Designation: ~~D5776 – 14a~~ D5776 – 21

Standard Test Method for Bromine Index of Aromatic Hydrocarbons by Electrometric Titration[1]

This standard is issued under the fixed designation D5776; 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.

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 35. Materials with a higher bromine index can be analyzed by this method; however, the precision section does not apply.~~

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.~~materials having bromine indexes below 35. Materials with a higher bromine index can be analyzed by this method; however, the precision section does not apply.

1.2.1 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.

1.3 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.* For a specific hazard statement see Section 8.

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:*[2]

D1159 Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration

D1193 Specification for Reagent Water

D3437 Practice for Sampling and Handling Liquid Cyclic Products

[1] This test method is under the jurisdiction of ASTM Committee D16 on ~~Aromatic Hydrocarbons~~ Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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[2] 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.

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

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Document:*
OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *bromine index, n*—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,~~specifications, 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 1 to ~~50 µA~~ 50 µA across two platinum plate electrodes or a combination platinum electrode and with a sensitivity such that a voltage change of approximately ~~500 mV~~ 500 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 Test Method D1159 for a list of expected bromine indexes of various compounds.

6.2 *Titration Vessel*—A tall form glass beaker of approximately ~~250-mL~~250 mL capacity or a water jacketed titration vessel of approximately ~~250-mL~~250 mL capacity connected to a refrigerated circulating water bath controlling the temperature at 0 to ~~5°C.~~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.[4] 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~~ I or II of Specification D1193.

[3] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

[4] ~~*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 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.

7.3 *Bromide-Bromate Standard Solution (0.10 N)*[5]—Dissolve 10.1 g of potassium bromide (KBr) and 2.8 g potassium bromate ($KBrO_3$) 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~~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~~50 mL buret 40 to ~~45 mL~~ 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.~~ 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 ($Na_2S_2O_3$) 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~~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 an 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. 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 ($Na_2S_2O_3$) 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 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 ($Na_2S_2O_3 \cdot 5H_2O$) in water and add 0.02 g of sodium carbonate (Na_2CO_3) 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*[6]—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 (H_gI_2) or ~~0.2 g~~ 0.2 g of salicylic acid can also be added. Boil for 5 to 10 min, allow to cool and then decant the clear supernatant liquid into glass stoppered bottles.

7.8 *Sulfuric Acid (1 + 5)*—Carefully add 1 volume of concentrated sulfuric acid (H_2SO_4 sp gr 1.84) to 5 volumes of water and thoroughly mix.

7.9 *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_2SO_4 (1 + 5).

NOTE 3—Dichloromethane, 1,1,1-trichloroethane, carbon tetrachloride or chloroform can be used to replace 1-methyl-2-pyrrolidinone in the titration solvent to improve miscibility with the sample.

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8. Hazards

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

[5] The 0.10 *N* bromide-bromate standard solution is available commercially from laboratory chemical suppliers.
[6] Arrow-root starch indicator solution may also be purchased prepared from chemical suppliers.

8.2 Acidic liquid and vapors are extremely corrosive to skin and mucous membranes. Research the safe handling of the specific acid prior to use.

8.3 Chlorohydrocarbons such as carbon tetrachloride and chloroform, can be toxic by inhalation, ingestion and dermal exposure and are suspected carcinogens. Research the safe handling of the specific chemical prior to use.

9. Sampling

9.1 Sample the material in accordance with Practice D3437.

10. Procedure

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

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

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 4). 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.

NOTE 4—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~~ 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~~ 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 = volume of bromide-bromate solution, mL,
A_2 = $Na_2S_2O_3$ solution required for titration of the bromide-bromate solution, mL, and
N_2 = normality of the $Na_2S_2O_3$ solution.

11.2 Calculate the bromine index as follows:

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

where:

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