Designation: D 1396 – 92 (Reapproved 1998)

Standard Test Methods for Chemical Analysis of Poly(Vinyl Butyral)[1]

This standard is issued under the fixed designation D 1396; 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 methods cover procedures for the determination of poly(vinyl alcohol), poly(vinyl acetate), and butyraldehyde in poly(vinyl butyral).

1.2 The procedures appear in the following order:

	Sections
Poly(vinyl alcohol)	4
Poly(vinyl acetate)	5
Butyraldehyde	6

1.3 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

3. Reagents

3.1 *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.[3] 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.

3.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

4. Poly(Vinyl Alcohol)

4.1 *Reagents*:

4.1.1 *Ethylene Dichloride*, technical grade.

4.1.2 *Phenolphthalein Indicator Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in 100 mL of ethanol (95 %), methanol, or isopropanol.

4.1.3 *Potassium Hydroxide, Standard Alcoholic Solution* (0.5 *N*)—Dissolve 33 g of KOH in methanol and dilute to 1 L. Standardize against potassium acid phthalate using phenolphthalein indicator solution.

4.1.4 *Pyridine Acetic Anhydride Reagent*—Mix slowly 1000 mL of pyridine and 87 mL of acetic anhydride. Make only about a week's supply, and keep it in a brown bottle.

4.2 *Procedure*:

4.2.1 Transfer 2.2 g of the dry sample to a clean, dry, 500-mL glass-stoppered flask. Add 25.0 mL of pyridine-acetic anhydride reagent. Insert the stopper, and heat the flask on a sand or steam bath below the boiling point for 5½ h. Swirl gently until the sample is completely dissolved. Vent the flask occasionally during the first part of the heating period to prevent the stopper from blowing out.

4.2.2 At the end of the 5½-h period, add 25 mL of ethylene dichloride and shake well. Add 100 mL of water, and shake vigorously immediately after adding the water. Let the flask stand for ½ h.

4.2.3 Add a few drops of phenolphthalein solution and titrate with 0.5 *N* alcoholic KOH solution. Shake vigorously during the titration.

4.2.4 *Blank*—Run a blank determination on the reagents, following the same procedure as for the sample.

4.3 *Calculation*—Calculate the percentage of poly(vinyl alcohol) as follows:

$$\text{Poly(vinyl alcohol), \%} = ([B - V)\, N \times 4.4]/\, S \qquad (1)$$

where:

B = KOH solution required for titration of the blank, mL,
V = KOH solution required for titration of the sample, mL,
N = normality of the KOH solution, and
S = specimen weight, g.

5. Poly(Vinyl Acetate)

5.1 *Apparatus*:

[1] These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *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.

5.1.1 *Flask, Wide-Mouth*, 500-mL capacity, equipped with a metal reflux condenser.

5.2 *Reagents*:

5.2.1 *Hydrochloric Acid Standard Alcoholic Solution* (0.5 *N*).

5.2.2 *Methanol*:

5.2.3 *Phenolphthalein Solution* (10 g/L)—See 4.1.2.

5.2.4 *Potassium Hydroxide Alcoholic Solution* (28 g KOH/L)—Dissolve 33 g of potassium hydroxide (85 % KOH in ethyl alcohol and dilute to 1 L with methanol. This solution is approximately 0.5 *N* so standardized solution (4.1.3) may be used if desired.

5.3 *Procedure*:

5.3.1 Transfer 2.15 g of the dry sample to the 500-mL flask. Add 200 mL of methanol, measured in a graduate. Measure from a buret 25.0 mL of KOH solution (4.2.3). Reflux on a sand or water bath for 2 h.

5.3.2 Rinse down the condenser and flask with a small amount of water, add a few drops of phenolphthalein solution, and backtitrate, using 0.5 *N* alcoholic HCl.

5.3.3 *Blank*—Run a blank determination on the reagents, following the same procedure as for the sample.

5.4 *Calculation*—Calculate the percentage of poly(vinyl acetate) as follows:

$$\text{Poly(vinyl acetate), \%} = [(B - V)N \times 8.6]/S \quad (2)$$

where:

B = HCl required for back-titration of the blank, mL,
V = HCl required for back-titration of the sample, mL,
N = normality of the HCl, and
S = sample used, g.

6. Total Butyraldehyde

6.1 *Reagents*:

6.1.1 *Bromphenol Blue Indicator Solution*—Dissolve 0.2 g of bromphenol blue indicator solution in 100-mL of methanol, ethanol, or isopropanol.

6.1.2 *n-Butanol*.

NOTE 1—The same lot of *n*-butanol should be used for all determinations that are to be compared.

6.1.3 *Hydroxylamine Hydrochloride Solution* (0.5 *N*).

6.1.4 *Methanol*.

6.1.5 *Sodium Hydroxide Standard Solution* (0.5 *N*)—Dissolve 20 g of NaOH in water and dilute to 1 L. Standardize against potassium acid phthalate.

6.2 *Blank Determination*:

6.2.1 Place 50 mL of *n*-butanol and 50 mL of the hydroxylamine hydrochloride solution in a 500-mL Erlenmeyer flask, and fit by means of the ground-glass joint to a 12-in. (305-mm) reflux condenser. Be sure the ground-glass joint is dry. Add a porous plate boiling chip, and reflux for 2 h on a hot plate. Cool to 24 ± 2°C.

6.2.2 Add exactly 5 drops of bromphenol blue indicator solution and 50 mL of methanol to the solution and titrate with 0.5 *N* NaOH solution to a green end point (Note 2). Run at least two blank determinations checking to within 0.5 mL of each other, titrating to the same end point at 24 ± 2°C (Note 3).

NOTE 2—The pH value of the blank and sample vary with temperature; if the temperature is raised the green end point will turn yellow and if the temperature is lowered the green end point will turn blue. The pH value of the blank changes more quickly than the pH of the sample solution for a given change in temperature. Therefore, the blank is titrated and kept at 24 ± 2°C and the sample is titrated at the same temperature.

NOTE 3—The color change of the indicator will be a gradual one from yellow to green to blue. No sharp transition point will be found. Choose a point of yellow green to green coloration. A buffer solution containing 2.05 g of potassium acid phthalate 24 mL of 0.1 *N* H_2SO_4, and 50 mL of methanol gives a color matching a blank titrated with 6.85 mL of 0.0938 *N* NaOH solution. The color in the buffer solution will fade out but the regular blank may be kept as a standard for the determination.

6.3 *Procedure for Analysis of Sample*:

6.3.1 Transfer 2 g of the dry sample, weighed to the nearest 0.1 mg, to the 500-mL Erlenmeyer flask. Add 50 mL of *n*-butanol and 50 mL of hydroxylamine hydrochloride solution, and attach the 12-in. (305-mm) reflux condenser. Be sure the ground-glass joint is dry. Add a boiling chip, and reflux for 2 h.

NOTE 4—The resin gradually forms a milky emulsion. At this point, the reaction tends to bump and must be watched. After approximately 1.5 h the bumping lessens considerably and the mixture clears.

6.3.2 Cool, add 5 drops of bromphenol blue solution and titrate with 0.5 *N* NaOH solution until at least two-thirds of the expected requirement has been run in. Add 50 mL of methanol. At the first appearance of a green tinge, bring the flask to 24 ± 2°C (Note 5). Titrate to the same color as the blank (Note 6).

NOTE 5—The heat of neutralization changes the temperature during the titration.

NOTE 6—The blank may be diluted to give the same intensity of color as in the analysis of the sample if the percentage of butyraldehyde in all determinations is fairly constant. Otherwise, adjust the intensity of color by the amount of indicator present.

6.4 *Calculation*—Calculate the percent of total butyraldehyde as follows:

$$\text{Butyraldehyde, \%} = [(V - B)N \times 7.2]/S \quad (3)$$

where:

V = NaOH solution required for titration of the specimen, mL,
B = NaOH solution required for titration of the blank, mL,
N = normality of the NaOH solution, and
S = specimen weight, g.

7. Precision and Bias

7.1 The precision of the three determinations has not been determined.

7.2 Bias cannot be determined as no standards are available.

8. Keywords

8.1 poly(vinyl acetate); poly(vinyl butyral)