Designation: D6657 – 16

Standard Test Method for pH of Wet Blue and Wet White[1]

This standard is issued under the fixed designation D6657; 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 pH of all types of Wet Blue and Wet White.

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

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:*[2]

D6659 Practice for Sampling and Preparation of Wet Blue for Physical and Chemical Tests

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

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

3. Terminology

3.1 *Definitions of Term Specific to this Standard:*

3.1.1 The pH of a solution has been defined as the negative logarithm of the hydrogen ion activity. A solution of pH 7 is neutral at 24 °C. Lower numbers indicate increasing acidity; higher numbers, increasing alkalinity.

4. Significance and Use

4.1 This test method is designed to measure the pH of a distilled-water extract of Wet Blue and Wet White. This is considered to be a measure of the acidity or alkalinity of the Wet Blue or Wet White. Excessive acidity or alkalinity may have a deleterious effect on the aging characteristics of Wet Blue and Wet White and the leather made from it.

4.2 This test method is suitable for development, control, and service evaluation of wet blue.

5. Apparatus

5.1 *Electronic pH Meter,* with a suitable electrode. The meter shall have an accuracy of at least 0.01 pH unit and reproducibility of 0.05 pH unit.

5.2 *Analytical Balance,* sensitive to 0.01 g or greater.

6. Reagents

6.1 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity. Distilled water shall have a pH value of not less than 5.5 nor more than 7.0 and shall give a residue of not more than 0.5 mg, when 100 mL is evaporated and dried in a platinum dish.

6.2 *Commercially Standardized pH Solutions*[3]:

6.2.1 *Alkaline Phosphate Buffer Solution (0.01 M trisodium phosphate, pH = 11.72 at 25 °C)*—Dissolve 1.42 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4) in 100 mL of a 0.1 *N* carbonate-free solution of sodium hydroxide (NaOH) and dilute to 1 L with water.

6.2.2 *Borax Buffer Solution (0.01 M, pH = 9.18 at 25 °C)*—Dissolve 3.81 g of sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) in water and dilute to 1 L.

6.2.3 *Hydrochloric Acid (pH = 1.10 at 25 °C)*—Add 2 g of concentrated hydrochloric acid (HCl, sp gr 1.19) to 450 g of water. Standardize and dilute to 0.1 *N*.

6.2.4 *Phosphate Buffer Solution (0.025 M with respect to each phosphate, salt pH = 6.86 at 2.5 °C)*—Dissolve 3.40 g of monobasic potassium phosphate (KH_2PO_4) and 3.55 g of anhydrous dibasic sodium phosphate (Na_2HPO_4) in water and dilute to 1 L.

6.2.5 *Potassium Hydrogen Phthalate Buffer Solution (0.05 M, pH = 4.01 at 25 °C)*—Dissolve 10.21 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in water and dilute to 1 L.

[1] This test method is under the jurisdiction of ASTM Committee D31 on Leather and is the direct responsibility of Subcommittee D31.02 on Wet Blue.

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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] Commercial buffer salts and solutions prepared in accordance with National Bureau of Standards recommendations are sold by reputable laboratory supply houses and may be used.

7. Test Specimen

7.1 The specimen shall consist of a composite sample prepared according to Practice D6659.

7.1.1 *Practice D6659*—Sample Preparation Method A (as received in wet state, diced): use 10 ± 1 g.

7.1.2 *Practice D6659*—Sample Preparation Method B (oven or air dried, ground): use 2 - 5 g.

8. Standardization

8.1 Use manufacturer's directions for establishing two point standardization with standard pH solutions that read on either side of the anticipated pH of the solution to be tested. Wash electrodes by immersing in three changes of water and establish a fresh liquid junction after blotting electrodes if using sleeve type electrode prior to testing each solution.

8.2 Check for electrode drift with either of the buffers and restandardize if necessary.

9. Procedure

9.1 Weigh the specimen to the nearest 0.01 g and transfer to a 250 mL Erlenmeyer flask.

9.1.1 If specimen was obtained as in 7.1.1 add water in the amount of ten times the mass of the specimen.

9.1.2 If specimen was obtained as in 7.1.2 add water in the amount of twenty times the mass of the specimen.

9.1.3 Stopper the flask and agitate thoroughly. Let stand at the Standard Laboratory Temperature, 23.0 ± 1°C (73.4 ± 1.8°F), with occasional agitation for not less than 4 nor more than 24 h. Agitate thoroughly and if necessary transfer to a clean beaker or decant if possible.

9.2 Determine the pH of the Wet Blue (or Wet White) water mixture or solution, reading the meter to the closest 0.05 unit.

9.3 If a pH difference figure (Delta pH) is desired, remove a 5 ml to 10 ml aliquot of the liquid into a beaker and dilute ten fold. Mix well and determine the pH. Calculate the difference in pH from the initial reading.

NOTE 1—If the pH difference figure is 0.7 or greater, it is an indication that strong free acid is present.

10. Report

10.1 Report the following information:

10.1.1 The pH of the sample shall be reported to the nearest 0.05 pH unit.

10.1.2 The pH difference figure (Delta pH) shall be reported to the nearest 0.05 pH unit.

11. Precision and Bias

11.1 This test method is adopted from the leather tanning industry where it has long been in use and approved for dissemination as a standard method before the inclusion of precision and bias statements was mandated. The pH of Wet Blue can change significantly over time after removal from the chrome-tanning vessel. This change happens because chemical reactions involving the basicity of the chromium sulfate complex continue to occur within the Wet Blue. The amount and rate of these pH changes is dependent on the specific processes and materials used to manufacture the Wet Blue. The user is cautioned to verify that the precision and bias (or reproducibility) of this method is adequate for the contemplated application.

11.2 A real world precision statement was determined through statistical examination[4] of 145 results from 9 laboratories, on 16 materials over nearly 2 years. Practice E691 was followed for the design and analysis of the data. The terms below (repeatability and reproducibility) are used as specified in Practice E177.

11.2.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

11.2.2 *Reproducibility (R)*—the difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

Repeatability (r)	Reproducibility (R)
0.04	0.29

11.3 The precision of this test method is based on an intralaboratoy study of ASTM WK40322, New Standard Test Method for the Determination of pH in Wet Blue and Wet White, conducted in 2012. Nine laboratories participated in this study, testing 16 Wet Blue samples. Every "test result" represents an individual determination. The laboratories were asked to report a single test result for 13 materials and duplicate test results for 3 materials. Except for the absence of replicate test results from all of the study materials, Practice E691 was followed for the design and analysis of the data; the details are give in an ASTM research report.[4]

11.3.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

11.3.1.1 Repeatability can be interpreted as maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

11.3.1.2 Repeatability limits are listed in Table 1.

11.3.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D31-1021. Contact ASTM Customer Service at service@astm.org.

TABLE 1 pH

Material	Average[A] $\bar{x}$	Repeatability Standard Deviation S_r	Reproducibility Standard Deviation S_R	Repeatability Limit r	Reproducibility Limit R
Wet Blue 1–24–12	3.54		0.18		0.50
Wet Blue 1–31–12	3.35		0.11		0.30
Wet Blue 11–9–12	3.55		0.09		0.24
Wet Blue 12–22–11	3.45		0.18		0.50
Wet Blue 2–21–12	3.47		0.12		0.32
Wet Blue 2–5–13	3.60		0.12		0.33
Wet Blue 3–13–12	3.58		0.02		0.06
Wet Blue 4–18–12	3.68		0.05		0.15
Wet Blue 5–16–12	3.67		0.06		0.17
Wet Blue 6–28–12	3.43		0.13		0.35
Wet Blue 8–15–12	3.54		0.09		0.24
Wet Blue 9–24–12	3.70		0.07		0.18
Wet Blue 4–13–13	3.55		0.12		0.33
Wet Blue 6–13–13	3.60	0.00	0.06	0.01	0.18
Wet Blue 8–7–13	3.58	0.03	0.16	0.08	0.46
Wet Blue 9–25–13	3.62	0.01	0.13	0.03	0.37
Average	**3.56**	**0.01**	**0.10**	**0.04**	**0.29**

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

11.3.2.1 Reproducibility can be interpreted as maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

11.3.2.2 Reproducibility limits are listed in Table 1.

11.3.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

11.3.4 Any judgment in accordance with 11.3.1 would normally have an approximate 95 % probability of being correct, however the precision statistics obtained in this ILS must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The limited number of materials for which replicate results were reported essentially guarantees that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95 % probability limit would imply. Consider the repeatability limit as a guide, and the associated probability of 95 % as only a rough indicator of what can be expected.

11.4 *Bias*—No information can be presented on the bias of the procedure in Test Method D6657 for measuring pH because no material having an accepted reference value was included in the analysis.

11.5 The precision statement was determined through statistical examination of 145 results, from 9 laboratories, on 16 materials over nearly 2 years.

12. Keywords

12.1 acidity; alkalinity; blue stock; Delta pH; pH; pH difference; Wet Blue; Wet White