



Standard Test Method for Colorimetric Determination of *p*-*tert*-Butylcatechol In Styrene Monomer or AMS (α -Methylstyrene) by Spectrophotometry¹

This standard is issued under the fixed designation D 4590; 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 ppm range. Any other compound known to produce color 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 The following applies to all specified limits in this standard: for purposes of determining conformance with this standard, an observed value or a calculated 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.

1.3 *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 7.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 3437 Practice for Sampling and Handling Liquid Cyclic Products³

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁴

2.2 Other Document:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200⁵

3. Summary of Method

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

4. Significance and Use

4.1 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.

5. Apparatus

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

5.2 *Volumetric Pipets*, 5 mL.

5.3 *Pipetors*, 0.1 and 0.2 mL.

6. Reagents and Materials

6.1 *Purity of Reagents*—Where unspecified, chemicals shall be reagent grade and conform to recognized specifications if such exist.⁶ If found to have no adverse effect on accuracy, other grades may be used.

6.2 *4-Tertiary-Butylcatechol*, Mp 52-55°C.

6.3 *Toluene*, ACS reagent grade.

6.4 *Methanol*, reagent grade.

6.5 *n-Octanol*, reagent grade.

6.6 *Sodium Hydroxide Pellets*, reagent grade.

6.7 *Alcoholic Sodium Hydroxide*, approximately 0.15 N. Dissolve 0.3 g NaOH in 25 mL methanol. Add 25 mL of *n*-octanol and 100 μ L of water. Let this reagent mature for two days before use. This solution is stable for two weeks.

6.8 *TBC Stock Standard*—Weigh 0.5 g of TBC into 500 g of toluene. This solution will contain 1000 ppm TBC. This standard should have a shelf life of one year or better if stored in a refrigerator or freezer. Storing standards in amber bottles

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.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.04.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

⁶ *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.

significantly reduces degradation of standards with time.

6.9 Unless otherwise indicated, references to water shall be understood to mean any reagent water as defined in Specification D 1193.

7. Hazards

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

7.2 *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.

7.3 *Flammable Hazards*—Styrene monomer is flammable and polymerizes exothermally in the presence of peroxide, mineral acids, and aluminum chloride.

8. Sampling

8.1 Collect the samples in accordance with Practice D 3437.

9. Preparation of Calibration Curve

9.1 Prepare standards of 5, 10, 20, 30, 40, 50, 70, and 100 ppm (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.

9.2 Determine the absorbance of each standard solution and one reagent blank in accordance with Section 10.

9.3 Plot absorbance versus concentration on standard graph paper.

NOTE 1—The plot is close to a straight line. Higher concentrations will definitely yield a curve up to about 300 ppm, then it drops off.

10. Procedure

10.1 Zero the spectrophotometer with the specimen to be analyzed.

10.2 Add 5 mL of specimen to a clean container.

NOTE 2—Use acetone or the purest methanol available for glassware cleaning as low results are caused by inferior methanol presence.

10.3 Shake the alcoholic NaOH reagent to ensure homogeneity.

NOTE 3—The turbidity formed as the sodium hydroxide ages does not appear to be harmful.

10.4 Add 100 μ L of alcoholic NaOH reagent to the container and mix vigorously for 30 s.

NOTE 4—A vortex mixer is beneficial if round cells are used.

10.5 Add 200 μ L of methanol to the container and shake for 15 s.

NOTE 5—If a blue color persists before the methanol is added, the concentration range has been exceeded. Dilute the specimen 1:10 with toluene and repeat.

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

NOTE 6—Color intensity will increase about 15 % per minute after the first 5 min. Calibration standards and specimens should be determined at the same time interval after the methanol addition.

10.7 Read the concentration in parts per million TBC from the graph.

11. Report

11.1 Report the inhibitor content as parts per million (mg/kg) of *p-tert*-butylcatechol.

12. Precision and Bias ⁷

12.1 *Intermediate Precision*—Data obtained from an inter-laboratory study with twelve laboratories analyzing six samples, three of known concentration and three of unknown concentration of TBC indicate that at the 95 % confidence level,

$$\text{Intermediate precision} = 0.50 + 0.020(x),$$

where x = concentration of TBC, mg/kg.

Precision values are estimates determined by multiplying the standard deviation by 2.8.

12.2 *Reproducibility*—Data obtained by this procedure indicate that:

$$\text{Reproducibility} = 1.75 + 0.074(x),$$

where x = concentration of TBC, mg/kg (see Table 1).

TABLE 1 Intermediate Precision and Reproducibility

TBC Concentration, mg/kg	Intermediate Precision	Reproducibility
12	0.74	2.64
30	1.10	3.97
60	1.70	6.19

12.3 *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.

13. Keywords

13.1 alpha-methylstyrene; AMS; styrene, inhibitor content; styrene, TBC content; TBC in styrene

⁷ Supporting data are available from ASTM International Headquarters. Request RR: D16-1009.

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