~~Designation:D6144–04~~ Designation: D 6144 – 08

Standard Test Method for Analysis of AMS (α-Methylstyrene) by Capillary Gas Chromatography[1]

This standard is issued under the fixed designation D 6144; 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 E 29.

~~1.4~~

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.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 3437 Practice for Sampling and Handling Liquid Cyclic Products
D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals
D 6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials
E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E 355 Practice for Gas Chromatography Terms and Relationships
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

2.2 *Other Document:*

~~OSHA Regulations, 29CFR, paragraphs 1910.1000 and 1910.1200~~OSHA Regulations, 29CFR paragraphs 1910.1000 and 1910.1200[3]

3. Terminology

3.1 See Terminology D 4790 for definition of terms used in this test method.

4. Summary of Test Method

4.1 AMS ~~(alpha-methylstyrene)~~(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

---

[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 ~~C_9~~C9 and ~~C_{10} Aromatic Hydrocarbons.~~C10 Atomatic Hydrocarbons .

Current edition approved ~~Jan.~~June 1, ~~2004.~~2008. Published ~~January 2004.~~June 2008. Originally approved in 1997. Last previous edition approved in ~~1997~~2004 as ~~D6144-97.~~D 6144 - 04.

[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	Reproducibility	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
*n*Propylbenzene (NPB)	2.11 + 0.03*NPB	–7.81 + 0.37*NPB	55 – 195
Phenol	1.84	3.65 + 0.58*Phenol	1 – 40
*tert*Butylbenzene (TBB)	–1.22 + 0.035*TBB	3.63 + 0.087*TBB	150 – 650
*sec*Butylbenzene (SBB)	4.23 + 0.019*SBB	21.60 + 0.25*SBB	200 – 765
*m*Cymene	0.31 + 0.035*mCymene	2.34 + 0.35*mCymene	2 – 50
*o*Cymene	1.63	8.00	29 – 31
*p*Cymene	5.12	15.79	10 – 18
cis-2-Phenyl-2-Butene (CPB)	0.17 + 0.030*CPB	5.39 + 0.11*CPB	50 – 225
trans-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
para-tert-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
~~Alpha Methylstyrene Oxide (AMSO)~~	~~4.61~~	~~6.51 + 0.23*AMSO~~	~~13 – 32~~
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

of the impurities are measured and converted to concentrations via an external standard methodology. Purity by GC (the AMS 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. Unless the analyst can be sure of peak identity, for example by gas chromatography-mass spectrometry (GC-MS), the use of the column in Table 2 is strongly recommended.

TABLE 2 Instrumental Parameters

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

6.3 *Recorder*—Electronic integration is recommended.

6.4 *Injector*—The specimen must be precisely and repeatably 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, 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*~~— Chromatographic grade helium is recommended.~~ — 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*~~— Chromatographic grade.~~ — Purify air to remove water and hydrocarbons. Air for a FID should contain less than 0.1 ppm THC.

7.4 *Hydrogen*~~—High purity.~~ —99.999 % minimum purity.

8. Hazards

8.1 Consult current OSHA regulation~~,~~s, 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 D 3437.

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 E 1510 for more information on column installation. See Practice E 355 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.~~D 4307. 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*-proplybenzene, 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:

$$Rfi = Ci/Ai \tag{1}$$

where:

Rfi = ~~response factor for impurity i,~~ response factor for impurity i,
Ci = concentration of impurity i in the calibration mixture, and
Ai = ~~peak area of impurity i.~~peak area of impurity i.

11.4 Initially analyze the calibration solution a minimum of three times and calculate an average Rfi. Subsequent calibrations may be a single analysis as long as the Rfis for all components of interest are within ±5 % of the initial validation Rfis. A "rolling" average as defined by most modern chromatographic software may also be used. The Rfi 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.

---

[4] *Reagent Chemicals, American Chemical Society Specifications*~~,~~ , American Chemical Society, Washington, DC. For ~~s~~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.