



Designation: D 5135 – 95

Standard Test Method for Analysis of Styrene by Capillary Gas Chromatography¹

This standard is issued under the fixed designation D 5135; 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 impurities in, and the purity of styrene by gas chromatography. It is applicable to styrene in the range from 99 to 100 % purity and to impurities at concentrations of 0.001 to 1.00 %. This test method may be used for lower purity but not all the impurities may be readily identified and the use of an internal standard becomes more difficult.

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 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 a specific hazard statement, see Section 7.

2. Referenced Documents

2.1 ASTM Standards:

D 3437 Practice for Sampling and Handling Liquid Cyclic Products²

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications³

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs³

2.2 Other Document

OSHA Regulations—29CFR paragraphs 1910.1000 and 1910.1200⁴

3. Summary of Test Method

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

4. Significance and Use

4.1 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.

4.2 This test method will detect the following impurities: non-aromatic hydrocarbons containing ten carbons or less, ethylbenzene, *p*- and *m*-xylene, cumene, *o*-xylene, *n*-propylbenzene, *m*- and *p*-ethyltoluene, alpha-methyl-styrene, *m*- and *p*-vinyltoluene and others where specific impurity standards are available. Absolute purity cannot be determined if unknown impurities are present.

5. Apparatus

5.1 *Gas Chromatograph*—Any gas chromatograph having a flame ionization detector and a splitter injector suitable for use with a fused silica capillary column may be used, provided the system has sufficient sensitivity to obtain a minimum peak height response of 0.1 mV for 0.010 % internal standard when operated at the stated conditions. Background noise at these conditions is not to exceed 3 μ V.

5.2 *Column*—Capillary columns have been found to be satisfactory. For example, 60 m of 0.32-mm inside diameter polar-fused silica capillary internally coated to a 0.5- μ m thickness with a bonded (cross-linked) polyethylene glycol can be used (see Table 1 for parameters). Other columns may be used after it has been established that such a column is capable of separating all major impurities and the internal standard from the styrene under operating conditions appropriate for the column (see Practice E 1510).

5.3 *Electronic Integration*, with tangent capabilities is recommended.

5.4 *100-mL Volumetric Flask*.

5.5 *Microsyringes*, assorted volumes.

6. Reagents and Materials

6.1 *Carrier Gas*—a carrier gas (minimum purity of 99.95

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 06.04.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

TABLE 1 Typical Instrument Parameters

Carrier gas	helium
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 µm bonded polyethylene glycol-fused silica capillary
Column temperature, °C	110
Chart speed, cm/min	1
Sample size, µL	0.6

mol %) appropriate to the type of detector used should be employed.

Precaution—If hydrogen is used, take special safety precautions to ensure that the system is free of leaks and that the effluent is properly vented or burned.

6.2 *Hydrogen* and air for the flame ionization detector (FID).

6.3 *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.

6.4 *Styrene*, the highest purity available, but not less than 99.6 % as determined by freezing point.

6.5 *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.

7. Hazards

7.1 Consult the latest OSHA regulations, suppliers' Material Safety Data Sheets, and local regulations for all materials used in this procedure.

8. Sampling

8.1 Sample the material in accordance with Practice D 3437.

9. Procedure

9.1 Prepare a calibration mixture containing approximately 99.5 weight % styrene and the expected significant impurities at their expected concentration. Weigh all components to the accuracy required to calculate the concentration of each to the nearest 0.001 %.

9.2 With a microsyringe, add 50 µL of internal standard to a 100-mL volumetric flask about three-fourths full of the 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 weight % *n*-heptane.

9.3 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.

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

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

9.6 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 = weight percent internal standard in calibration mixture, and

C_i = weight percent impurity in calibration mixture.

10. Sample Preparation

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

10.2 Prepare sample as described in 9.2.

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

11. Calculation

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

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

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

where:

A_i = area of impurity,

A_s = area of internal standard,

RF_i = response factor for impurity, relative to the internal standard, and

C_s = concentration of internal standard, in weight percent.

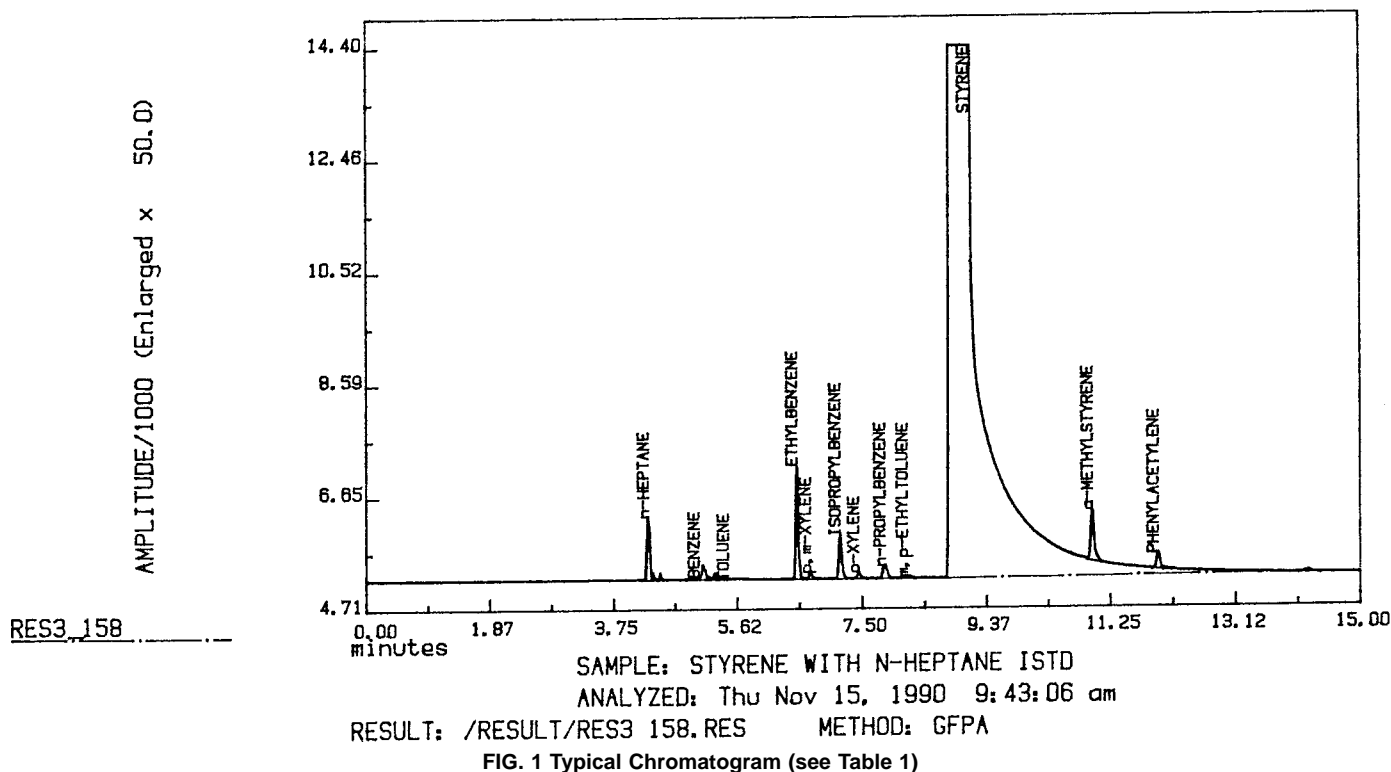
11.3 Calculate the styrene content by subtracting the sum of the impurities from 100.00. Styrene weight percent = 100.00 – (sum of impurities).

12. Report

12.1 Report the concentration of impurities to the nearest 0.001 % and the styrene content to the nearest 0.01 %.

13. Precision and Bias

13.1 *Precision*—The following criteria should be used to judge the acceptability (95 % probability level) of results obtained by this test method. The criteria were derived from a



round robin among six laboratories. The data were run on two days using different operators.

13.2 *Intermediate Precision*—Results in the same laboratory should not be considered suspect unless they differ by more than the normal amount shown in Table 2 and Table 3.

13.3 *Reproducibility*—The results by each of two laboratories should not be considered suspect unless they differ by

TABLE 2 Precision for Styrene and Impurities at Stated Levels

Component	Concentration, weight %	Intermediate Precision, %	Reproducibility, %
Styrene	99.74	0.017	0.054
Ethylbenzene	0.043	0.002	0.001
α-methylstyrene	0.028	0.0001	0.004
Isopropylbenzene	0.008	0.001	0.001
n-propylbenzene	0.004	0.0003	0.001
m- and p-ethyltoluene	0.014	0.001	0.005
p, m-xylene	0.125	0.005	0.007
o-xylene	0.030	0.001	0.042

TABLE 3 Precision for High Purity Styrene and Impurities at Stated Levels

Component	Concentration, weight %	Intermediate Precision, %	Reproducibility, %
Styrene	99.96	0.024	0.033
Ethylbenzene	0.014	0.003	0.004
α-methylstyrene	0.007	0.002	0.003

more than the amount shown in Table 2 and Table 3.

13.4 No statement is made about bias since no acceptable reference material and value is available.

14. Keywords

14.1 analysis by gas chromatography; impurities in styrene; purity of styrene; styrene; styrene monomer

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