Designation: D 5776 – 95

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

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 (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 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 1193 Specification for Reagent Water
D 1159 Test Method for Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration
D 3437 Practice for Sampling and Handling Liquid Cyclic Products
E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
2.2 Other Document:
OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200

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 μA 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 180 to 200 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 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...
the addition takes between 90 and 120 s. Stopper the flask thiosulphate (Na₂S₂O₃) solution. Near the end of the walls of flask, and titrate promptly with the standard sodium the lip of the flask. After 5 min remove the flask from the ice immediately, shake the contents, place it again in the ice solution, estimated to the nearest 0.01 mL, at a rate such that 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, lid, and walls of flask, and titrate promptly with the standard sodium thiosulphate (Na₂S₂O₃) 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 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 slowly 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, lid, and walls of flask, and titrate promptly with the standard sodium thiosulphate (Na₂S₂O₃) solution. Near the end of the titration add 1 mL of starch indicator solution and titrate slowly to the disappearance of the blue color.

7.5 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 (Na₂S₂O₃·5H₂O) in water and add 0.02 g of sodium carbonate (Na₂CO₃) 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—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 (HgI₂) 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.

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

9.1 Sample the material in accordance with Practice D 3437.

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 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 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:

\[ N_1 = \frac{A_2N_2}{A_1} \]  

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:

\[ \text{Bromine index} = \frac{(A - B)N \times 7990}{W} \]  

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

13.1 Precision—Based on limited information (32 analysis by one operator) from one laboratory, the absolute standard deviation of 0.24 at the 2.8 mg/100 g bromine index level was obtained.

13.1.1 Intermediate Precision (formerly called Repeatability)—The 95 % repeatability limits at the 2.8 mg/100 g levels are approximately \( \pm 0.7 \).

13.1.2 Reproducibility—The reproducibility of this test method is being determined.

13.2 Bias—Since there is no accepted reference material suitable for determining the bias of the procedure in this test method, bias has not been determined.

14. Keywords

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

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