



Designation: D5135 – 21

Standard Test Method for Analysis of Styrene by Capillary Gas Chromatography¹

This standard is issued under the fixed designation D5135; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method covers the determination of the impurities typically found in styrene and uses those values to determine the purity of styrene by difference by gas chromatography. Typical impurities in commercial styrene are found in [Table 1](#).

1.2 This test method is applicable to impurity concentrations up to 1 %.

1.2.1 The limit of detection is 0.0003 mass % and the limit of quantitation is 0.0010 mass %.

1.2.2 LOD and LOQ were calculated using data from ILS results for *n*-propylbenzene in [Table 3](#).

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For a specific hazard statement, see [Section 9](#).

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This test method is under the jurisdiction of ASTM Committee [D16](#) on Aromatic, Industrial, Specialty 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 1910.1200](#)³

3. Terminology

3.1 See [Terminology D4790](#) for definitions of terms used in this test method.

4. Summary of Test Method

4.1 In this test method, the chromatogram peak area for each impurity is compared to the peak area of the internal standard (*n*-heptane or other suitable known) added to the sample. From the response factors of these impurities relative to that of the internal standard and the amount of internal standard added,

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>.

TABLE 1 Impurities Known or Suggested to be Present in Commercial Styrene

Ethylbenzene
<i>o</i> -xylene
<i>m</i> -xylene
<i>p</i> -xylene
Isopropylbenzene
<i>n</i> -propylbenzene
<i>m</i> -ethyltoluene
<i>p</i> -ethyltoluene
α -methylstyrene
<i>m</i> -vinyltoluene
<i>p</i> -vinyltoluene
Phenylacetylene

the concentration of the impurities are calculated. The styrene content is obtained by subtracting the total amount of all impurities from 100.00.

5. Significance and Use

5.1 This test method is designed to obtain styrene purity on the basis of impurities normally present in styrene and may be used for final product inspections and process control.

5.2 This test method will detect the impurities shown in **Table 1**, non-aromatic hydrocarbons containing ten carbons or less, and others where specific impurity standards are available. Absolute purity cannot be determined if unknown impurities are present.

6. Interferences

6.1 The internal standard chosen must be satisfactorily resolved from any impurity as well as the product peak. A peak will be satisfactorily resolved from a neighboring peak if the distance from the valley to the baseline between the two peaks is not greater than 50 % of the peak height of the smaller of the two peaks.

7. Apparatus

7.1 *Gas Chromatograph*—Any instrument having a flame ionization detector that can be operated at the conditions given in **Table 2**.

TABLE 2 Recommended Operating Conditions

Carrier gas	helium, nitrogen, or hydrogen ^A
Carrier gas flow rate at 110°C, mL/min	1.2
Detector	flame ionization
Detector temperature, °C	240
Injection port temperature, °C	230
Hydrogen flow rate, mL/min	30
Air flow rate, mL/min	275
Make up gas	nitrogen
Make up gas flow rate, mL/min	23
Split flow, mL/min	150
Column	60 m × 0.32 mm ID × 0.5 μ m bonded polyethylene glycol-fused silica capillary
Column temperature, °C	110
Chart speed, cm/min	1
Sample size, μ L	0.6

^A **Warning**—Helium carrier gas was used to develop this standard. Use of nitrogen or hydrogen carrier gas requires different conditions. The user must conduct the necessary evaluation to determine that equivalent results are obtained.

7.2 *Column*—A capillary column containing a stationary phase of cross-linked polyethylene glycol has been found to be satisfactory. Any column can be used that is capable of resolving all significant impurities from styrene and from the internal standard. The choice of column is based on resolution requirements. Any column may be used that is capable of resolving all significant impurities from the major component. The column and conditions described in **Table 2** have been used successfully and shall be used as a referee in cases of dispute.

7.2.1 “Total non-aromatics” are defined as all components eluting before *o*-xylene, excluding benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, and cumene. The internal standard used for calibration is also excluded. Generally, non-aromatics are summed and reported as a group. In certain cases, one or more individual non-aromatic components, such as 1,4-dioxane, may be reported separately. In those cases, the grouping would not include the separately reported component(s), and the remaining non-aromatics would be reported as “Nonaromatics other than (component(s)).”

7.2.2 “Total C9-plus aromatics” are defined as cumene, plus all components eluting after *o*-xylene. Generally, C9-plus aromatics are summed and reported as a group. In certain cases, one or more individual C9-plus aromatic components, such as cumene or *p*-diethylbenzene, may be reported separately. In those cases, the grouping would not include the separately reported component(s) and the remaining C9-plus aromatics would be reported as “C9-plus aromatics other than (component(s)).” Very heavy non-aromatics may also elute in this region, but they are not common in materials within the scope of Committee D16, and are not considered in the definition.

7.3 *Recorder*—Chromatographic data systems are preferred but electronic integration may be used if the user can demonstrate that the results are consistent with the precision statement.

7.4 *100-mL Volumetric Flask*.

7.5 *Microsyringes*, assorted volumes.

8. Reagents and Materials

8.1 *Purity of Reagent*—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 Committee on Analytical Reagents of the American Chemical Society,⁴ where such specifications are available.

8.2 *Carrier Gas*, makeup and detector gases 99.999 % 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.

8.3 *Air*; purify to remove hydrocarbons and water. Air should contain less than 0.1 ppm THC.

⁴ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

8.4 *n*-Heptane, 99.0 % minimum purity, or other internal standard, such as *n*-octane, previously analyzed to be free of compounds coeluting with impurities in the sample.

8.5 Styrene, the highest purity available, but not less than 99.7 %.

8.6 *Pure Compounds*, for calibration, shall be those compounds that are typically present in commercial styrene. These should be at least 99 % pure as they are to be used for determining response factors.

8.7 *Equipment Setup Check Sample:*

8.7.1 The purpose is to:

(a) Determine retention times for the components measured in GC standards;

(b) Verify there is adequate resolution to measure the components of interest in GC standards; and

(c) Determine that the equipment has the sensitivity specified in the scope of the standard.

8.7.2 The equipment setup check sample should contain all the expected impurities and should contain a component with a concentration that is approximately two times the LOD stated in the scope of the standard. When the equipment setup check sample is analyzed, an acceptable result for the trace component is ± 50 % of the expected concentration.

8.7.2.1 If styrene can be purified or obtained with one of the expected impurities undetectable, then use that impurity to determine sensitivity. If this is not possible, then:

(a) Add an impurity that is not present in the primary material. Determine that the impurity has the following properties:

The impurity is essentially inert and unreactive in the primary material;

The retention time is sufficiently separated from other impurities so that there will be no mistake in identification;

The impurity is completely vaporized in the injection port; and

The impurity is well behaved on the column. That is, no fronting or tailing.

9. Hazards

9.1 Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this procedure.

10. Sampling

10.1 Sample the material in accordance with Practice D3437.

11. Preparation of Apparatus

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

12. Calibration

12.1 Prepare a calibration mixture containing approximately 99.5 mass % styrene and the expected significant impurities at

their expected concentration (see Practice D4307). Weigh all components to the accuracy required to calculate the concentration of each to the nearest 0.001 %.

12.2 With a microsyringe, add 50 μ L of internal standard to a 100-mL volumetric flask about three-fourths full of calibration mixture. Mix well. Add calibration mixture to mark and again mix well. If *n*-heptane is used as the internal standard, using a density of 0.684 for *n*-heptane and 0.906 for styrene, this solution will contain 0.0377 mass % *n*-heptane.

12.3 Also prepare a sample of the styrene used for the calibration blend with and without *n*-heptane to determine the concentration of existing impurities and interfering compounds with internal standard. If impurities in the styrene emerge with the chosen internal standard, an alternate internal standard must be used.

12.4 Inject an appropriate amount of sample into the chromatograph and obtain a chromatogram.

12.5 Measure the areas of all peaks, including the internal standard, except the styrene peak.

12.6 Calculate the response factors for each impurity relative to the internal standard as follows:

$$RF_i = \frac{C_i}{(C_s) \left(\frac{A_i}{A_{si}} - \frac{A_b}{A_{sb}} \right)} \quad (1)$$

where:

RF_i = response factor relative to the internal standard,

A_{si} = area of internal standard in calibration mixture,

A_i = area of impurity peak in calibration mixture,

A_{sb} = area of internal standard in styrene used in making calibration mixture,

A_b = area of impurity in styrene used to make calibration mixture,

C_s = mass percent internal standard in calibration mixture, and

C_i = mass percent impurity in calibration mixture.

13. Procedure

13.1 Establish stable instrument operation at the prescribed or selected operating conditions. Reference should be made to instructions provided by the manufacturer of the chromatograph.

13.2 Prepare sample as described in 12.2.

13.3 Inject appropriate amount of sample into the chromatograph and obtain the chromatogram. A typical chromatogram is shown in Fig. 1.

14. Calculation

14.1 Measure the areas of all peaks, including the internal standard, except the styrene peak.

14.2 Calculate the weight percent of the individual impurities, C_i , as follows:

$$C_i = \frac{(A_i) (RF_i) (C_s)}{A_s} \quad (2)$$