



Standard Test Method for Analysis of AMS (α -Methylstyrene) by Capillary Gas Chromatography¹

This standard is issued under the fixed designation D6144; 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 covers the determination of the purity of AMS (α -methylstyrene) by gas chromatography. Calibration of the gas chromatography system is done by the external standard calibration technique.

1.2 This test method has been found applicable to the measurement of impurities such as cumene, 3-methyl-2-cyclopentene-1-one, *n*-propylbenzene, *tert*-butylbenzene, *sec*-butylbenzene, *cis*-2-phenyl-2-butene, acetophenone, 1-phenyl-1-butene, 2-phenyl-2-propanol, *trans*-2-phenyl-2-butene, *m*-cymene, *p*-cymene, and phenol, which are common to the manufacturing process of AMS. The method has also been found applicable for the determination of para-tertiary-butylcatechol typically added as a stabilizer to AMS. The impurities in AMS can be analyzed over a range of 5 to 800 mg/kg by this method. (See Table 1.) The limit of detection for these impurities is typically in the range of 5 to 10 mg/kg. (See Table 1.)

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 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 hazard statements, see Section 8.

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. Referenced Documents

2.1 ASTM Standards:²

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

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

E355 Practice for Gas Chromatography Terms and Relationships

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

2.2 Other Document:

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200³

3. Terminology

3.1 See Terminology D4790 for definition of terms used in this test method.

4. Summary of Test Method

4.1 AMS (α -methylstyrene) is analyzed by a gas chromatograph (GC) equipped with a flame ionization detector (FID). A precisely repeatable volume of the sample to be analyzed is injected onto the gas chromatograph. The peak areas of the impurities are measured and converted to concentrations via an external standard methodology. Purity by GC (the AMS

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

TABLE 1 Summary of Precision Data (mg/kg)

Compound	Repeatability (<i>r</i>)	Reproducibility (<i>R</i>)	Range Studied
Acetone	1.61 + 0.035*Acetone	0.47 + 1.10*Acetone	0.5 – 26
Cumene	–0.46 + 0.031*Cumene	7.88 + 0.19*Cumene	45 – 290
<i>n</i> Propylbenzene (NPB)	2.11 + 0.03*NPB	–7.81 + 0.37*NPB	55 – 195
Phenol	1.84	3.65 + 0.58*Phenol	1 – 40
<i>tert</i> Butylbenzene (TBB)	–1.22 + 0.035*TBB	3.63 + 0.087*TBB	150 – 650
<i>sec</i> Butylbenzene (SBB)	4.23 + 0.019*SBB	21.60 + 0.25*SBB	200 – 765
<i>m</i> Cymene	0.31 + 0.035*mCymene	2.34 + 0.35*mCymene	2 – 50
<i>o</i> Cymene	1.63	8.00	29 – 31
<i>p</i> Cymene	5.12	15.79	10 – 18
<i>cis</i> -2-Phenyl-2-Butene (CPB)	0.17 + 0.030*CPB	5.39 + 0.11*CPB	50 – 225
<i>trans</i> -2-Phenyl-2-Butene (TPB)	1.57	0.54 + 0.20*TPB	19 – 70
1-Phenyl-1-Butene (PB)	4.00 + 0.018*PB	0.17 + 0.19*PB	0.2 – 735
Acetophenone (AP)	–1.09 + 0.15*AP	1.17 + 0.63*AP	15 – 115
<i>para-tert</i> -Butylcatechol (PTBC)	2.21	17.82	10 – 19
2-Methylbenzofuran (MBF)	0.33 + 0.76*MBF	0.75 + 0.60*MBF	1 – 2
2-Phenylpropion aldehyde (PPA)	0.59 + 0.11*PPA	0.29 + 0.23*PPA	1.5 – 15
α -Methylstyrene Oxide (AMSO)	4.61	6.51 + 0.23*AMSO	13 – 32
DimethylBenzyl Alcohol (DMBA)	0.38	0.55 + 2.03*DMBA	0.1 – 1

content) is calculated by subtracting the sum of the impurities from 100.00. Results are reported in weight percent.

5. Significance and Use

5.1 This test method is suitable for setting specifications on the materials referenced in 1.2 and for use as an internal quality control tool where AMS is produced or is used in a manufacturing process. It may also be used in development or research work involving AMS.

5.2 This test method is useful in determining the purity of AMS with normal impurities present. If extremely high boiling or unusual impurities are present in the AMS, this test method would not necessarily detect them and the purity calculation would be erroneous.

6. Apparatus

6.1 *Gas Chromatograph*—Any instrument having a flame ionization detector that can be operated at the conditions given in Table 2. The system should have sufficient sensitivity to obtain a minimum peak height response for 10 mg/kg acetophenone of twice the height of the signal background noise.

6.2 *Columns*—The choice of column is based on resolution requirements. Any column may be used that is capable of resolving all significant impurities from AMS. The column described in Table 2 has been used successfully and shall be used as a referee in cases of dispute.

6.3 *Recorder*—Electronic integration is recommended.

6.4 *Injector*—The specimen must be precisely and repeatedly injected into the gas chromatograph. An automatic sample injection device is highly recommended. Manual injection can be employed if the precision stated in Table 1 can be reliably and consistently satisfied.

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,

TABLE 2 Recommended Operating Conditions

Detector	flame ionization
Injection Port	capillary splitter
Column A:	
Tubing	fused silica
Stationary phase	crosslinked methylsilicone
Film thickness, μm	1.0
Length, m	60
Diameter, mm	0.32
Temperatures:	
Injector, °C	250
Detector, °C	300
Oven, °C	85 hold for 13 min Ramp 1 = 6°C/min to 125°C, hold for 2 min Ramp 2 = 30°C/min to 250°C, hold for 7.5 min
Carrier gas	helium
Flow rate, mls/min	3
Split ratio	60:1
Sample size, μl	1.0

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 *Carrier Gas, Makeup, and Detector Gases*—Helium, hydrogen, nitrogen, or other carrier, makeup and detector gases 99.999 % minimum purity. Oxygen in carrier gas less than 1 ppm, less than 0.5 ppm is preferred. Purify carrier, makeup, and detector gases to remove oxygen, water, and hydrocarbons.

7.3 *Compressed Air*—Purify air to remove water and hydrocarbons. Air for a FID should contain less than 0.1 ppm THC.

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.

7.4 Pure Compounds for Calibration—The purity of all reagents should be 99.9 % or greater. If the purity is less than 99 %, the concentration and identification of impurities must be known so that the composition of the standard can be adjusted for the presence of the impurities.

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 and Handling

9.1 Sample the material in accordance with Practice D3437.

10. Preparation of Apparatus

10.1 Follow manufacturer's instructions for mounting and conditioning the column into the chromatograph and adjusting the instrument to the conditions described in Table 2 allowing sufficient time for the equipment to reach equilibrium. See Practice E1510 for more information on column installation. See Practice E355 for additional information on gas chromatography practices and terminology.

11. Calibration

11.1 Prepare a synthetic mixture of high purity AMS containing impurities at concentrations representative of those expected in the samples to be analyzed in accordance with Practice D4307. The weight of each hydrocarbon impurity must be measured to the nearest 0.1 mg. Because the availability of stock AMS with a purity higher than 99.80 % is problematic, the method of standard additions may be required for impurities such as *tert*-butylbenzene and *n*-propylbenzene, as well as for a number of the other impurities listed in 1.2 that are commonly present. In addition, nearly all commercially available AMS is stabilized with 10 to 30 mg/kg of para-tertiary-butylcatechol, requiring a standard addition methodology for this component as well unless AMS can be obtained safely and directly from the point of manufacture.

11.2 Inject the resulting solution from 11.1 into the gas chromatograph, collect and process the data. A typical chromatogram is illustrated in Fig. 1 based on the conditions listed in Table 2.

11.3 Determine the response factor for each impurity in the calibration mixture as follows:

$$R_{fi} = C_i/A_i \quad (1)$$

where:

R_{fi} = response factor for impurity i ,

C_i = concentration of impurity i in the calibration mixture, and

A_i = peak area of impurity i .

11.4 Initially analyze the calibration solution a minimum of three times and calculate an average R_{fi} . Subsequent calibrations may be a single analysis as long as the R_{fi} s for all components of interest are within ± 5 % of the initial validation R_{fi} s. A "rolling" average as defined by most modern chromato-

graphic software may also be used. The R_{fi} for *tert*-butylbenzene is used for the quantification of unknown impurities.

12. Procedure

12.1 Inject into the gas chromatograph an appropriate amount of sample as previously determined according to 6.1 and start the analysis.

12.2 Obtain a chromatogram and peak integration report. Fig. 1 illustrates a typical analysis of AMS using the column and conditions outlined in Table 2.

13. Calculations

13.1 Of the impurities identified in AMS, only the butenylbenzene isomers are not available commercially. However, pure samples of these isomers can be prepared, and testing has shown that all three isomers have the same response factor ± 5 %, and that it is equivalent to that for *tert*-butylbenzene ± 5 %.⁵

13.2 Calculate the concentration of each impurity as follows:

$$C_i = (A_i) (R_{fi}) \quad (2)$$

where:

C_i = concentration of component i , in mg/kg,

A_i = peak area of component i , and

R_{fi} = response factor for component i .

13.3 Calculate the total concentration of all impurities in wt. % as follows:

$$C_t = \Sigma C_i / 10000 \quad (3)$$

where:

C_t = total concentration of all impurities.

13.4 Calculate the purity of AMS as follows:

$$\text{AMS, weight percent} = 100.00 - C_t \quad (4)$$

14. Report

14.1 Report the individual impurities to the nearest 0.1 mg/kg.

14.2 Report the purity of AMS to the nearest 0.01 wt. %.

15. Precision and Bias⁵

15.1 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 the conditions listed in Table 1 which included five laboratories analyzing six samples in triplicate by the same operator on the same day. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D16-1022.

15.2 *Repeatability*—Results in the same laboratory should not be considered suspect unless they differ by more than the

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1022.

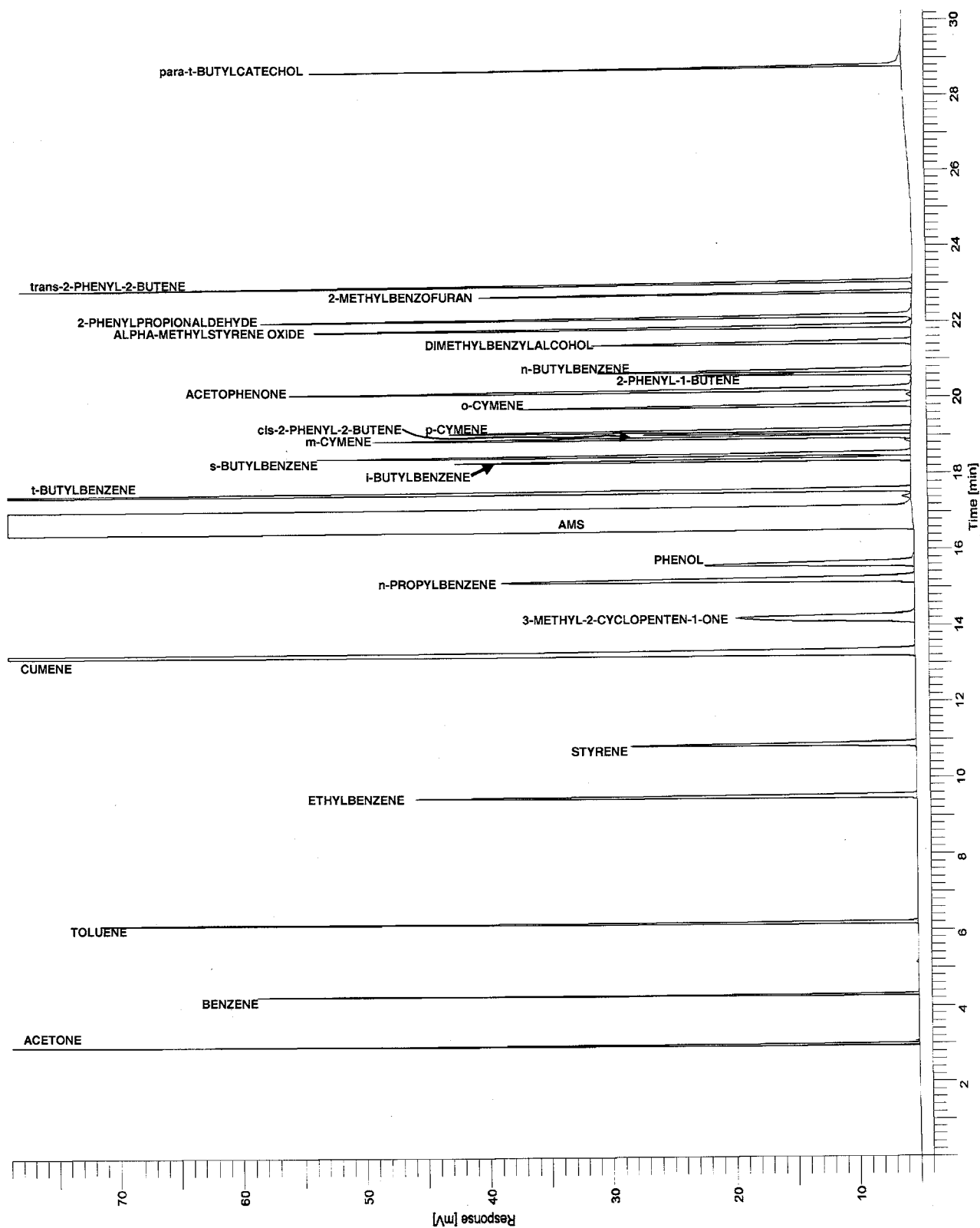


FIG. 1 Typical AMS Chromagram, AMS Method

amounts calculated from the appropriate equations in **Table 1**. Results differing by less than “*r*” have a 95 % probability of being correct.

15.3 Reproducibility—Results submitted by two laboratories should not be considered suspect unless they differ by more than the amounts calculated from the appropriate equations in **Table 1**. Results differing by less than “*R*” have a 95 % probability of being correct.

15.4 Bias—Since there is no accepted reference material suitable for determining the bias in this test method for measuring these impurities, bias has not been determined.

16. Quality Guidelines

16.1 Laboratories shall have a quality control system in place.

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

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

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

16.1.4 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.

17. Keywords

17.1 acetophenone; alpha methylstyrene; AMS; analysis by gas chromatography; benzene; butenylbenzene; butylbenzene; catechol; cumene; cymene; phenol; propylbenzene; toluene

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D6144 – 08) that may impact the use of this standard. (Approved December 1, 2012.)

(1) Sections 6, 7, 15 and 16 updated to current Editorial Guidelines.

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