1. Scope

1.1 This test method covers the determination of the impurities in, and the purity of styrene by gas chromato-
graphy. 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 responsi-
bility 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 6.

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 deter-
mined 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 μV.

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-μm
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 appro-
priate 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.

<table>
<thead>
<tr>
<th>TABLE 1 Typical Instrument Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier gas</td>
</tr>
<tr>
<td>Carrier gas flow rate at 110°C, mL/min</td>
</tr>
<tr>
<td>Detector</td>
</tr>
<tr>
<td>Detector temperature, °C</td>
</tr>
<tr>
<td>Injection port temperature, °C</td>
</tr>
<tr>
<td>Hydrogen flow rate, mL/min</td>
</tr>
<tr>
<td>Air flow rate, mL/min</td>
</tr>
<tr>
<td>Make up gas</td>
</tr>
<tr>
<td>Make up gas flow rate, mL/min</td>
</tr>
<tr>
<td>Split flow, mL/min</td>
</tr>
<tr>
<td>Column</td>
</tr>
<tr>
<td>Column temperature, °C</td>
</tr>
<tr>
<td>Chart speed, cm/min</td>
</tr>
<tr>
<td>Sample size, μL</td>
</tr>
</tbody>
</table>

1 This test method is under the jurisdiction of ASTM Committee D-16 on
Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of
Subcommittee D16.04 on Styrene, Ethylbenzene, and C9 and C10 Aromatic
Hydrocarbons.

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4 Available from Superintendent of Documents, U.S. Government Printing
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6. Hazards
6.1 Consult the latest OSHA regulations, suppliers' Material Safety Data Sheets, and local regulations for all materials used in this procedure.

7. Reagents and Materials
7.1 Carrier Gas—a carrier gas (minimum purity of 99.95 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.

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

7.3 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.

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

7.5 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.

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 the chromatogram. A typical chromatogram is shown in Fig. 1.

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:

\[
C_i = \frac{(A_i)(RF_i)(C_s)}{A_s}
\]

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 2A.

13.3 Reproducibility—The results by each of two laboratories should not be considered suspect unless they differ by more than the amount shown in Table 2 and 2A.

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.
TABLE 2 Precision for Styrene and Impurities at Stated Levels

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration, weight %</th>
<th>Intermediate Precision, %</th>
<th>Reproducibility, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>99.74</td>
<td>0.017</td>
<td>0.054</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.043</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>α-methylstyrene</td>
<td>0.028</td>
<td>0.0001</td>
<td>0.004</td>
</tr>
<tr>
<td>Isopropybenzene</td>
<td>0.008</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>n-propybenzene</td>
<td>0.004</td>
<td>0.0003</td>
<td>0.001</td>
</tr>
<tr>
<td>m- and p-ethyltoluene</td>
<td>0.014</td>
<td>0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>p, m-xylene</td>
<td>0.125</td>
<td>0.005</td>
<td>0.007</td>
</tr>
<tr>
<td>o-xylene</td>
<td>0.030</td>
<td>0.001</td>
<td>0.042</td>
</tr>
</tbody>
</table>

TABLE 2A Precision for High Purity Styrene and Impurities at Stated Levels

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration, weight %</th>
<th>Intermediate Precision, %</th>
<th>Reproducibility, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>99.96</td>
<td>0.024</td>
<td>0.033</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.014</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>α-methylstyrene</td>
<td>0.007</td>
<td>0.002</td>
<td>0.003</td>
</tr>
</tbody>
</table>

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