index	Sample Size, g
0 to 20	50
20 to 100	30 to 40
100 to 200	20 to 30
200 to 500	8 to 10

NOTE 3—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. The sample mass may be determined by obtaining the density of the sample and calculating the mass of a measured volume.

10.3 Start the titration with the bromide-bromate solution according to the optimized instrument conditions. Continue the titration until a significant change in potential persisting for 30 s marks the endpoint of the titration.

10.4 *Blanks*—Make duplicate blank titrations on each batch of titration solvent and reagents. Make sure that less than 0.10 mL of bromide-bromate solution is required.

## 11. Calculations

11.1 Calculate the normality of the bromide-bromate solution as follow:

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

where:

$N_1$  = normality of the bromide-bromate solution,

$A_1$  = bromide-bromate solution, mL,

$A_2$  =  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the bromide-bromate solution, mL, and

$N_2$  = normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

11.2 Calculate the bromine index as follows:

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

where:

$A$  = bromide-bromate solution required for titration of the sample, mL,

$B$  = bromide-bromate solution required for titration of the blank, mL,

$N$  = normality of bromide-bromate solution,

$W$  = sample, g, and

7990 = molecular weight of bromine  $\times$  100.

## 12. Report

12.1 Report the following information:

12.1.1 Bromine index to the nearest 0.5 mg/100 g.

## 13. Precision and Bias <sup>10</sup>

13.1 *Precision*—The following criteria should be used to judge the acceptability at the 95 % probability level of the results obtained by this test method. The precision criteria were derived from an interlaboratory study between 7 laboratories conducted in accordance with Practice E 691.

13.2 *Repeatability*—Results in the same laboratory should not be considered suspect unless they differ by more than plus or minus the amount shown in Table 2.

13.3 *Reproducibility*—Results submitted by two laboratories should not be considered suspect unless they differ by more than plus or minus the amount shown in Table 2.

13.4 *Bias*—Since there is no acceptable reference material suitable for determining the bias in this test method for measuring bromine index in aromatic hydrocarbons, bias has not been determined.

## 14. Keywords

14.1 aromatic hydrocarbons; bromine index; bromine-reactive; electrometric titration

<sup>10</sup> Supporting data available from ASTM Headquarters. Request RR:D16-1026.

**TABLE 2 Bromine Index Repeatability and Reproducibility**

Concentration, mg Bromine /100 g	Repeatability	Reproducibility
7.5	1.1	4.6
20	1.6	4.3
25	2.1	3.6
35	2.0	11.5

## SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue that may impact the use of this standard.

(I) Section 13 and Table 2 include the revised precision and bias statements from the interlaboratory study conducted.

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