Designation: D4026 − 06 (Reapproved 2017)

Standard Test Method for Rubber Latex—Styrene-Butadiene Copolymer—Determination of Residual Styrene[1]

This standard is issued under the fixed designation D4026; 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 residual styrene content of styrene butadiene (SBR) latex. This test method is based upon direct injection of a diluted latex into a gas chromatograph. The amount of residual styrene is calculated using an internal standard technique.

1.2 The range of residual styrene covered is approximately 100 to 3000 mg/kg (ppm) with a lower detection limit of approximately 50 mg/kg (ppm).

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

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 specific safety statements, see Section 8.)

1.5 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

3. Summary of Test Method

3.1 A sample of latex is mixed with a wetting agent and an internal standard of vinyl toluene. It is then injected into a gas chromatograph equipped with a flame ionization detector. The amount of residual styrene is determined by the internal standard technique.

4. Significance and Use

4.1 The amount of residual styrene (unreacted styrene) in an SBR latex must be studied from health, safety, economic, and environment viewpoints. This test method is useful in studying these aspects of residual styrene and also in research, development, and factory processing problems.

5. Interferences

5.1 Materials that interfere with the complete separation of styrene and vinyl toluene must be absent. Matrix effects (anything in the latex that affects the release of styrene or vinyl toluene, or both) may be minimized by the use of an addition technique.

6. Apparatus

6.1 *Gas Chromatograph:*

6.1.1 Any gas chromatograph whose operating parameters and columns provide well-resolved, narrow, styrene and vinyl toluene peaks, free of interference, may be used. The chromatograph must be equipped with a flame ionization detector (FID) and preferably with some means of electronic or microprocessor type of integration. Detectors must be operated in the 200 to 300°C range and injection ports must be operated in the 200 to 210°C range.

NOTE 1—It is understood that the gas chromatograph will be operated in accordance with the manufacturer's instructions for optimum performance and that the equipment will be operated by persons knowledgeable in the techniques of gas chromatography. Practice E260 and Practice E355, manufacturer's literature, and standard texts on gas chromatography are especially helpful.

6.1.2 Equip the chromatograph with removable glass liners for easy cleaning. *Cleaning will be required when spurious*

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[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and Rubber-like Materials and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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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.

TABLE 1 Parameters for the Gas Chromatograph

NOTE 1—Packings and supports may also be obtained from most companies that supply gas chromatographic supplies and equipment.

Chromatograph	*A*	*B*	*C*	*D*	*E*
Column:					
Glass	X				X
Stainless steel		X	X	X	
Length, cm	300	300	300	180	150
Outside diameter, mm	6	3	3	3	6
Inside diameter, mm	2	—	—	—	2
Packed with	20 % SP 2100^{A,B} or OV-101/0.1 %^{C,B} Carbowax 1500$^{D, B}$	20 % SP 2100 or OV-101/0.1 % Carbowax 1500	10 % OV 225^{C,B}	10 % Apiezon L^{E,B}	5 % SP 1200/ 1.7 % Bentone 34^{F,B}
Support type	Supelcoport^{A,B}	Supelcoport	(1) Chromosorb W-HP^{G,B} (2) Chromosorb P-NAW^{G,B}	Chromosorb W	Supelcoport
Mesh size, µm^{H}	150/125	150/125	(1) 150/125 (2) 180/150	180/150	125
Carrier gas	helium	helium	helium	helium	helium
Carrier gas flow, cm^3/min	30	30	15	30	—
Detector, °C	250	250	250	200	300
Program:					
Initial, °C	80–90	80–90		50	85
Initial time, min	5	5		2	19
Rate,° C	8	8		16	50
Final, °C	120	120	135	150	165
Isothermal	No	No	Yes	No	No

[A] The sole source of supply of the apparatus (SP 2100 and Supelcoport) known to the committee at this time is Supelco, Inc., Supelco Park, Bellefonte, PA 16823.

[B] If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[C] The sole source of supply of the apparatus (OV-101 and 225) known to the committee at this time is Pierce Chemical Co., P.O. Box 117, Rockford, IL 61105.

[D] The sole source of supply of the apparatus (Carbowax 1500) known to the committee at this time is Union Carbide Corp., 270 Park Ave., New York, NY 10017.

[E] The sole source of supply of the apparatus (Apiezon L) known to the committee at this time is the James G. Biddle Co., Township Line & Jolly Rds., Plymouth Meeting, PA 19462.

[F] The sole source of supply of the apparatus (Bentone 34) known to the committee at this time is the National Lead Co., Baroid Div., Box 1675, Houston, TX 77001.

[G] The sole source of supply of the apparatus (Chromosorb P-NAW and W-HP) known to the committee at this time is Johns-Mansville, 22 E. 40 St., New York, NY 10016.

[H] Specification E11; Sieve designations: No. 80 180µ m, No. 100 150 µm, No. 120 125 µm.

peaks begin to appear and usually after about 20 injections. If glass liners are not available, metal liners, packed with glass wool, may be used.

6.2 *Gas Chromatographic Columns, Packings, and Programs*—Any column, packing, or program listed in Table 1 is satisfactory, as long as it produces narrow, well-resolved styrene and vinyl toluene peaks. Other columns, packings, and programs may be used, as long as they satisfy these requirements.

6.3 *Syringes,* capable of delivering 1 mm^3 (1µL).

NOTE 2—Syringes may be cleaned by drawing water into the syringe barrel, then ejecting it, while heating the syringe needle with a small flame.

6.4 *Pipets,* capable of accurately delivering 0.1 cm^3.

6.5 *Glass Vials,* of 20-cm^3 capacity, equipped with self-sealing septa.

6.6 *Analytical Balance,* capable of weighing to ±0.1 mg.

6.7 *Ordinary Laboratory Glassware,* necessary for carrying out this procedure.

6.8 *Mechanical Shaker,* that will accept the vials of 6.5. (Desirable, but not mandatory.)

7. Reagents and Materials

7.1 *Deionized Water* or equivalent.

7.2 *Nonionic Wetting Agent (iso*octyl phenyl polyethoxy ethanol).[3]

7.3 *Styrene* (*p*-tert butyl catechol, inhibited)—There shall be no chromatographic peaks that interfere with vinyl toluene and it shall show no turbidity when mixed with methanol.

7.4 *Vinyl Toluene* (polymerization grade—28 % *p*-vinyl toluene and 72 % *m*-vinyl toluene) and pure *o*-vinyl toluene. Both chemicals elute from the chromatograph as one sharp peak and have the same response to the FID. Neither of these chemicals shall show turbidity when mixed with methanol.

8. Safety Precautions

8.1 Special care should be exercised in the use of compressed gases required for the operation of the gas chromatograph. Styrene and vinyl toluene should be handled in well-ventilated areas or in fume hoods, to minimize health and safety hazards.

9. Sampling and Selection of Test Portions

9.1 Since the use of this test method may be required for any purpose listed under Section 4, the analyst may choose the

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[3] The sole source of supply of nonionic wetting agent (Triton X100) known to the committee at this time is Rohm and Haas, Philadelphia, PA 19105. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

sample and test portion at his discretion. A necessary requirement is that the test portion be as representative of the sample as possible.

10. Calibration

10.1 For a series of analyses, sufficient stock and calibration solutions are made prior to test portion preparation. The concentrations of these solutions are tabulated as follows, but may be different if the analyst so chooses. In any case, the exact concentrations of styrene and vinyl toluene must be known.

10.2 *Stock Solutions:*

10.2.1 *Stock Solution A*—Dissolve 20 g of nonionic wetting agent (7.2) in 180 g of water (7.1).

10.2.2 *Stock Solution B*—Weigh approximately 250 ± 0.1 mg of styrene (7.3) into a 50-cm^3 volumetric flask and dilute to the mark with Stock Solution A (10.2.1).

10.2.3 *Stock Solution C*—Weigh approximately 150 ± 0.1 mg of vinyl toluene (7.4) into a 50-cm^3 volumetric flask and dilute to the mark with Stock Solution A (10.2.1).

NOTE 3—In the subsequent analyses, if the addition of Stock Solution A coagulates the latex, do not use. Substitute an equivalent volume of water (7.1). The use of this wetting agent is especially helpful in reducing plugging of the syringe needles and aids in the homogeneous dispersion of added styrene and vinyl toluene.

10.3 *Calibration Mixtures*—To each of four bottles, add 5 cm^3 of water (7.1), 5 cm^3 of Stock Solution A (10.2.1). Proceed as follows:

10.3.1 Label one bottle, D, and add 0.1 cm^3 of Stock Solution B (10.2.2) and 1.0 cm^3 of Stock Solution C (10.2.3).

10.3.2 Label another bottle, E, and add 0.4 cm^3 of Stock Solution B (10.2.2) and 1.0 cm^3 of Stock Solution C (10.2.3).

10.3.3 Label another bottle, F, and add 0.6 cm^3 of Stock Solution B (10.2.2) and 1.0 cm^3 of Stock Solution C (10.2.3).

10.3.4 Label the last bottle, G, and add 1.5 cm^3 of Stock Solution B (10.2.2) and 1.0 cm^3 of Stock Solution C (10.2.3).

NOTE 4—These calibration mixtures provide concentrations of styrene similar to the expected content in the latex and provide good dispersion of the styrene and vinyl toluene in the water phase. They also provide internal standard concentrations in the same general range as styrene and can be used to check response factors and detector linearity. The calibration standards correspond to the following styrene and vinyl toluene levels when mixed with 5 g of latex:

Calibration mixture	Styrene, mg/kg	Vinyl toluene, mg/kg
D	100	600
E	400	600
F	600	600
G	1500	600

10.4 *Response Factors*—Inject 1 mm^3 (1 µL) of each calibration mixture D through G into the gas chromatograph and determine the response factor for styrene and vinyl toluene. See the Annex for examples of response factor calculations.

11. Procedure

11.1 Dry an aliquot of the sample latex to constant mass at lLa105°C. Calculate the total solids according to 12.3. (The total solids content of the latex must be known if the residual styrene on a dry rubber basis is required.)

11.2 Accurately weigh approximately 5 g of latex to ±0.1 mg into a sample vial (6.5); then add 5.0 cm^3 of Stock Solution A (10.2.1) and 1.0 cm^3 of Stock Solution C (10.2.3).

NOTE 5—It has been observed that adjusting the internal standard content to give a peak height of approximately the peak height of the styrene in the sample, improves quantitative recovery.

11.3 Agitate the vial for 5 min, either manually or mechanically.

11.4 Inject 1 mm^3 (1 µL) of this solution into the gas chromatograph and obtain the area of the styrene and vinyl toluene peaks. If injection is difficult, dilute with additional Stock Solution A (10.2.1) or water (7.1).

11.5 Check for matrix effects periodically according to 11.5.1 and 11.5.2. (Adverse matrix effects have not been observed in most latex systems.)

11.5.1 Repeat 11.2 for test portion preparation; then add 0.4 cm^3 of Stock Solution B and an additional 1.0 cm^3 of Stock Solution C. Continue as in 11.3 and 11.4. This preparation will contain added styrene at 400 mg/kg (ppm) and additional vinyl toluene at 600 mg/kg (ppm). If the analyst so desires, additional vinyl toluene need not be added, provided the styrene and vinyl toluene ratios will remain within the calibration range.

11.5.2 Calculate according to 12.1 for residual styrene. If the results indicate that the matrix does affect these results (an increase of residual styrene by three times the standard deviation over that found in 11.2 through 11.4), the latex must be analyzed with this addition technique. See the Annex for sample calculation.

12. Calculations

12.1 Calculate the residual styrene on an as-received, wet, basis as follows:

$$\text{Residual styrene, mg/kg (ppm)} = (A \times B \times C \times 1000/M \times D) \quad (1)$$

where:

A = milligrams of vinyl toluene added as internal standard,
B = response factor for styrene,
C = area of the styrene peak,
M = mass of the latex in grams, and
D = area of the vinyl toluene peak.

12.2 Calculate the residual styrene on the dry rubber as follows:

$$\text{Residual styrene, mg/kg (ppm)} = (A \times B \times C \times 1000/(M \times T) \times D) \quad (2)$$

where:

A = milligrams of vinyl toluene added as internal standard,
B = response factor for styrene,
C = area of the styrene peak,
M = mass of the latex in grams,
D = area of the vinyl toluene peak, and
T = decimal equivalent of the percent total solids.

12.3 Calculate the total solids (T) of the sample as follows:

$$\text{Total solids, \%} = (M_d \times 100/M_w) \quad (3)$$

TABLE 2 Type 1 Precision

NOTE 1—
S_r =within laboratory standard deviation.
r = repeatability (in measurement units).
(r) = repeatability (in percent).
S_R = between laboratory standard deviation.
R = reproducibility (in measurement units).
(R) = reproducibility (in percent).

Material	Mean Value, mg/kg	Within Laboratories			Between Laboratories		
		S_r	*r*	(*r*)	S_R	*R*	(*R*)
1	375	37.67	106.6	28.4	71.4	202.1	53.9
2	631	34.55	97.9	15.5	45.9	129.9	20.6
3	2711	172.5	488.0	18.0	223.0	631.0	23.3

where:
M_d = mass of the dried sample in grams, and
M_w = mass of the wet latex in grams.

13. Report

13.1 The report shall contain the following information:

13.1.1 Full identification of the sample and date of analysis,

13.1.2 Average residual styrene from two determinations, that fall within the precision found in Section 14,

13.1.3 Whether the residual styrene has been calculated on a wet or dry basis, and

13.1.4 Total solids content of the latex.

14. Precision and Bias[4]

14.1 This precision and bias section has been prepared in accordance with Practice D4483. Refer to Practice D4483 for terminology and other statistical calculation details.

14.2 A Type 1 (interlaboratory) precision was evaluated. Both repeatability and reproducibility are short term, a period of a few days separates replicate test results. A test result is the average value, as specified by this test method, obtained on two determinations or measurements of the property or parameter in question.

14.3 Three different materials were used in the interlaboratory program, these were tested in five laboratories on two different days.

14.4 The results of the precision calculations for repeatability and reproducibility are given in Table 2, in ascending order of material average or level, for each of the materials evaluated.

14.5 The precision of this test method may be expressed in the format of the following statements which use what is called an "appropriate value" of *r, R, (r),* or (*R*), that is, that value to be used in decisions about test results (obtained with this test method). The appropriate value is that value of *r* or *R* associated with a mean level in Table 2 closest to the mean level under consideration at any given time, for any given material in routine testing operations.

14.6 *Repeatability*—The repeatability, *r*, of this test method has been established as the appropriate value for any parameter tabulated in Table 2. Two single test results, obtained under normal test method procedures, that differ by more than this tabulated *r* (for any given level) must be considered as derived from different or nonidentical sample populations.

14.7 *Reproducibility*—The reproducibility, *R*, of this test method has been established as the appropriate value tabulated in Table 2. Two single test results obtained in two different laboratories, under normal test method procedures, that differ by more than the tabulated *R* (for any given level) must be considered to have come from different or nonidentical sample populations.

14.8 Repeatability and reproducibility expressed as a percentage of the mean level, *(r)* and *(R)*, have equivalent application statements as above for *r* and *R*. For the *(r)* and *(R)* statements, the difference in the two single test results is expressed as a percentge of the arithmetic mean of the two test results.

14.9 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values do not exist for this test method since the value (of the test property) is exclusively defined by the test method. Bias, therefore, cannot be determined.

15. Keywords

15.1 styrene; styrene-butadiene rubber (SBR); styrene-butadiene rubber latex

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D11-1018.

ANNEX

(Mandatory Information)

A1. EXAMPLE OF CALIBRATION PROCEDURE AND CALCULATIONS

A1.1 Calibration of Gas Chromatograph

A1.1.1 The following stock solutions were used to calibrate the gas chromatograph:

A1.1.1.1 *Stock Solution A*—A 20.0-g sample of Triton X-100 was dissolved in 180 g of water.

A1.1.1.2 *Stock Solution B*—A sample of 0.2667 g of fresh styrene was weighed in a tared 50-cm^3 volumetric flask and diluted to volume with Stock Solution A. This solution contains 5.334 mg of styrene/cm^3.

A1.1.1.3 *Stock Solution C*—A sample of 0.1660 g of *o*-vinyl toluene was weighed in a tared 50-cm^3 volumetric flask and diluted to volume with Stock Solution A. This solution contains 3.32 mg of vinyl toluene/cm^3.

A1.1.2 The following calibration standards were prepared and analyzed in accordance with this test method:

	Calibration standard			
Solutions	1	2	3	4
Stock Solution A, cm^3	5.0	5.0	5.0	5.0
Stock Solution B, cm^3	0.10	0.40	0.60	1.50
Stock Solution C, cm^3	1.00	1.00	1.00	1.00
Water, cm^3	5.0	5.0	5.0	5.0
Styrene added, mg	0.53	2.13	3.20	8.00
Vinyl toluene added, mg	3.32	3.32	3.32	3.32

Based on a 5.0-g latex sample:

Styrene, mg/kg (ppm)	105	426	640	1600
Vinyl toluene, mg/kg (ppm)	664	664	664	664

Injections of 1 mm^3 (µL) of each standard had the following areas:

Styrene area	2 109	7 879	13 716	31 206
Vinyl toluene area	11 588	10 489	12 402	11 490

A1.1.3 *Example of Response Factor Calculation*—From the preceding table, the weight ratio (R_W) of styrene/vinyl toluene is calculated. The area ratio of styrene/vinyl toluene is calculated from the chromatographic peak areas (integrator, computer, etc.).

A1.1.3.1 The mass ratio (R_W) for the calibration standard 1 is as follows:

$$(\text{mg styrene/mg vinyl toluene}) \text{ or } (0.53/3.32) = 0.1596 \tag{A1.1}$$

A1.1.3.2 The area ratio (R_A) for the same standard is:

$$(\text{area styrene/area vinyl toluene}) \text{ or } (2109/11588) = 0.1820 \tag{A1.2}$$

and the response factor (R_f) is R_W/R_A or:

$$0.1596/0.1820 = 0.877 \tag{A1.3}$$

A1.1.3.3 Similarly, the response factors of the other standards may be calculated:

Standard	1	2	3	4
Response factor	0.877	0.855	0.870	0.887

Average response factor: 0.872

A1.1.4 *Example of Residual Styrene Calculation:*

$$\text{Residual styrene, mg/kg} = (\text{mg vinyl toluene} \times 0.872 \times \text{area styrene peak} \times 1000/\text{g latex} \times \text{area vinyl toluene peak}) \tag{A1.4}$$

A1.1.4.1 *For Calibration Standard #1:*

$$\text{Styrene, mg/kg} = (3.32 \times 0.872 \times 2109 \times 1000/5.00 \times 11\ 588) = 105 \tag{A1.5}$$

A1.1.5 *Example of Addition Technique and Calculations for Matrix Effects:*

A1.1.5.1 A sample of 5.0253 g of an SBR latex, to which 1.0 cm^3 of Stock Solution C had been added, was found to contain 753 mg/kg of residual styrene. The addition of 0.40 cm^3 of Stock Solution B (2.13 mg of styrene) should increase the residual styrene to:

$$753 + (2.13\ \text{mg}/5.0253\ \text{g}) \times 1000 = 1177\ \text{mg/kg} \tag{A1.6}$$

A1.1.5.2 Duplicate injections of 1 mm^3 (µL) of the "spiked" sample gave the following areas:

	Styrene	Vinyl toluene
(1)	22 966	11 483
(2)	25 127	12 378

(1) Styrene found = $(3.32 \times 0.872 \times 22\ 966 \times 1000/5.0253 \times 11\ 483) = 1152$ mg/kg

(2) Styrene found = $(3.32 \times 0.872 \times 25\ 127 \times 1000/5.0253 \times 12\ 378) = 1169$ mg/kg

A1.1.5.3 Comparison:

Styrene added: 1177 − 753 = 424 mg/kg
Styrene found: 1152 − 753 = 399 mg/kg
Average: 1169 − 753 = 416 mg/kg

A1.1.5.4 Since the difference in styrene found from styrene added (−25 mg/kg) is well within the limit of three times the standard deviation as found in Section 14, the latex need not be analyzed by the addition technique. This exercise also serves to show the analyst that the operating parameters of the chromatograph are correct for his problem and that the analysis is being carried out properly.

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