Designation: D4590 – 13

Standard Test Method for Colorimetric Determination of *p-tert*-Butylcatechol In Styrene Monomer or AMS (α–Methylstyrene) by Spectrophotometry[1]

This standard is issued under the fixed designation D4590; 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 is applicable to the determination of residual 4-tertiary-butylcatechol (TBC) in styrene monomer or AMS in the 1 to 100 mg/kg range. Any other compound producing color at 490 nm when contacted with aqueous sodium hydroxide solution will interfere. It may be compensated for by including it in the preparation of the standard solutions, if its identity and concentration in the sample are known.

1.2 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.

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

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 statements on hazards, see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

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 See Terminology D4790 for definition of terms used in this standard.

4. Summary of Method

4.1 Color is developed in the specimen by the addition of caustic in a methanol-octanol solvent. The intensity of the pink color is measured with a spectrometer and compared to a calibration curve for quantitation.

5. Significance and Use

5.1 This test method is suitable for determining the quantity of TBC inhibitor, both for the protection against polymerization while in transit and storage, and for internal quality control.

6. Apparatus

6.1 *Visible Range Spectrometer,* equipped with absorption cells providing light paths from 1 to 5 cm for use at approximately 490 nm.

6.2 *Volumetric Pipets and Pipetors*—The sample pipet volume should be sized to fill the spectrometer absorption cell. Pipetor volumes must be scaled to the sample volume. This procedure is written using a 15 mL sample volume. The following table shows how reagent pipetor volumes could be scaled to use a 5 mL sample volume.

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.07 on Styrene, Ethylbenzene and C9 and C10 Aromatic Hydrocarbons.

Current edition approved June 1, 2013. Published June 2013. Originally approved in 1986. Last previous edition approved in 2009 as D4590 – 09. DOI: 10.1520/D4590-13.

[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.

[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.

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

Sample Pipet, mL	0.15 NaOH Pipetor, µL	Methanol Pipetor, µL
15	300	600
5	100	200

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 specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] 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 *4-Tertiary-Butylcatechol,* Mp 52 to 55°C.

7.3 *Toluene,* ACS reagent grade.

7.4 *Methanol,* reagent grade.

7.5 *n-Octanol,* reagent grade.

7.6 *Aqueous Sodium Hydroxide, 10 Normal (10N),* reagent grade.

7.7 *Alcoholic Sodium Hydroxide,* approximately 0.15 N: Mix 0.75 mL of 10N Aqueous Sodium Hydroxide with 25 mL methanol. With stirring, add 25 mL of *n*-octanol and then 0.75 mL of water. Store the reagent in an amber glass bottle. This reagent can be used immediately after preparation and is stable for at least 2 months. To reduce exposure of the reagent to the atmosphere, transfer enough for several samples to a small clean vial.

7.8 *TBC Stock Standard*—This standard may be purchased if desired. Prepare a stock solution by weighing 0.500 ± 0.001 g of TBC to the nearest 0.0001 g into 500 ± 1 g of toluene (weighed to the nearest 0.1 g). This solution will have a concentration of approximately 1000 mg/kg TBC in toluene and the exact concentration can be calculated using Eq 1. This standard should have a shelf life of one year or better if stored in a refrigerator or freezer. Storing standards in amber bottles significantly reduces degradation of standards with time.

$$mg\ TBC/kg\ toluene = [(g\ of\ TBC) \times (Purity\ of\ TBC) \times (10^6)]/g\ of\ toluene \quad (1)$$

7.9 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean any reagent conforming to type I as defined in Specification D1193.

8. Hazards

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

8.2 *Handling Precautions—p-tert* -butylcatechol, particularly when molten or in concentrated solution, is very corrosive to the skin. It is also a systemic poison when taken orally or absorbed in quantity through the skin.

8.3 *Flammable Hazards*—Styrene monomer is flammable and can polymerize exothermally under a variety of conditions, most especially in the presence of peroxides, mineral acids, and Lewis acids such as aluminum chloride.

9. Sampling and Handling

9.1 Sample the material in accordance with Practice D3437.

10. Preparation of Calibration Curve

10.1 Prepare standards of approximately 5, 10, 20, 30, 40, 50, 70, and 100 mg/kg TBC in toluene by diluting 0.5, 1, 2, 3, 4, 5, 7, and 10 mLs of TBC stock standard to 100 mLs with toluene. Record the actual concentrations generated to the nearest 0.5 mg/kg.

NOTE 1—Both the stock solution and toluene diluent should be at room temperature. Temperature differences will cause dilution errors due to variations in density.

10.2 Determine the absorbance of each standard solution and one reagent blank in accordance with Section 11.

10.3 Plot absorbance versus concentration on standard graph paper.

NOTE 2—The plot should be close to a straight line. The maximum absorbance should be within the absorbance range of the spectrometer. If not, repeat the calibration with a spectrometer cell that has less path length.

11. Procedure

11.1 Zero the spectrometer with the specimen to be analyzed.

11.2 Add 15 mL of specimen to a clean round container.

11.3 Verify that the alcoholic NaOH reagent and pipetor are free of particulates.

NOTE 3—The particulates formed in the sodium hydroxide reagent from exposure to carbon dioxide in the atmosphere will scatter light and may cause an error in the determination.

11.4 Add 300 µL of alcoholic NaOH reagent to the container and mix vigorously with a vortex mixer for 30 s.

NOTE 4—If a vortex mixer is not available, continuous vigorous shaking for 30 s is required. Rapid reaction completion depends on the formulation of an emulsion of aqueous NaOH in the sample mixture.

11.5 Add 600 µL of methanol to the container and shake for about 15 s, creating a clear solution from the reaction emulsion.

11.6 Measure the absorbance at 490 nm as soon as possible and within 5 min.

11.7 Read the concentration in mg/kg TBC from the graph. Calculate the inhibitor content using Eq 2 for density correction:

$$Inhibitor\ Content,\ mg/kg = (Value\ from\ curve) \times [(toluene\ density)/(sample\ density)] \quad (2)$$

12. Report

12.1 Report the inhibitor content as mg/kg (or ppm) of *p-tert*-butylcatechol.

[4] *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.

13. Precision and Bias

13.1 The following criteria should be used to judge the acceptability of results obtained by this test method (95 % confidence level). The precision criteria were derived from an ILS that was conducted using six laboratories analyzing three sample of unknown concentration of TBC with two determinations for each sample. Each determination was the result of one measurement as specified in this standard. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D16-1009.[5]

TABLE 1 Intermediate Precision and Reproducibility

TBC Observed Concentration	Repeatability	Reproducibility
4.7	0.23	0.94
15.2	0.47	5.08
24.5	1.55	4.91
94.6	3.98	9.94

13.2 *Intermediate Precision (formerly called Repeatability)*—Results in the same laboratory should not be considered suspect unless they differ by more than the values shown in Table 1. Results differing by less than "*r*" have a 95 % probability of being correct.

13.3 *Reproducibility*—Results submitted by two laboratories should not be considered suspect unless they differ by more than the values shown in Table 1. Results differing by less than "*R*" have a 95 % probability of being correct.

13.4 *Bias*—There is a bias associated with running the test method that is statistically significant at the 95 % confidence level. The bias for the unknown samples is an average absolute value of 0.6 mg/kg with the observed results lower than the actual amounts added. However, at the 99 % confidence level, the bias is not statistically significant.

14. Quality Guidelines

14.1 Laboratories shall have a quality control system in place.

14.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines for standard statistical quality control practices.

14.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

14.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

14.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

15. Keywords

15.1 alpha-methylstyrene; AMS; para-tertiary butyl catechol; PTBC; styrene, inhibitor content; styrene, TBC content; TBC in styrene

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1009.

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D4590–09) that may impact the use of this standard. (Approved June 1, 2013.)

(1) All sections updated to current D16 Editorial Guidelines.