Designation: D2121 – 16

Standard Test Methods for Polymer Content of Styrene Monomer[1]

This standard is issued under the fixed designation D2121; 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 These test methods cover the determination of the polymer content of styrene monomer. It should be noted, however, that dimers and trimers are not measured by these test methods.

1.2 *Test Method A,* which is based on the use of a spectrophotometer or photometer, is intended for the quantitative determination of the polymer content of styrene monomer in concentrations up to 15 mg/kg. Samples containing more than 15 mg/kg of polymer must be suitably diluted before measurement.

1.3 *Test Method B* is a rapid visual procedure that is intended for the approximate evaluation of polymer to a maximum concentration of 1.0 mass %. Samples having a polymer content of 1.0 mass % or greater should be suitably diluted prior to measurement.

1.4 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.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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 specific hazard statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2827 Specification for Styrene Monomer

D3437 Practice for Sampling and Handling Liquid Cyclic Products

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

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Document:*

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

3. Terminology

3.1 See Terminology D4790 for definition of terms used in this test method.

TEST METHOD A—DETERMINATION OF POLYMER IN STYRENE MONOMER PHOTOMETER METHOD

4. Summary of Test Method

4.1 This test method utilizes the fact that polymers present in the monomers are insoluble in methanol. The polymer content of styrene monomer is determined by measurement of the degree of turbidity produced by the addition of dry methanol to the styrene sample.

5. Significance and Use

5.1 This test method can be used for determining polymer concentrations in styrene monomer.

5.2 This test method will not detect dimers and trimers.

5.3 This test method can be used for plant control and for specification analysis.

6. Interferences

6.1 Small changes in turbidity may occur with time. It is, therefore, important that the absorbance of calibration mixtures and samples be determined after standing the same length of time.

[1] These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and are the direct responsibility of Subcommittee D16.07 on Styrene, Ethylbenzene and C9 and C10 Aromatic Hydrocarbons.

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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, http://www.access.gpo.gov.

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

6.2 Hexane is used for two reasons:
6.2.1 To block out any color in the styrene, and
6.2.2 To indicate dissolved water in the styrene.

7. Apparatus

7.1 *Pipets,* 10 and 15-mL.

7.2 *Bottles or Flasks,* of suitable size equipped with glass stoppers.

7.3 *Spectrophotometer or Photometer Cells,* with 50 to 150-mm light path.

7.4 *Spectrophotometer or Photometer,* capable of absorbance measurements in wavelength region of 420 nm and sensitive to 1 mg polymer/kg monomer.

8. Reagents and Materials

8.1 *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 specifications 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.

8.2 *Hexane,* dry.

8.3 *Methanol,* dry.

8.4 *Polystyrene:*
8.4.1 Prepare polystyrene as follows: wash 50 mL of styrene monomer twice with equal volumes of 1 *N* NaOH solution and twice with equal volumes of water. After the second water wash, filter the styrene through two layers of rapid filtering ready folded filter paper. Pour about 20 mL of this styrene monomer into a test tube and heat in an oven at 100°C for 24 h to promote polymerization. At the end of this time, remove the polystyrene from the test tube by breaking the tube and discarding all glass. Grind the polymer plug to a fine powder in an agate mortar.
8.4.2 Commercially available high-purity polystyrene pellets can be used; however, high-molecular weight polystyrene (>150 000 molecular weight) should be specified.

8.5 *Styrene Monomer,* conforming to Specification D2827.

8.6 *Toluene,* dry.

9. Hazards

9.1 Styrene monomer is flammable and polymerizes exothermically on contact with peroxides, mineral acids and aluminum chloride.

9.2 Styrene monomer both in liquid and vapor state, when in sufficient concentrations, acts as an irritant to the eyes and respiratory tract.

9.3 Consult current OSHA regulations, local regulations, and suppliers' Safety Data Sheets for all materials used in these test methods.

10. Sampling and Handling

10.1 Sample the material in accordance with Practice D3437.

11. Calibration

11.1 *Apparatus*—Prepare and operate the spectrophotometer or photometer in accordance with the manufacturer's instructions.

11.2 *Reference Standards and Blanks:*
11.2.1 Dissolve 0.0905 g of polystyrene in 1000 mL of toluene measured at 25°C, which is equivalent to 100 mg/kg of polymer in monomer. This serves as the standard for polymer in styrene.
11.2.2 Make standard solutions containing 1, 3, 6, 9, 12, and 15 mg/kg of styrene polymer by diluting 1, 3, 6, 9, 12, and 15 mL of the 100 mg/kg standard solution to 100 mL with toluene in a volumetric flask at 25°C.

11.3 *Calibration Curves and Tables:*
11.3.1 Into each of a series of bottles equipped with glass stoppers pipet 15 mL of dry methanol and 10 mL of a polymer standard and mix thoroughly. Into another series of bottles pipet 15 mL of hexane and 10 mL of each polymer standard and mix thoroughly. Other volumes may be used, depending on the capacity of the spectrophotometer cell as long as the 3:2 proportion is maintained.
11.3.2 Allow the solutions to stand in the stoppered bottles for 15 min ± 1 min (Note 1). At the end of this time, pour the solutions into the spectrophotometer cells and measure the absorbance of each at a wavelength of 420 nm using the hexane/polymer standard as the blank (Note 2).

NOTE 1—Small changes in turbidity may occur with time. It is, therefore, important that the absorbance of calibration mixtures and samples be determined after standing the same length of time.

NOTE 2—The hexane is used for two reasons: *(1)* to blank out any color in the styrene, and *(2)* to indicate dissolved water in the styrene.

11.3.3 Prepare a calibration curve by plotting the absorbance against the milligrams per kilogram of polymer.

12. Procedure

12.1 Pipet 15 mL of hexane into a bottle equipped with a glass stopper.

12.2 Into a second bottle, pipet 15 mL of dry methanol.

12.3 Add 10 mL of styrene monomer to each bottle and mix thoroughly.

12.4 Proceed as described in 11.3.2 using the hexane mixture as the blank.

13. Calculation

13.1 Read the milligrams per kilogram of polymer directly from the calibration curve.

NOTE 3—Milligrams per kilogram can be converted to mass percent by dividing by 10 000.

[4] *Reagent Chemicals, American Chemical Society Specifications*, 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.

TABLE 1 Styrene (*mg/kg*)

Material	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Sample 1 — 0.4 mg/kg	1.673	1.796	2.827
Sample 2 — 2 mg/kg	2.413	1.711	3.792
Sample 3 — 4 mg/kg	3.759	4.268	5.090
Sample 4 — 10 mg/kg	10.143	3.254	9.037

[A] The average of the laboratories' calculated averages.

TABLE 2 % Recovery

Material	Average[A] (mg/kg)	Average Recovery (%)
Sample 1 — 0.4 mg/kg	1.673	418.2
Sample 2 — 2 mg/kg	2.413	120.6
Sample 3 — 4 mg/kg	3.759	94.0
Sample 4 — 10 mg/kg	10.143	101.4

[A] The average of the laboratories' calculated averages.

14. Report

14.1 Report the polymer content of the sample as milligrams of polymer per kilogram of monomer to the nearest mg/kg. For results less than 1 mg/kg, report <1 mg/kg.

15. Precision and Bias[5]

15.1 An ILS was conducted which included ten laboratories analyzing four samples three times. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D16-1053.

15.2 *Repeatability:*

15.2.1 Results should not be suspect unless they differ by more than shown in Table 1. Results differing by less than *r* have a 95 % probability of being correct.

15.3 Reproducibility results submitted by two labs should not be considered suspect unless they differ by more than shown in Table 1. Results differing by less than *R* have a 95 % probability of being correct.

15.4 Reproducibility limits are listed in Table 1.

15.5 *Bias*—Since there is no accepted reference material suitable for determining bias for the procedure in these test methods, bias has not been determined.

16. Quality Guidelines

16.1 Laboratories shall have a quality control system in place.

16.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

16.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

16.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

16.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

TEST METHOD B—VISUAL EVALUATION OF POLYMER CONTENT OF STYRENE MONOMER

17. Summary of Test Method

17.1 This test method utilizes the fact that styrene polymers are insoluble in methanol. The polymer content of a sample of styrene monomer is evaluated by visual observation of the degree of turbidity produced by the addition of methanol to the sample. The order of magnitude of the polymer content of styrene monomer in the incremental steps 0.001, 0.01, 0.1, and 1.0 mass % may readily be differentiated visually. For 0 % observe pure dry methanol.

18. Apparatus

18.1 *Test Tube,* 25 by 150-mm.

18.2 *Pipets,* 2 and 10-mL.

18.3 *Daylight Fluorescent Tube,* equipped with curved reflector.

19. Reagents

19.1 *Methanol,* dry.

19.2 *Polystyrene,* uncolored, unfilled, unlubricated (see 8.4).

19.3 *Toluene,* dry.

20. Procedure

20.1 Pipet 2 mL of sample into a clean, dry test tube, add 10 mL of dry methanol by means of a pipet, stopper the test tube with a cork covered with aluminum foil, and shake vigorously for a few seconds.

20.2 After shaking the test tube, inspect the mixture visually by looking through it toward a source of artificial daylight. Compare the observed turbidity of the mixture with the descriptions of turbidity given in Table 3 or against known

TABLE 3 Relationship Between Polymer Content of Styrene Monomer and Turbidity of Mixture of Two Parts by Volume Styrene Monomer and Ten Parts by Volume Dry Methanol

Polymer Content of Styrene Monomer by Weight, %[A]	Description of Turbidity of Styrene-Methanol Mixture
1.0 or greater	milk-white opaque liquid with heavy white precipitate
0.1	milk-white opaque liquid with no evidence of sedimentation
0.01	cloudiness readily visible, but mixture still transparent
0.001	faint trace of cloudiness; detectable only by comparison with pure dry methanol
None	no cloudiness discernible by comparison with pure dry methanol

[A] It is suggested that the analyst initially perform the test using reference mixtures described in this table as a guide. An experienced analyst can estimate the polymer content reliably without the use of reference mixtures.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1053. Contact ASTM Customer Service at service@astm.org.

standards. If standards are desired, they may be prepared using polystyrene and toluene.

21. Report

21.1 From Table 3 select the turbidity description that most nearly approximates that of the sample, and report the corresponding polymer content.

22. Keywords

22.1 polymer; polymer content; styrene; styrene monomer

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D2121–15) that may impact the use of this standard. (Approved June 1, 2016.)

(1) Section 11.2.1 — The mass of polymer was revised.

Committee D16 has identified the location of selected changes to this standard since the last issue (D2121–07) that may impact the use of this standard. (Approved March 15, 2015.)

(1) All references to AMS removed.
(2) Section 3 Terminology added.
(3) Section 11.2 — mass for stock solution corrected.
(4) Section 15 — new precision statements.
(5) Section 16 — revised to match D16 Editorial Guidelines.