Designation: D 3797 – 04

Standard Test Method for Analysis of *o*-Xylene by Gas Chromatography[1]

This standard is issued under the fixed designation D 3797; 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 analysis of normally occurring impurities in, and the purity of, *o*-xylene by gas chromatography. Impurities determined include nonaromatic hydrocarbons, benzene, toluene, *p*- and *m*-xylenes, cumene, styrene, and ethylbenzene.

1.2 This test method is applicable for impurities at concentrations from 0.001 to 2.000 % and for *o*-xylene purities of 98 % or higher.

1.3 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.

1.4 *This standard does not purport to address all of 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 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

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

2.2 *Other Documents:*

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

3. Terminology

3.1 *Definitions:*

3.1.1 For definition of terms used in this test method see Terminology D 4790.

4. Summary of Test Method

4.1 A known amount of internal standard is added to the sample. A gas chromatograph equipped with a flame ionization detector and a polar-fused silica capillary column is used for the analysis. The impurities are measured relative to the internal standard. To calculate *o*-Xylene purity subtract the impurities found from 100.00 %.

5. Significance and Use

5.1 This test method is suitable for setting specifications on *o*-xylene and for use as an internal quality control tool where *o*-xylene is used in a manufacturing process. It may be used in development or research work involving *o*-xylene.

5.2 Purity is commonly reported by subtracting the determined expected impurities from 100 %. Absolute purity cannot be determined if unknown impurities are present.

6. Apparatus

6.1 *Gas Chromatography*—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.

6.2 *Chromatographic Column*, fused silica capillary, 60-m long, 0.32-mm inside diameter, internally coated to a 0.5-µm thickness with a bonded (cross-linked) polyethylene glycol. Other columns may be used after it has been established that such column is capable of separating all major impurities and

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[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 D16.01 on Benzene, Toluene, Xylenes, Cyclohexane and Their Derivatives.

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[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.

***A Summary of Changes section appears at the end of this standard.**

the internal standard from the *o*-xylene under operating conditions appropriate for the column.

6.3 *Recorder*, optional.

6.4 Electronic integration with tangent capabilities (required).

6.5 *Microsyringes*, 10-µL, and 50-µL.

6.6 *Volumetric Flask*, 50-mL.

7. Reagents and Materials

7.1 *Carrier Gas*, hydrogen or helium, 99.999 % minimum purity. Oxygen content in carrier less than 1 ppm (less than 0.5 ppm preferred). Purify to remove hydrocarbons and water.

7.2 *Compressed Air*, 99.999 % minimum purity. Purify to remove hyrdocarbons and water.

7.3 *Hydrogen*, 99.999 % minimum purity. Purify to remove hydrocarbons, oxygen, and water.

7.4 *Nitrogen*, 99.999 % minimum purity. Purify to remove hydrocarbons, oxygen, and water.

7.5 Pure compounds for calibration shall include *n*-nonane (Note 1), toluene, styrene, ethylbenzene, *p*-xylene, *m*-xylene, *o*-xylene, cumene (isopropylbenzene), *iso*-octane (2,2,4-trimethylbenzene), (Note 2), and *n*-undecane (Note 2), of a purity not less than 99 %. If the purity of the calibration compounds is less than 99 %, the concentration and identification of impurities must be known so that the composition of the final weighed blends can be adjusted for presence of the impurities.

NOTE 1—*n*-nonane represents the nonaromatic in a sample.

NOTE 2—Any of these compounds may be used as an internal standard provided it elutes free of contamination.

8. Hazards

8.1 Consult current OSHA regulations,local regulations, and supplier's Material Safety Data Sheets for all materials used in this test method.

9. Sampling

9.1 Guidelines for taking samples from bulk are given in Practice D 3437.

10. Calibration

10.1 Prepare a synthetic mixture in accordance with Practice D 4307 from pure hydrocarbons with all of the aromatic compounds present in the sample to be analyzed containing approximately 98.0 weight % *o*-xylene and the expected significant impurities at their expected concentration. A typical composition is given in weight percent. *o*-Xylene of a purity not less than 99 weight % must be used in preparing the calibration mixture. The pure material itself must be analyzed and corrections made in the composition of the calibration blend as required. Sample the material in accordance with Practice D 3437. The standard may be purchased if desired.

Typical Concentrations for Calibration Blend

o-xylene	98.25 %
toluene	0.2 %
p-xylene	0.2 %
m-xylene	0.4 %
ethylbenzene	0.2 %
cumene	0.3 %
n-nonane	0.2 %
styrene	0.05 %

10.2 Analyze the *o*-xylene used in preparing the calibration blend as described in 11.2 and 11.3. Calculate the purity of the stock *o*-xylene as shown in 12.3, using an assumed response factor of 1.00 for each impurity. This will verify that the *o*-xylene used in preparing this test method is 99 weight % or better.

10.3 Analyze the calibration blend as described in 11.3.

10.4 Calculate response factors as follows:

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

where:

R_i = response factor for impurity relative to internal standard,
A_i = area of impurity peak in calibration blend,
A_b = area of impurity in the stock *o*-xylene,
C_s = concentration of internal standard, weight %,
A_{si} = area of internal standard peak in calibration blend,
A_{sb} = area of internal standard peak in stock *o*-xylene, and
C_i = concentration of impurity, weight, %.

10.5 Calculate response factors to the nearest 0.001.

11. Procedure

11.1 Install the chromatograph column and establish stable instrument operation at the operating conditions shown in Table 1 (Note 1). Refer to instructions provided by the manufacturer of the gas chromatograph and Practices E 355 and E 1510.

11.2 Fill a 50-mL volumetric flask to the mark with test specimen. With a microsyringe, add 30 µL of the internal standard. Mix well. When using *iso*-octane as the internal standard and assuming densities of 0.692 for *iso*-octane and 0.880 for *o*-xylene, the resulting *iso*-octane concentration will be 0.05 weight %. When using *n*-undecane as the internal standard and assuming densities of 0.740 for *n*-undecane and 0.880 for *o*-xylene, the resulting *n*-undecane concentration will be 0.05 weight %.

TABLE 1 Typical Instrument Parameters

Carrier	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
Airflow rate, mL/min	275
Make-up gas	Nitrogen or Helium
Make-up gas flow rate, mL/min	23 (nitrogen or 30 (helium)
Split flow, mL/min	150
Column temperature program:	
Initial temperature, °C	70
Initial time, min	24
Programming rate, °C/min	20
Final temperature, °C	210
Chart speed, cm/min	1

NOTE 1—The flame ionization detector makeup gas flow rates for nitrogen and helium shown in Table 1 are suggested values. Analysts should refer to the instrument manufacturer's recommendation for the optimal values.

11.3 Inject between 0.5 to1.0 µL of solution into the gas chromatograph and obtain the chromatogram. A typical chromatogram is shown in Fig. 1. An injection size of 0.6 µL was used for Fig. 1 and for the intermediate precision described in 14 and Table 2.

TABLE 2 Intermediate Precision

Component	Concentration weight %	Intermediate Precision	Reproducibility
Styrene	0.005	0.001	0.002
Cumene	0.221	0.014	0.057
m-Xylene	1.066	0.058	0.26
p-Xylene	0.192	0.039	0.066
Ethylbenzene	0.011	0.001	0.005
Toluene	0.063	0.004	0.017
Benzene	0.091	0.005	0.026
Nonaromatics	0.088	0.026	0.065
o-Xylene	98.261	0.10	0.42

12. Calculation

12.1 Measure the areas of all peaks, including the internal standard, except for the *o*-xylene peak.

12.2 Sum all the peaks eluting between the *iso*-octane and toluene peaks. Identify this sum as nonaromatic hydrocarbons plus benzene.

12.3 Calculate the weight percent of the individual impurities, C_i to the nearest 0.001 % as follows:

$$C_i = \frac{IS\, A_i(R_i)}{(A_s)} \quad (2)$$

where:

IS = internal standard, weight %,
A_i = area of impurity,
R_i = response factor for impurity, and
A_s = area of internal standard.

12.4 Use the response factor determined for *n*-nonane for all the nonaromatic hydrocarbon plus benzene peaks.

12.5 Calculate the purity of the *o*-xylene by subtracting the sum of the impurities from 100.00.

13. Report

13.1 Report the following information:

13.1.1 The concentration of each impurity to the nearest 0.001 weight % , and

13.1.2 The purity of *o*-xylene to the nearest 0.01 % .

14. Intermediate Precision and Bias[4]

14.1 *Precision*—The following criteria should be used to judge the acceptability (95 % probability level) of the results obtained by this test method. The criteria were derived from a round robin between nine laboratories. The data were run over two days using different operators.

14.1.1 *Intermediate Precision formerly called Repeatability*—Results in the same laboratory should not be considered suspect unless they differ by more than the amount shown in Table 2.

14.1.2 *Reproducibility*—The results submitted by two laboratories should not be considered suspect unless they differ by more than the amount shown in Table 2.

14.2 *Bias*—No statement is made about bias since no acceptable reference material and value are available.

15. Keywords

15.1 gas chromatography; *o*-xylene; purity

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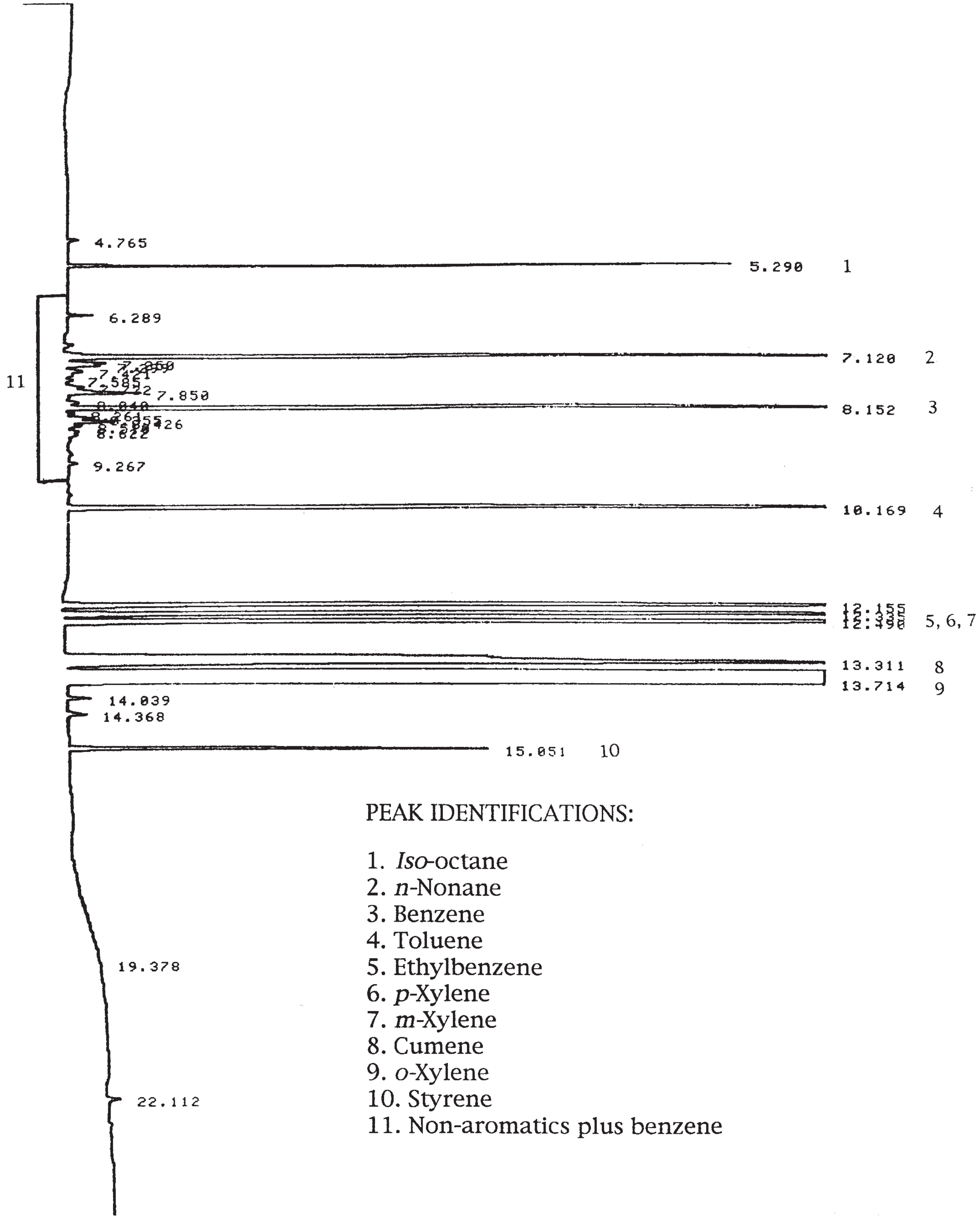
[4] Supporting data are available at ASTM International Headquarters. Request Research Report RR:D16 – 1019.



PEAK IDENTIFICATIONS:

1. *Iso*-octane
2. *n*-Nonane
3. Benzene
4. Toluene
5. Ethylbenzene
6. *p*-Xylene
7. *m*-Xylene
8. Cumene
9. *o*-Xylene
10. Styrene
11. Non-aromatics plus benzene

FIG. 1 Typical Chromatogram (See Table 1)

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D 3797 - 03) that may impact the use of this standard.

(1) Section 6.3 was modified to make the recorder optional
(2) Section 7.5 was modified to clarify chemical names.
(3) Section 10.1 was modified to change the description of the standard from suggested to typical.
(4) Section 10.1 was modified to removebenzene from the calibration blends.
(5) Section 11.2 was modified to describe the resulting internal standard concentration obtained when using the standard preparation procedure.
(6) Section 11.3 was modified to allow 0.5 to 1.0 µL injections instead of requiring exactly 0.6 µL.
(7) Note was added to Table 1 to indicate that the FID makeup flow rates in the tableare suggested values.

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